PREFACE

The second edition of *Chemistry* continues the substantial commitment of John Wiley and Sons Australia to local chemistry education. Students today require various multimedia activities, online resources and testing to maintain engagement. With this edition, the authors and Wiley have continued to expand the diverse ancillary resources available through *WileyPLUS* which complement the text. In addition to the text itself, Wiley has developed extensive new media content for *Chemistry, 2nd edition*. Written in close consultation with the authors and specifically designed for the new version 5 of *WileyPLUS*, the text and resources provide lecturers and students the complete and integrated tools to 'help teachers teach, and students learn'.

Chemistry, 2nd edition continues to provide the appropriate amount of organic, inorganic and physical chemistry for the majority of Australasian first-year Chemistry courses. In this edition a new chapter has been added to the text, chapter 14 'The *p*-block elements', for those courses that include more of this inorganic chemistry topic. The authors would like to acknowledge the assistance of Tony Wedd from the University of Melbourne in the preparation of this chapter.

Additionally more than half of the chapters have significant new content, and all chapters have been revised. Chapter 8 'Chemical thermodynamics' has been broken into smaller sections allowing mathematical content to be ignored if not required, and the thermodynamics material has been rewritten. New end-of-chapter questions have also been added throughout, including a number of visual problems, while all figures and artwork have been closely scrutinised and further enhanced.

The first edition introduced two features, 'Chemical Connections' and 'Chemistry Research', that proved popular and have been retained. The 'Chemical Connections' features highlight the connections between the chemical concepts within the chapter and applications of that chemistry in the world around you; chemistry does not stop at the laboratory door. In addition to the applications discussed through the body of the text, these separate pages give more in-depth descriptions of applications and cover many diverse subjects, including DNA profiling, desalination and nanotechnology. Complementing this, 'Chemistry Research' showcases inspirational work performed in research laboratories in Australia and New Zealand related to topics in each chapter. New contributions to 'Chemistry Research' in *Chemistry, 2nd edition* include protein recognition, computational chemistry and photoelectron spectroscopy.

Our thanks goes to the following researchers and contributors, who have provided information and/or materials for the 'Chemical Connections' and 'Chemistry Research' features.

Paul V Bernhardt, University of Queensland

Margaret Brimble, University of Auckland

Sally Brooker, University of Otago

Mark Buntine, Curtin University

Sam Carroll, CSIRO

John Carver, University of Adelaide

Michelle Coote, Australian National University

Deanna D'Allessandro, University of Sydney

James De Voss, University of Queensland

Chris Easton, Australian National University

Emilio Ghisalberti, University of Western Australia

Paul Haddad, University of Tasmania

Trevor Hambley, University of Sydney
Jason Harper, University of New South Wales
Richard Hartshorn, University of Canterbury
Craig Hawker, University of California, Santa Barbara
Tesse Hoekstra, CSIRO
Franca Jones, Curtin University
Scott Kable, University of Sydney
Cameron Kepert, University of Sydney
Simon W Lewis, Curtin University
Max Lu, University of Queensland
Marcel Maeder, University of Newcastle
Kathryn McGrath, Victoria University of Wellington
Mark Ogden, Curtin University
Roger Read, University of New South Wales
Carl H Schiesser, University of Melbourne
Tim Schmidt, University of Sydney
Frances Separovic, University of Melbourne
Daniel Southam, Curtin University
Claudine Stirling, University of Otago
Jeff Tallon, MacDiarmid Institute and Industrial Research Ltd
John Tsanaktsidis, CSIRO
Mark von Itzstein, Griffith University
Gordon Wallace, University of Wollongong
Jacqueline Anne Wilce, Monash University
(Richard) Ming Wah Wong, University of Singapore
Zhi Ping (Gordon) Xu, University of Queensland

Much of the popularity of the first edition can be attributed to the consultative nature of the authorial process. The second edition has also been through an extensive, thorough and rigorous review. Undertaken by academics teaching undergraduate Chemistry in Australia and New Zealand, more than 50 contributed their time in carefully reviewing draft chapters and making suggestions to the authors. In this context the authors and publishers would like to acknowledge the importance of the contributions made by:

Belinda Abbott, LaTrobe University
Phil Andrews, Monash University
Stuart Bailey, Curtin University
Stephen Best, University of Melbourne
Joanne Blanchfield, University of Queensland
Suzanne Boniface, Victoria University of Wellington
David Brown, Curtin University
Ron Clarke, Sydney University
James Crowley, University of Otago
Murray Davies, James Cook University

Greg Dicinoski, University of Tasmania
Peter Fredericks, Queensland University of Technology
Lawrie Gahan, University of Queensland
Bob Gilbert, University of Queensland
Lisbeth Grondhal, University of Queensland
Jason Harper, University of New South Wales
Hugh Harris, University of Adelaide
Toby Hudson, Sydney University
Geoff Jameson, Massey University
Lynne Jones, Curtin University
Richard Keene, James Cook University
Trevor Kitson, Massey University
Gerald Laurence, University of Adelaide
Kieran Lim, Deakin University
Max Massi, Curtin University
Ross McGeary, University of Queensland
Carla Meledandri, University of Otago
Julie Niere, RMIT University
Alan Payne, Curtin University
Sébastien Perrier, Sydney University
Stephen Ralph, University of Wollongong
Mark Riley, University of Queensland
Trevor Rook, RMIT University
David Salter, University of Auckland
Gary Schenk, University of Queensland
Tim Schmidt, Sydney University
Madeleine Schultz, Queensland University of Technology
Trevor Smith, University of Melbourne
Daniel Southam, Curtin University
Chris Sumby, University of Adelaide
Mattheus Timmer, Victoria University of Wellington
Mark Waterland, Massey University
Tony Wedd, University of Melbourne
Natalie Williamson, University of Adelaide
David Wilson, LaTrobe University
Danny Wong, Macquarie University

Allan Blackman, Steve Bottle, Siggi Schmid, Mauro Mocerino, and Uta Wille add the following:

We would like to thank the team at Wiley, especially Jason Gray, who have all worked so tirelessly in the development of this text. We would also like to give particular thanks to the many friends and professional colleagues whose names appear in this preface who have also made significant contributions to this project. Our goal to create a text that is rich in local contexts and examples and which matches the needs and expectations of chemists in Australia and New Zealand would not have been possible without this crucial input and for that we thank you and look forward to your further

feedback and future support.

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RESOURCES

WileyPLUS

WileyPLUS is a research-based, online environment for effective teaching and learning. Through a revised design, it enables students' confidence so they know what to do, how to do it, and that they have done it correctly. It has been developed as a result of significant educational research and focus group input to deliver a solution that offers both students and lecturers a superior online learning, homework and assessment system.

Research-based Design

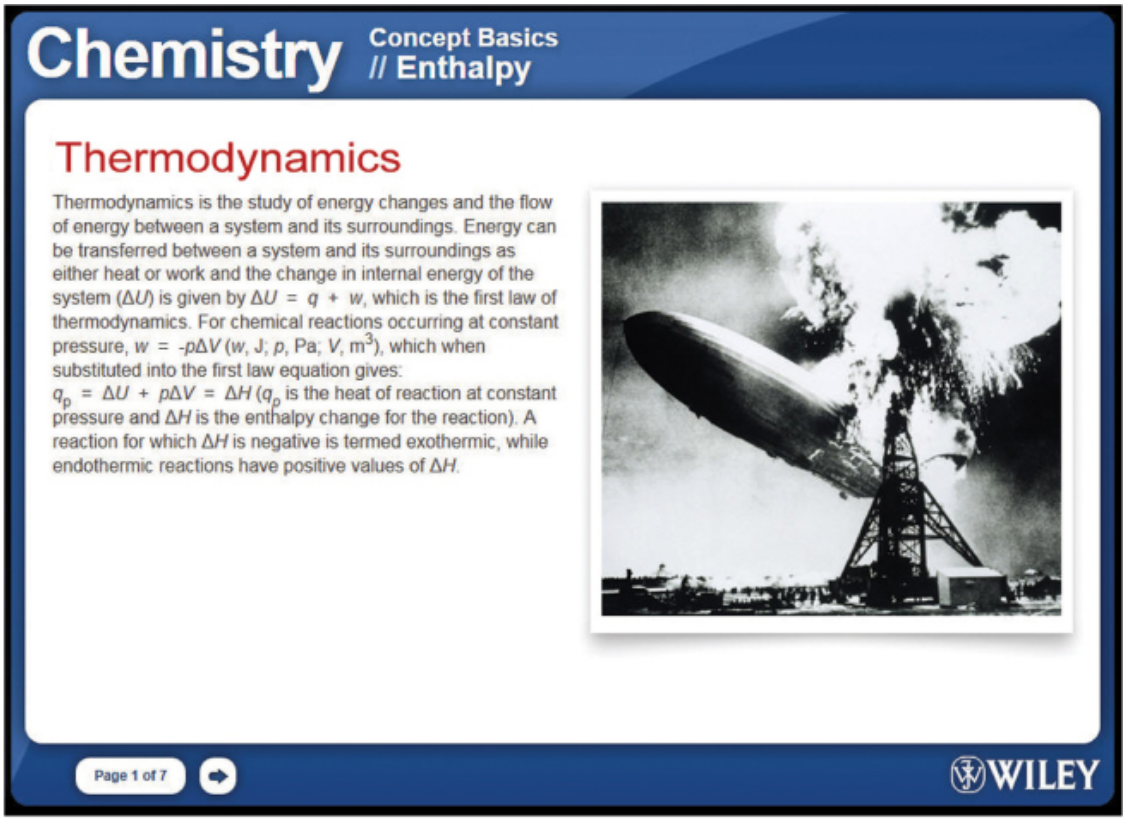
WileyPLUS provides an online environment that integrates relevant resources, including the entire digital textbook, in an easy-to-navigate framework that helps students study more effectively and so build confidence.

- *WileyPLUS* adds structure by organising the textbook content into smaller, more manageable ‘chunks’.
- Innovative features such as calendars, visual progress tracking and self-evaluation tools improve time management and strengthen areas of weakness.
- Related media, examples and sample practice items reinforce the learning objectives.

One-on-one Engagement

With *WileyPLUS* for *Chemistry, 2nd edition* students receive 24/7 access to resources that promote positive learning outcomes and engagement.

- In each chapter within *WileyPLUS*, **concept modules** are written around a clear learning objective, and start with a **Concept Basics**, a brief outline of the concept module. Within each module, **animated examples** walk the student through the concept. There is also **scaffolded practice**. The scaffolding variously takes the form of **hints, links to the text, guided online (GO) tutorials** helping the student step through a similar problem, **solutions** showing how the answer is reached, and the **answer**. These help the student understand 'how to do it'. When the lecturer comes to test students within *WileyPLUS*, they can choose what scaffolding help can be made available to the students for every question.

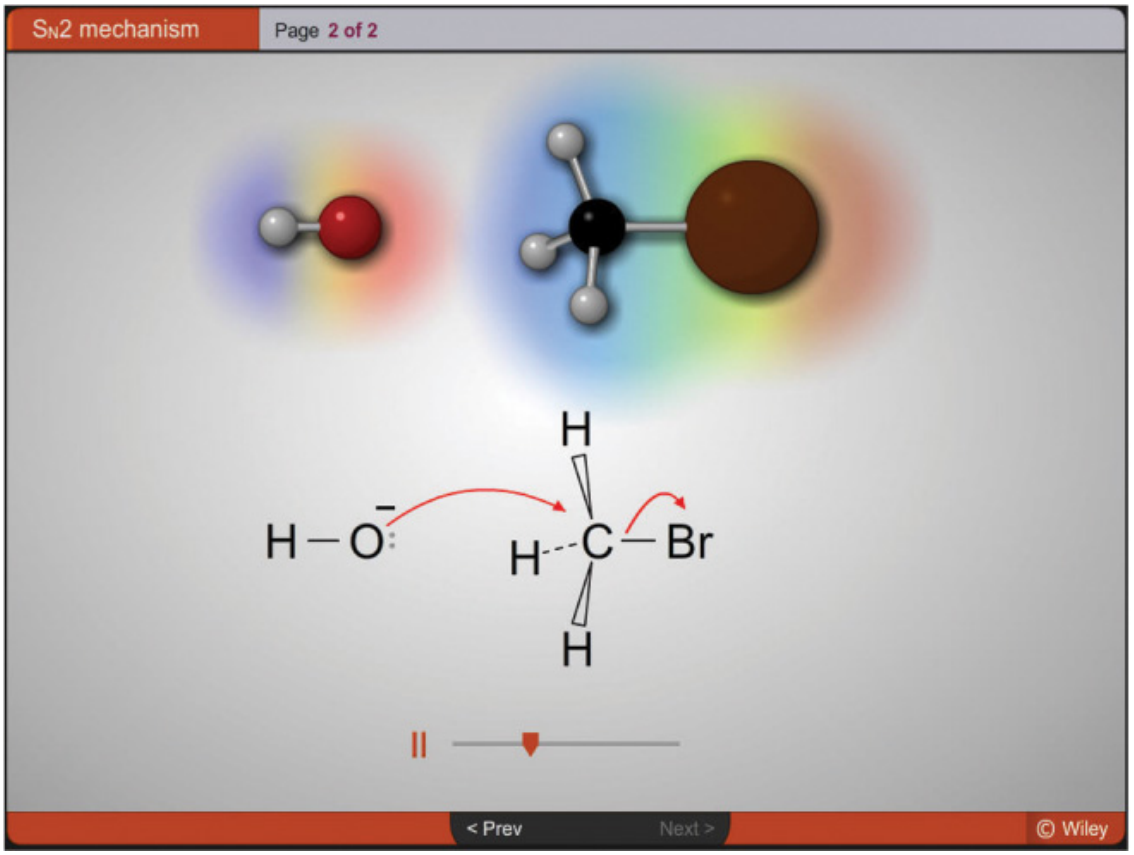


Concept Basics



Animated example

- Newly written **visualisations** give students an engaging format to gain both visual and conceptual understanding of key topics.



Visualisation

Measurable Outcomes

Throughout each study session, students can assess their progress and gain immediate feedback. *WileyPLUS* provides precise reporting of strengths and weaknesses, as well as individualised quizzes, so that students are confident they are spending their time on the right things. With *WileyPLUS*, students always know the exact outcome of their efforts.

Instructor Resources

WileyPLUS provides reliable, customisable resources that reinforce course goals inside and outside of the classroom as well as visibility into individual student progress. Pre-created materials and activities help instructors optimise their time:

Customisable course plan: *WileyPLUS* comes with a pre-created course plan designed by a subject matter expert uniquely for this course. Simple drag-and-drop tools make it easy to assign the course plan as is or modify it to reflect your course syllabus.

Pre-created activity types include:

- Questions
- Readings and resources
- **Concept Mastery** assignments test key concepts from multiple points of view (visual, symbolic, graphical, quantitative). Additionally, many organic questions include those which require students to draw using MarvinSketch.
- **Reaction Explorer** is an interactive system for learning and practising reactions, syntheses and mechanisms in organic chemistry, with advanced support for the automatic generation of random problems and curved-arrow mechanism diagrams.

WileyPLUS **gradebook:** *WileyPLUS* provides instant access to reports on trends in class performance, student use of course materials and progress towards learning objectives, helping inform decisions and drive classroom discussions.

Course Materials and Assessment Content

- Most problems in the *WileyPLUS* **Question Assignments** are coded algorithmically with hints, links to text, whiteboard/show work feature and instructor-controlled problem-solving help.
- *WileyPLUS* **Algorithmic questions** are available for every chapter.
- **PowerPoint slides** have been completely rewritten.
- The **Instructors' Solutions Manual** contains worked solutions to the end-of-chapter problems in the text.
- The **Test Bank** is available in Word, Blackboard, WebCT and Moodle. This is a separate test bank from that found in *WileyPLUS*.
- The **Computerised Test Bank** allows lecturers to produce hard copy tests from the test bank.
- The **Art Files** provides all images from the text in a format that allows easy integration into the lecturers' own resources.

Contributors to Chemistry, 2nd Edition Resources

The authors and publishers would like to thank John Hill, LaTrobe University, for his substantial contribution in providing the *WileyPLUS* concept modules and ‘Concept Basics’.

They would also like to thank the following for their time and contribution to the instructor resources:

- Solutions Manual: John Hill, LaTrobe University

- PowerPoint: Melissa Latter, University of Western Australia
- Test Bank: John Hill, LaTrobe University; Florence Laibe, Monash University; Joseph Lane, Waikato University; Melissa Latter, University of Western Australia; Shannan Maisey, University of Western Australia.

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ACKNOWLEDGEMENTS

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PROLOGUE

It is likely that you are reading these words because you have enrolled in a first-year chemistry course at university. It may be that you are starting on a career in chemistry, or you may be planning to study another subject for which chemistry is a prerequisite. Some of you will have studied chemistry throughout high school, while, for others among you, this may well be the first time you have encountered chemistry. But regardless of your background in chemistry, or the reasons you are studying the subject, you are all going to have to learn some chemistry over the coming months, and we sincerely hope that reading this book will make that task easier. Each member of the author team has been exactly where you are now; we all survived first-year chemistry and we all know which teaching and learning approaches worked for us. It is our aim to bring those approaches to this book so that they may assist you in your studies.



Those of you with your sights set on a career in chemistry will already know the importance of the subject and the kind of work that chemists do. Chemists are people trained in the science of chemistry, and they are interested in many different aspects of matter. Some chemists are primarily concerned with chemical synthesis, the preparation of new types of matter that have not previously existed. Examples include new drugs for the treatment of disease; new strong, lightweight materials for use in constructing everything from yachts to skyscrapers; and plastics that can conduct electricity or emit light. Other chemists are primarily interested in measuring the properties and amounts of matter — for example, how much heat a particular material can hold or how much carbon dioxide is in the atmosphere. A growing number of chemists never even venture into the chemical laboratory, preferring to use computers to predict, with great accuracy, properties of matter that has yet to be made. These examples serve to illustrate the fact that chemistry is an expanding subject. In the not-too-distant past, chemistry was viewed as a narrowly defined science carried out by men (always men) in white coats (always white coats) who inhabited labs filled with flasks containing all kinds of noxious chemicals. Thankfully, this is no longer the case; nowadays, there are likely to be more women than men in a first-year chemistry class, and the scope of chemistry has increased enormously. Indeed, chemistry now overlaps with many other sciences to the point where the margins between the different disciplines have become significantly blurred. This is shown by the following statistics concerning the most prestigious award in chemistry, the Nobel Prize. Of the 25 awardees over the period 2000–2009, fewer than half of them had a PhD in chemistry. Many had a medical degree or PhD in the biological sciences, one had a PhD in physics, while, remarkably, two had no PhD at all. The prizes were awarded for topics as diverse as discoveries about how water and other small molecules can pass through the walls of cells, how proteins are degraded in cells, the structure and function of the ribosome, the discovery and development of a protein in jellyfish that glows green, and the development of methods to determine the structure of large molecules. Many of these subjects would usually be thought of as the domain of biological scientists, but their basis is undeniably chemistry. And herein lies the reason that chemistry is a prerequisite for a large number of science courses.

Consider medicine, for example. If you are training to be a doctor, a knowledge of chemistry is crucial — we are, after all, made up of atoms. The human body plays host to a dizzying variety of chemical reactions, all of which play a particular role in a quality that we call life. We are able to see, thanks in part to a molecule called retinal, which undergoes a chemical reaction when it is exposed to light. We maintain a body temperature of approximately 37 °C primarily due to a molecule called adenosine triphosphate, which undergoes a chemical reaction in the body that releases energy. Our nerves function as they do because of the very delicate balance of sodium and potassium ions in the body. Current medical research is not just about better surgical techniques; it aims to find cures for diseases such as cancer, HIV/AIDS and Alzheimer's through an understanding of the molecular basis of such diseases. Medical students must learn about the myriad processes that enable the human body to function and appreciate the role that chemistry plays in many of them.



If you are hoping to become a dentist, you will need to be familiar with the chemistry of calcium hydroxyapatite, an important component of tooth enamel. Dentists need to appreciate the uses and possible dangers of mercury fillings — more and more people are choosing to have mercury fillings replaced with white fillings because of the possible health risk, and any dentist must be able to advise patients on this subject. Also of current interest is the question of fluoridation of water supplies to reduce the incidence of tooth decay, particularly in young children. What are the risks and what are the benefits? What is the role of fluoride in reducing tooth decay? What form of fluoride is added to city water supplies? Again, dentists need to have an understanding of this very emotive issue. As a dentist, you will encounter a large number of new polymeric materials used in fillings, implants and prostheses, and you will have to understand the chemistry of these to make appropriate choices of material for particular applications.

Those of you studying to be pharmacists and pharmacologists will encounter significant amounts of chemistry in your courses. Obviously, drugs and the way in which they are manufactured are important in these disciplines, but how these drugs interact with molecules in the body also constitutes a significant portion of your study, and you will certainly require an appreciation of chemical kinetics to

understand the different rates at which particular drugs act.

Biochemistry and genetics are concerned mainly with huge molecules such as DNA, RNA and proteins, and the importance of chemistry in these disciplines is self-evident. To understand how these molecules function, biochemists and geneticists need a knowledge of chemical principles such as acid–base chemistry, hydrogen bonding and molecular recognition, as well as an appreciation of the basics behind the methods used for structural determination of these molecules. Biochemical applications in forensics, most notably DNA fingerprinting, have significant chemistry components; samples must be kept scrupulously clean to avoid contamination, and highly pure reagents and stringently controlled techniques must be used to obtain usable evidence. People's lives depend on the skill and understanding of the person carrying out these analyses.

The chemistry of the environment continues to increase in importance as we grow to appreciate the significant impacts that mankind is having on the Earth. Recognition and confirmation of the damaging consequences of greenhouse gases in the atmosphere, for example, are due to the careful and painstaking measurements by scientists all around the globe. Because of this, we now use terms such as ‘carbon footprint’ and ‘food miles’, which were unheard of only two decades ago. Likewise, chlorofluorocarbons (CFCs) have now been all but banned because of their capacity to destroy the ozone layer, a fact recognised as a result of experiments in the chemistry laboratory. It is because of this work that the ozone hole in the vicinity of Australia and New Zealand has slowed its growth and is showing some signs of recovery.



It is certain that we will run out of accessible fossil fuels at some stage, possibly in your lifetime; what we urgently need is not more efficient use of this dwindling resource but an entirely new source of energy. Both Australia and New Zealand are perfectly situated to exploit solar power. Chemists are at the forefront of research in this area and are developing new materials that can cleanly and efficiently convert sunlight to electricity. Again, those of you studying environmental science or ecology will learn about these subjects and the chemistry behind them.

In short, the majority of sciences have some chemistry component; indeed, you will find chemical names, chemical formulae and chemical diagrams in most scientific textbooks. But chemistry also crops up in quite unexpected places — law, for example. Scientific discoveries with any commercial potential are usually immediately patented, and this process is carried out by patent attorneys. Given that many of the most valuable patents concern drugs, it is obviously vital that the patent attorneys involved have an appreciation of chemistry, and graduates who trained in both patent law and chemistry are currently in great demand. Similarly, an understanding of both chemistry and commerce is a major advantage in manufacturing industries, and a significant number of commerce students now opt to include some science units in their degrees. Given the importance of chemistry in our modern world, we would hope

that our leaders would have at least some appreciation of the subject. The subject of climate change, for example, must be addressed on the basis of science, rather than economics, and, in an ideal world, politicians would be sufficiently versed in the chemistry of climate change to be able to make informed decisions. After all, the future of the planet is at stake.

But what of chemistry as a discipline in itself? Why do people choose to be chemists? There is no simple answer to this question, but it is probably true to say that most chemists are fascinated by the nature of matter and seek an understanding of it using chemical principles, such as the synthesis of new molecules, determination of the structures of chemical species and studies of the reactivity of a particular molecule. Trained chemists go on to a remarkable variety of jobs, not necessarily in chemistry labs, and the demand for chemistry graduates is always strong.

So now that you have an appreciation of just what chemistry is, it is time to begin our study. We will start with a fundamental concept which underpins all of chemistry — the atom.

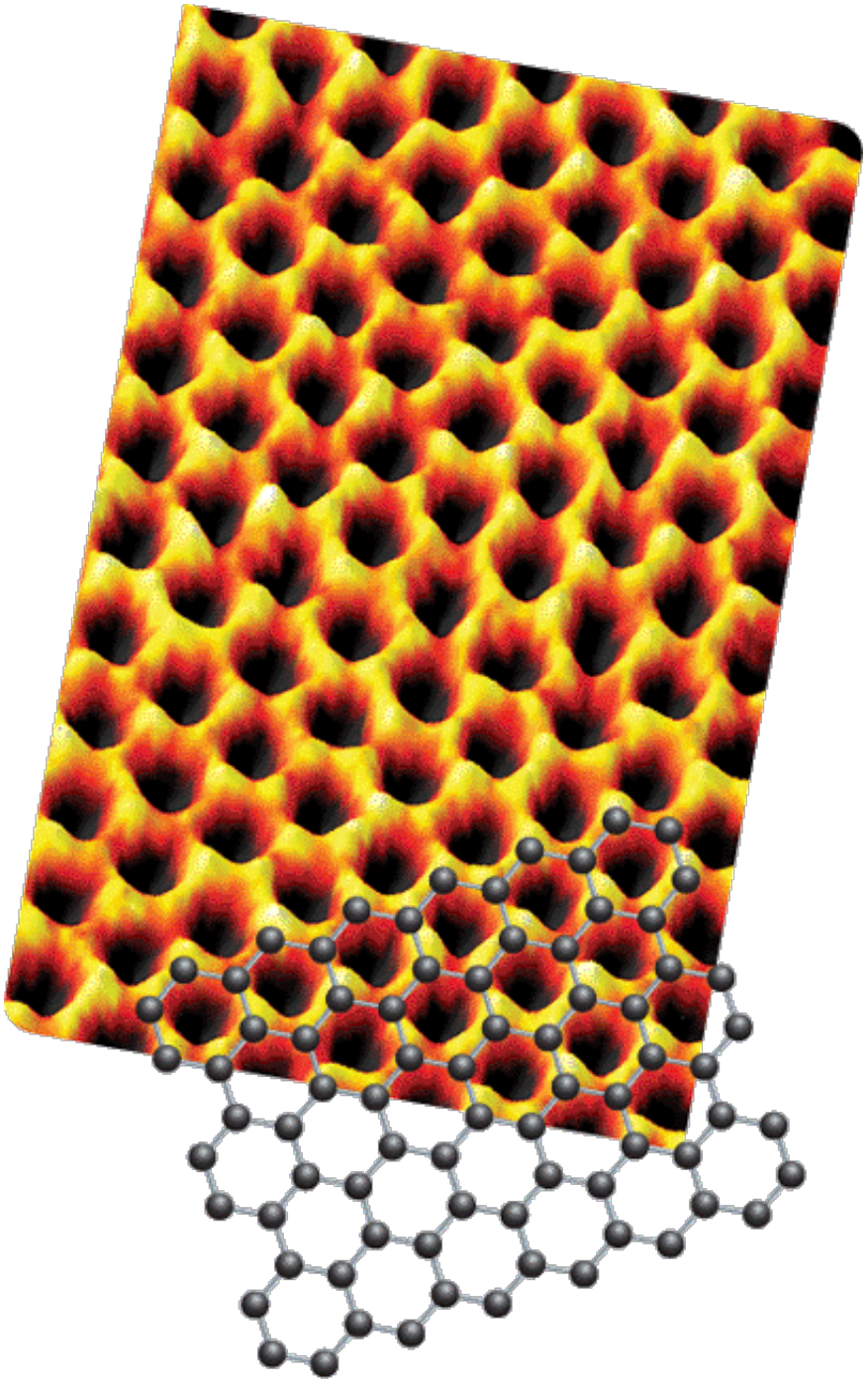
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CHAPTER

1 The Atom

Chemistry is the science concerned with the study of matter. Matter is anything that takes up space and has mass — everything you can see, smell, touch or taste. Central to the work of chemists is the structure of matter — in other words, the ways in which matter is constructed from the fundamental building block, the atom.

Although atoms are truly tiny, and cannot be seen using conventional means of magnification, modern technology allows visualisation of individual atoms. For example, the electron microscope image at right shows a sheet of graphene, a material composed entirely of carbon atoms. Each hexagon comprises six carbon atoms and the whole sheet is just a single atom thick, as shown in the accompanying ball-and-stick model. Such atomic-scale images can aid understanding of the properties of graphene, including its unusual strength and conductivity.



NASA Ozone Hole Watch, http://ozonewatch.gsfc.nasa.gov

In contrast to Andre Geim and Konstantin Novoselov, who were awarded the Nobel Prize in physics in 2010 for their work on graphene, the early twentieth century pioneers did not have recourse to our modern hi-tech methods. Our understanding of the structure of the atom, and the way in which atoms pack together in three-dimensional space, owes much to experiments carried out by two Australasian-born scientists, Ernest Rutherford (1871–1937, Nobel Prize in chemistry 1908) and William Lawrence Bragg (1890–1971, Nobel Prize in physics 1915), using equipment that would now be considered primitive. The New Zealand-born Rutherford was the first to show that the atom consists of a positively charged nucleus surrounded by tiny negatively charged electrons, while Bragg (born in Australia), together with his British-born father William Henry Bragg, developed the technique of X-ray crystallography, in which X-rays are used to determine the three-dimensional structure of solid matter on the atomic scale. The contribution of the Braggs will be outlined further in chapter 7. This chapter is primarily concerned with the atom. It will examine the contribution of Rutherford and others to the determination of the structure of the atom, and will show how a particular

structural feature of the atom forms the basis of the periodic table of the elements.

KEY TOPICS

1.1 Atoms, molecules, ions, elements and compounds
1.2 The atomic theory
1.3 The structure of the atom
1.4 The periodic table of the elements
1.5 Electrons in atoms

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1.1 Atoms, Molecules, Ions, Elements and Compounds

Chemistry is the study of **matter**. Chemists view matter as being composed of various chemical entities. Before we embark on our study of chemistry, we will briefly define some terms used to describe these entities. This will aid our understanding of the material in this chapter; we will look at these concepts again, in greater detail, in subsequent chapters. **Atoms** are discrete chemical species comprising a central positively charged nucleus surrounded by one or more negatively charged **electrons**. Atoms are always electrically neutral, meaning that the number of electrons is equal to the number of protons in the nucleus. Chemists regard the atom as the fundamental building block of all matter, so it may surprise you to learn that individual atoms are rarely of chemical interest; free atoms (with the exception of the elements helium, neon, argon, krypton, xenon and radon) are usually unstable. Of much greater interest to chemists are **molecules**, which are collections of atoms with a definite structure held together by chemical bonds. The smallest molecules contain just two atoms, while the largest can consist of literally millions. Most gases and liquids consist of molecules, and most solids based on carbon (organic solids) are also molecular. Like atoms, molecules are electrically neutral and are, therefore, uncharged. Molecules are held together by **covalent bonds**, which involve the sharing of electrons between neighbouring atoms.

Ions are chemical species that have either a positive or negative electric charge. Those with a positive charge are called **cations**; those with a negative charge are called **anions** (respectively designated by a $^{+}$ or $^{-}$). Ions can be formally derived from either atoms or molecules by the ad dition or removal of one or more electrons. For example, removing an electron (e^{-}) from a sodium, Na, atom gives the Na^{+} cation.

$$Na \rightarrow Na^{+} + e^{-}$$

Adding an electron to an oxygen molecule, which consists of two oxygen atoms bonded together and is designated O_2, gives the superoxide anion.

$$O_2 + e^{-} \rightarrow O_2^{-}$$

Elements are collections of one type of atom only, and the 118 elements known at the time of writing are listed in the periodic table on the inside front cover. **Compounds** are simply substances containing two or more elements in a definite and unchanging proportion. Compounds may be composed of molecules, ions or covalently bonded networks of atoms. Note that we do not have individual 'molecules' of an ionic compound such as sodium chloride. The chemical formula of sodium chloride, NaCl, simply represents the smallest repeating unit in an enormous three-dimensional array of Na^{+} ions and Cl^{-} ions. The same applies to certain covalently bonded structures. For example, quartz, which is composed of an 'infinite' three-dimensional network of covalently bound Si and O atoms, has the chemical formula SiO_2, which refers not to individual SiO_2 'molecules' but to the smallest repeating unit in the network.

All of the above chemical entities (atoms, molecules, ions, elements and compounds) may be involved as **reactants** in **chemical reactions**, processes in which they undergo transformations generally involving the making and/or breaking of chemical bonds, and which usually result in the formation of different chemical species called **products**.

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1.2 The Atomic Theory

Today, we take the existence of atoms for granted. We can explain many aspects of the structure of the atom and, in fact, current technology allows us to 'see' and even manipulate individual atoms. However, scientific evidence for the existence of atoms is relatively recent, and chemistry did not progress very far until that evidence was found.

The concept of atoms began nearly 2500 years ago when the Greek philosopher Leucippus and his student Democritus expressed the belief that matter is ultimately composed of tiny indivisible particles; the word 'atom' is derived from the Greek word *atomos*, meaning 'not cut'. The philosophers' conclusions, however, were not supported by any scientific evidence; they were derived simply from philosophical reasoning. The concept of atoms remained a philosophical belief, having limited scientific usefulness, until the discovery of two laws of chemical combination in the late eighteenth century — the law of conservation of mass and the law of definite proportions. These may be stated as follows:

- the **law of conservation of mass**: No detectable gain or loss of mass occurs in chemical reactions. Mass is conserved.
- the **law of definite proportions**: In a given chemical compound, the elements are always combined in the same proportions by mass.

The French chemist Antoine Lavoisier (1743–1794) proposed the law of conservation of mass as a result of his experiments involving the individual reactions of the elements phosphorus, sulfur, tin and lead with oxygen. He used a large lens to focus the Sun's rays on a sample of each element contained in a closed jar, and the heat caused a chemical reaction to take place. He weighed the closed jar and its contents before and after the chemical reaction and found no difference in mass, leading him to propose the law. (Lavoisier was beheaded following the French Revolution, the judge at his trial reputedly saying 'the Republic has no need of scientists'.) The law of conservation of mass can be alternatively stated as 'mass is neither created nor destroyed in chemical reactions'.

Another French chemist, Joseph Louis Proust (1754–1826), was responsible for the law of definite proportions, following experiments that showed that copper carbonate prepared in the laboratory was identical in composition to copper carbonate that occurs in nature as the mineral malachite. He also showed that the two oxides of tin, SnO and SnO_2, and the two sulfides of iron, FeS and FeS_2, always contain fixed relative masses of their constituent elements. The law states that chemical elements always combine in a definite fixed proportion by mass to form chemical compounds. Thus, if we analyse *any* sample of water (a compound), we *always* find that the ratio of oxygen to hydrogen (the elements that make up water) is 8 to 1 by mass. Similarly, if we form water from oxygen and hydrogen, the mass of oxygen consumed will always be 8 times the mass of hydrogen that reacts. This is true even if there is a large excess of one of them. For instance, if 100 g of oxygen is mixed with 1 g of hydrogen and the reaction to form water is initiated, all the hydrogen would react but only 8 g of oxygen would be consumed; there would be 92 g of oxygen left over. No matter how we try, we cannot alter the chemical composition of the water formed in the reaction.

WORKED EXAMPLE 1.1

Applying the Law of Definite Proportions

The element molybdenum, Mo, combines with sulfur, S, to form a compound commonly called molybdenum disulfide that is useful as a dry lubricant, similar to graphite. It is also used in specialised lithium batteries. A sample of this compound contains 1.50 g of Mo for each 1.00 g of S. If a different sample of the compound contains 2.50 g of S, what mass of

Mo does it contain?

Analysis

The law of definite proportions states that the proportions of Mo and S by mass must be the same in both samples. To solve the problem, we will set up the mass ratios for the two samples. In the ratio for the second sample the mass of molybdenum will be an unknown quantity. We will equate the two ratios and solve for the unknown quantity.

Solution

The first sample has a Mo to S mass ratio of:

$$\frac{1.50\ \text{g Mo}}{1.00\ \text{g S}}$$

We know the mass of S in the second sample, but the mass of Mo is unknown. We do know, however, that the Mo to S mass ratio is the same as that in the first sample. We set up the ratio for the second sample using x for the unknown mass of Mo. Therefore, from the law of definite proportions, we can write:

$$\frac{1.50\ \text{g MO}}{1.00\ \text{g S}} = \frac{x}{2.50\ \text{g S}}$$

We can solve for x by multiplying both sides of the equation by 2.50 g S, to give:

$$x = \frac{2.50\ \text{g S} \times 1.50\ \text{g Mo}}{1.00\ \text{g S}}$$

$$= 3.75\ \text{g Mo}$$

Is our answer reasonable?

To avoid errors, it is always wise to do a rough check of the answer. Usually, some simple reasoning is all we need to see if the answer makes sense. This is how we might do such a check here: Notice that the mass of sulfur in the second sample is more than twice the mass in the first sample. Therefore, we should expect the mass of Mo in the second sample to be somewhat more than twice what it is in the first. The answer we obtained, 3.75 g Mo, is more than twice 1.50 g Mo, so our answer seems to be reasonable.

PRACTICE EXERCISE 1.1

Cadmium sulfide is a yellow compound that is used as a pigment in artists' oil colours. A sample of this compound is composed of 1.25 g of cadmium, Cd, and 0.357 g of sulfur, S. If a second sample of the same compound contains 3.50 g of sulfur, what mass of cadmium does it contain?

The laws of conservation of mass and definite proportions served as the experimental foundation for the atomic theory. They prompted the question, ‘What must be true about the nature of matter, given the truth of these laws?’ In other words, ‘What is matter made of ?’ At the beginning of the nineteenth

century, John Dalton (1766–1844), an English scientist, used the Greek concept of atoms to make sense of the laws of conservation of mass and definite proportions. Dalton reasoned that, if atoms really exist, they must have certain properties to account for these laws. He described such properties, and the following list constitutes what we now call **Dalton's atomic theory**.

1. Matter consists of tiny particles called atoms.
2. Atoms are indestructible. In chemical reactions, the atoms rearrange but they do not themselves break apart.
3. In any sample of a pure element, all the atoms are identical in mass and other properties.
4. The atoms of different elements differ in mass and other properties.
5. When atoms of different elements combine to form a given compound, the constituent atoms in the compound are always present in the same fixed numerical ratio.

Dalton's theory easily explained the law of conservation of mass. According to the theory, a chemical reaction is simply a reordering of atoms from one combination to another. If no atoms are gained or lost, and if the masses of the atoms can't change, the mass after the reaction must be the same as the mass before. This explanation of the law of conservation of mass allows us to use a notation system of **chemical equations** to describe chemical reactions. A chemical equation contains the reactants on the left-hand side and the products on the right-hand side, separated by a forward arrow, as demonstrated in the following chemical equation for the formation of liquid water from its gaseous elements.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(1)$$

The law of conservation of mass requires us to have the same number of each type of atom on each side of the arrow; this being the case, the chemical equation above is described as balanced. We will discuss this concept in detail in chapter 3. Note that this chemical equation also specifies the physical states of the reactants and product. Gases, liquids and solids are abbreviated as (g), (l) and (s), respectively, after each reactant and product.

The law of definite proportions can also be explained by Dalton's theory. According to the theory, a given compound is always composed of atoms of the same elements in the same numerical ratio. Suppose, for example, that elements *X* and *Y* combine to form a compound in which the number of atoms of *X* equals the number of atoms of *Y* (i.e. the atom ratio is 1 to 1). If the mass of a *Y* atom is twice that of an *X* atom, then every time we encounter a sample of this compound, the mass ratio (*X* to *Y*) would be 1 to 2. This same mass ratio would exist regardless of the size of the sample so, in samples of this compound, elements *X* and *Y* are always present in the same proportion by mass.

Strong support for Dalton's theory came when Dalton and other scientists studied elements that can combine to give at least two compounds. For example, sulfur and oxygen can combine to form both sulfur dioxide, SO_2, and sulfur trioxide, SO_3. The former contains one atom of sulfur and two atoms of oxygen, while the latter contains one atom of sulfur and three atoms of oxygen. Although they have similar chemical formulae, they are different chemically; for example, at room temperature, SO_2 is a colourless gas while SO_3, which melts at 16.8 °C, is a solid or liquid, depending on the temperature of the room. If we analyse samples of SO_2 and SO_3 in which the masses of sulfur are the same, we obtain the results shown in table 1.1.

TABLE 1.1 Mass Composition of Sulfur Dioxide and Sulfur Trioxide

Compound	Mass of sulfur	Mass of oxygen
SO_2	1.00 g	1.00 g
SO_3	1.00 g	1.50 g

Note that the ratio of the masses of oxygen in the two samples is one of small whole numbers.

$$\frac{\text{mass of oxygen in sulfur trioxide}}{\text{mass of oxygen in sulfur trioxide}} = \frac{1.50\ \text{g}}{1.00\ \text{g}} = \frac{3}{2}$$

Similar observations are made when we study other elements that form more than one compound with each other. These observations form the basis of the **law of multiple proportions**, which states that: Whenever two elements form more than one compound, the different masses of one element that combine with the same mass of the other element are in the ratio of small whole numbers.

Dalton's theory explains the law of multiple proportions in a very simple way. Suppose a molecule of sulfur trioxide contains 1 sulfur and 3 oxygen atoms, and a molecule of sulfur dioxide contains 1 sulfur and 2 oxygen atoms (figure 1.1). If we had just one molecule of each, our samples would each have 1 sulfur atom and, therefore, the same mass of sulfur. Then, comparing the oxygen atoms, we find they are in a numerical ratio of 3 to 2. But because oxygen atoms all have the same mass, the mass ratio must also be 3 to 2. The law of multiple pro portions was not known before Dalton presented his theory, and its discovery demonstrates science in action. Experimental data suggested to Dalton the existence of atoms, and the atomic theory suggested the relationships that we now call the law of multiple proportions. When found by experiment, the existence of the law of multiple proportions added great support to the atomic theory. In fact, for many years, it was one of the strongest arguments in favour of the existence of atoms.

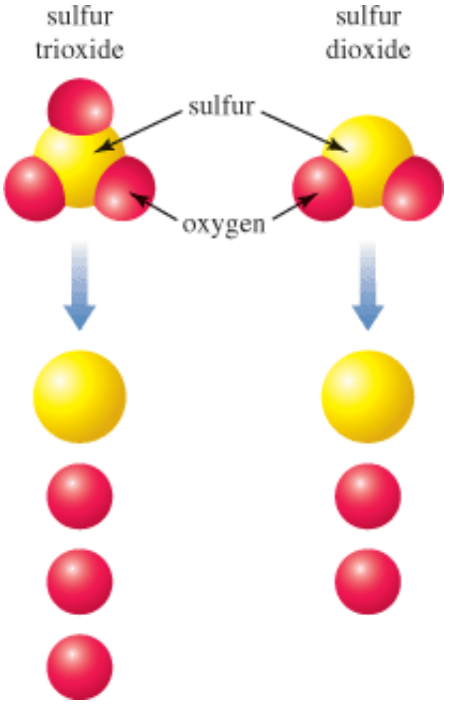


FIGURE 1.1 Compounds containing oxygen and sulfur demonstrate the law of multiple proportions. Represented here are molecules of sulfur trioxide, SO_3, and sulfur dioxide, SO_2. Each has one sulfur atom, and therefore the same mass of sulfur. The oxygen ratio is 3 to 2, both by atoms and by mass.

As outlined in the Chemical Connections feature on the next page, we are now able to ‘see’ and even manipulate individual atoms, thereby providing proof of the atomic nature of matter.

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1.3 The Structure of the Atom

Even though absolute proof of the existence of atoms was not available around the turn of the twentieth century, scientists were interested in the structure of the atom. While Dalton's theory said that atoms were indestructible and could not be broken apart, experiments around this time showed this was not necessarily true. In particular, the discovery of radiation in the form of X-rays by Wilhelm Röntgen (1845–1923) in 1895 (see figure 1.2) and radioactivity by Antoine Henri Becquerel (1852–1908, pictured in figure 1.3) in 1896 led scientists to believe that the atom was composed of discrete particles, as both forms of radiation involve the release of particles from atoms, thought at that time to be indivisible.



FIGURE 1.2 A reproduction of one of the first ever X-ray images, taken by Wilhelm Röntgen (Nobel Prize in physics, 1901) on 22 December 1895. The hand is that of his wife.

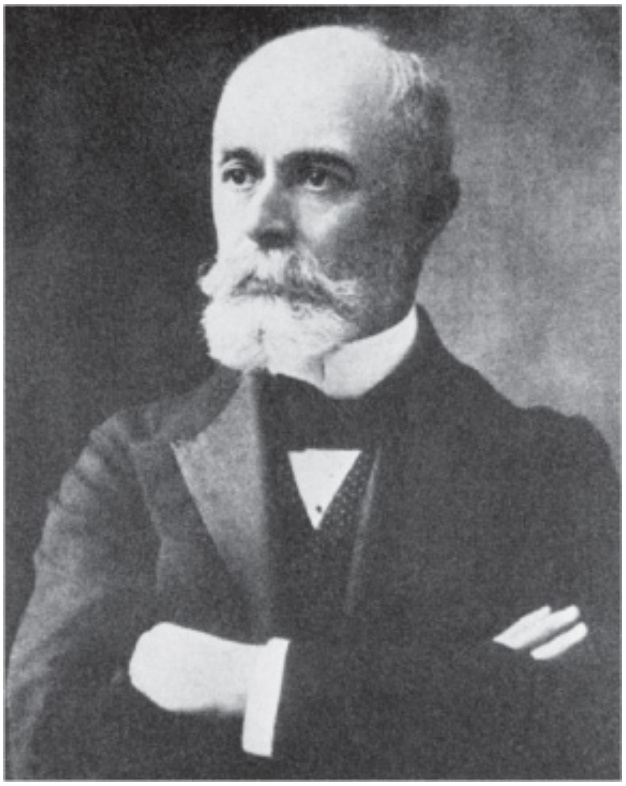


FIGURE 1.3 Antoine Henri Becquerel (Nobel Prize in physics, 1903) discovered radioactivity.

Chemical Connections

Nanotechnology: Controlling Structure at the Molecular Level

Nanotechnology is a word that is finding increasing use, especially in the popular media. As we shall see in chapter 2, the prefix ‘nano’ means 10^{-9}, and nanotechnology can therefore be broadly defined as the science of objects having dimensions on the nanometre (10^{-9} m) scale. Individual atoms have diameters of the order of 10^{-10} m — in other words, fractions of a nanometre. Nanoscale objects therefore have dimensions of perhaps tens to hundreds of atoms.

Nanotechnology deals with using such small-scale objects to accomplish useful tasks. One of the goals of nanotechnology is to build materials from the atom up. There are several reasons for the great interest in nanotechnology. For one, the properties of materials are related to their structures. By controlling structures at the atomic and molecular level, we can (in principle) tailor materials to have specific properties. Driving much of the research in this area are the continuing efforts by computer and electronics designers to produce ever smaller circuits. The reductions in size achieved through traditional methods are near their limit, so new ways to achieve smaller circuits and smaller electrical devices are being sought.

Another area of research of much interest today is the field of molecular self-assembly, in which certain molecules, when brought together, spontaneously arrange themselves into desirable structures. Biological systems employ this strategy in constructing structures such as cellular membranes. The goal of scientists is to mimic biology by designing molecules that will self-assemble into specific arrangements.

Visualising and manipulating nanoscale objects

We cannot use optical microscopes to observe nanoscale objects, because their dimensions are smaller than the wavelength of visible light. However, the invention of both the scanning tunnelling microscope (STM) and the atomic force microscope (AFM) in the late twentieth century has allowed us to 'see' and, more remarkably, manipulate individual atoms. The STM and AFM operate using the same basic principle — moving the tip of an extremely fine stylus across a surface at a distance of atomic dimensions. In the case of the STM, the surface must be electrically conducting, and this causes a current to flow between the surface and the tip. The magnitude of this current depends on the distance between the tip and the surface, so as the tip is moved across the surface, computer control of the current at a constant value will cause the tip to move up and down, thereby giving a map of the surface. Because of its tiny size, the tip can also be used to move individual atoms. One of the first demonstrations of nanotechnology came in 1989 when Don Eigler, a scientist at IBM, manipulated 35 atoms of xenon on a nickel surface using an STM to spell the name of his employer (figure 1.4).

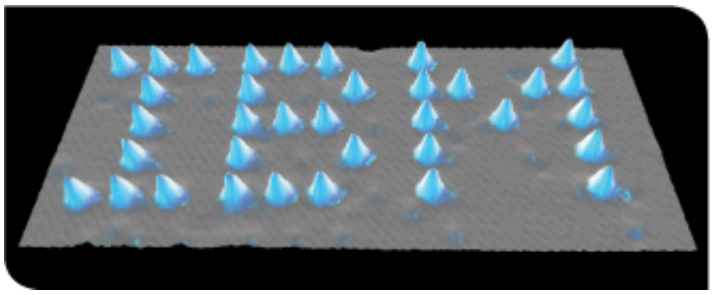


FIGURE 1.4 Individual Xe atoms (blue dots) on a nickel surface manipulated by an STM tip.

An AFM (illustrated in figure 1.5) is used to study nonconducting samples. The stylus is moved across the surface of the sample under study. Forces between the tip of the probe and the surface cause the probe to flex as it follows the ups and downs of the bumps that are the individual molecules and atoms. A mirrored surface attached to the probe reflects a laser beam at angles proportional to the amount of deflection of the probe. A sensor picks up the signal from the laser and translates it into data that can be analysed by a computer to give three-dimensional images of the sample's surface.

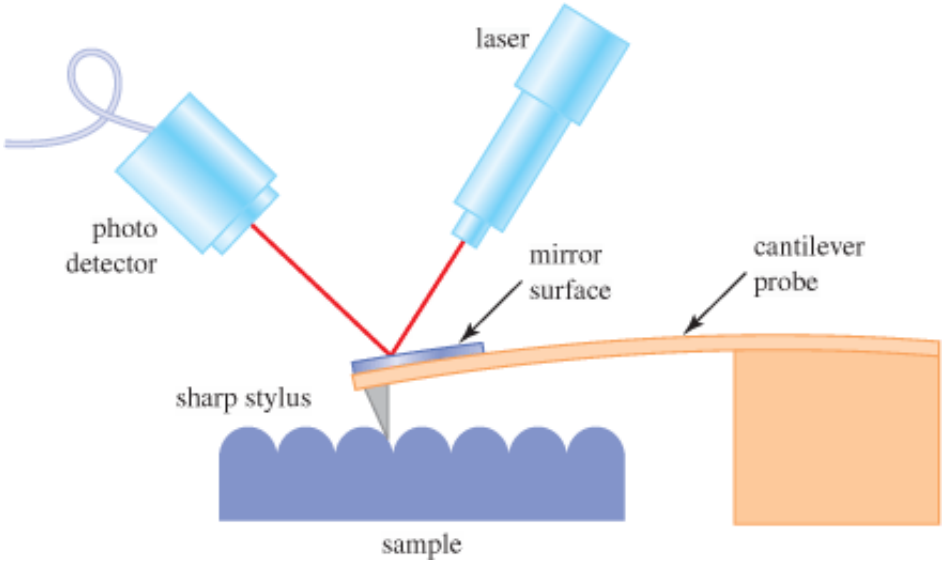


FIGURE 1.5 In an AFM, a sharp stylus attached to the end of a cantilever probe rides up and down over the surface features of the sample. A laser beam, reflected off a mirrored surface at the end of the probe, changes angle as the probe moves up and down. A photo detector reads these changes and sends the information to a computer, which translates the data into an image.

A typical AFM image is shown in figure 1.6. It involves manipulating single atoms to give

what is probably the smallest known writing.

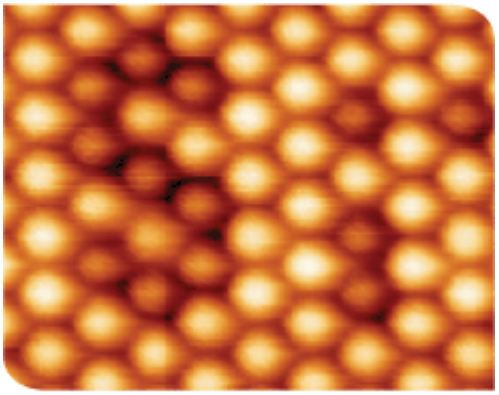


FIGURE 1.6 The world's smallest writing? The element symbol for silicon, Si, is spelled out with individual silicon atoms (dark) among tin atoms (light). The silicon atoms were manipulated with the tip of an AFM.

Further evidence for the presence of discrete particles in atoms came from experiments with gas discharge tubes, such as that shown in figure 1.7. When the tube was filled with a low pressure gas and a high voltage was applied between the electrodes, negatively charged particles flowed from the negative electrode (cathode) to the positive electrode (anode).

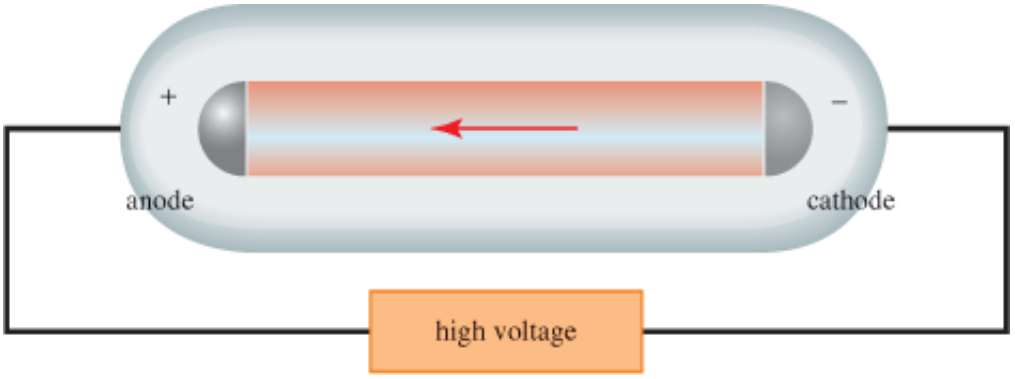


FIGURE 1.7 Diagram of a gas discharge tube.

Because they emanated from the cathode, the particles were called cathode rays. In 1897, the British physicist JJ Thomson passed cathode rays through a magnetic field using the modified discharge tube shown in figure 1.8. The magnetic field caused the path of the cathode rays to bend. Analysis of this effect allowed Thomson to determine the charge to mass ratio of the components of cathode rays, what we now know as electrons.

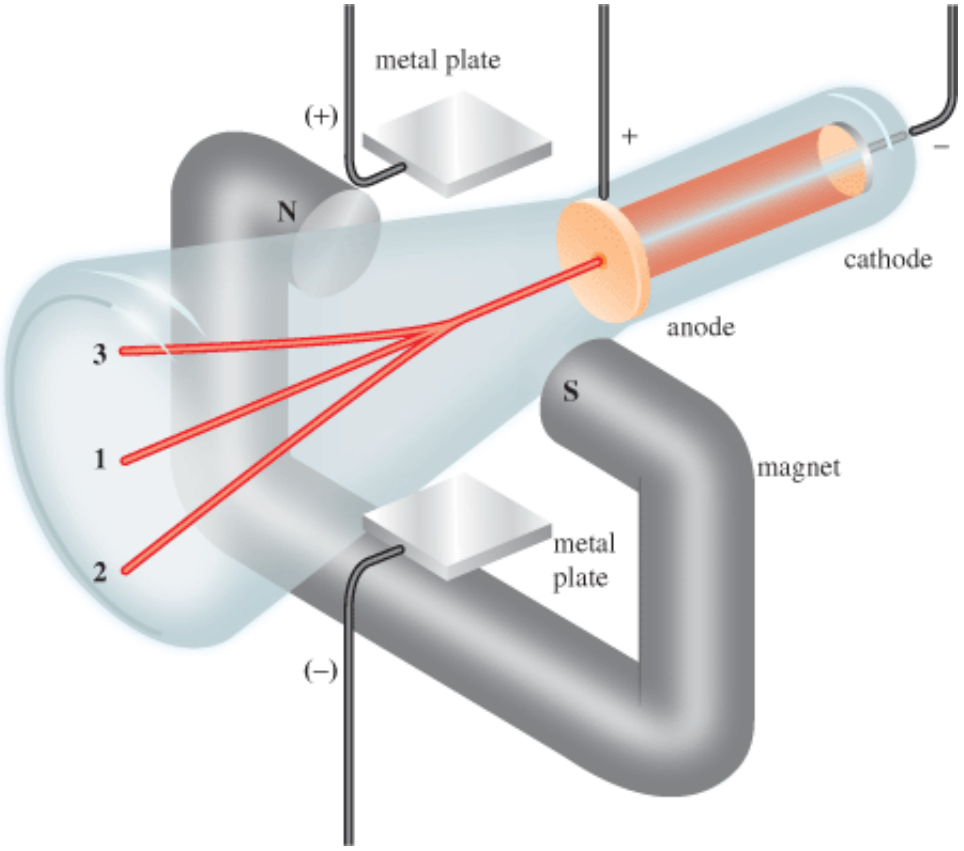


FIGURE 1.8 Diagram of the apparatus used by JJ Thomson to determine the charge to mass ratio of the electron. The cathode ray beam passes between the poles of a magnet and between a pair of metal electrodes that can be given electric charges. The magnetic field tends to bend the beam in one direction (to point 2) while the charged electrodes bend the beam in the opposite direction (to point 3). By adjusting the charge on the electrodes, the two effects can be made to cancel each other (point 1). The amount of charge on the electrodes required to balance the effect of the magnetic field can be used to calculate the charge to mass ratio.

In 1909, the American chemist Robert Millikan determined the charge on an individual electron by measuring the rates at which charged oil drops fell between electrically charged plates. This, combined with Thomson's results, allowed calculation of the mass of an electron as 9.09×10^{-31} kg. The knowledge that atoms were electrically neutral meant that the electron must have a positively charged counterpart, but its exact nature was not known by the early years of the twentieth century. It was the work of the New Zealand-born scientist Ernest Rutherford (1871–1937) that shed light not only on the positively charged component of the atom, but also on the structure of the atom itself. Around 1909, Rutherford, who had already won the Nobel Prize in chemistry in 1908 for his work on the theory of radioactivity, devised his famous gold foil experiment depicted in figure 1.9. Rutherford took an incredibly thin sheet of gold (only a few atoms thick) and bombarded it with a stream of positively charged particles called **alpha particles**.

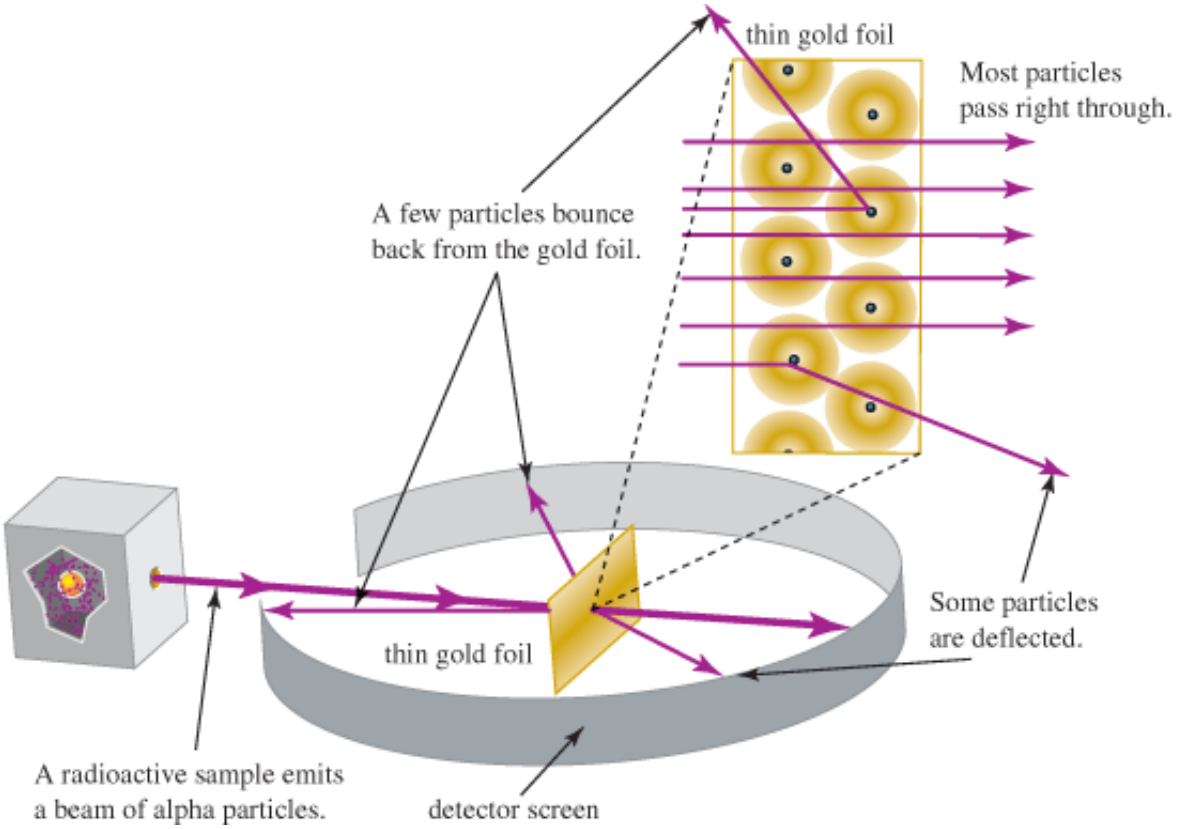


FIGURE 1.9 Schematic view of Rutherford's gold foil experiment. When a beam of positively charged alpha particles was 'shot' at a thin gold foil, most of them passed straight through the foil. Some, however, were deflected straight back towards the source.

Most of the particles went straight through the foil essentially undisturbed, some were deflected through various angles, and about 1 in 8000 was deflected almost straight back towards the source. Of this amazing observation, Rutherford said, 'It was almost as incredible as if you had fired a fifteen-inch [38.1-centimetre] shell at a piece of tissue paper and it came back and hit you'. To explain his observations, Rutherford proposed a new model of the atom. He suggested that every atom has a tiny positively charged central core, which he called the **nucleus**, that constitutes most of the mass of the atom. The positive charge in the nucleus is due to particles, which he called **protons**, and the number of these in the nucleus determines the identity of the atom. The electrical neutrality of the atom requires that there is the same number of electrons in an atom as there are protons in the nucleus, and these surround the central core, as shown schematically in figure 1.10.

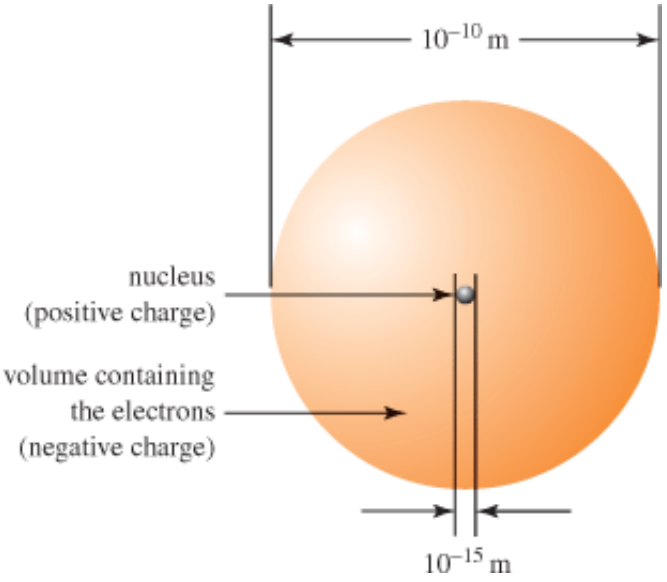


FIGURE 1.10 Diagram (not to scale) showing the nucleus and the volume occupied by the surrounding electrons. If this were drawn to scale, the nucleus would be invisible.

Electrons occupy a volume that is huge compared with the size of the nucleus, but each electron has such a small mass that alpha particles are not deflected by the electrons. Consequently, an alpha particle is deflected only when it passes very near a nucleus, and it bounces straight back only when it collides head-on with a nucleus. Because most of the volume of an atom is essentially empty space, most alpha particles pass through the foil without being affected. From the number of particles deflected and the pattern of deflection, Rutherford calculated that the positive nucleus occupies less than 0.1% of the total atomic volume. To give you an idea of what that means, an atom the size of a rugby stadium would have a nucleus the size of a pea. When Rutherford calculated the nuclear mass based on the number of protons in the nucleus, the value always fell short of the actual mass. In fact, Rutherford found that only about half of the nuclear mass could be accounted for by protons. This led him to suggest that there was another particle in the nucleus that had a mass close to or equal to that of a proton, but with no electric charge. This suggestion initiated a search that finally ended in 1932 with the discovery of the **neutron** by James Chadwick (1891–1974), a British physicist. Because they are found in the nucleus, protons and neutrons are sometimes called **nucleons**. Table 1.2 summarises the **subatomic particles** present in this model of the atom.

TABLE 1.2 Physical Data for the Electron, Proton and Neutron

Particle	Symbol	Charge (C)	Mass (kg)	Mass (u)
electron	e^-	-1.6022×10^{-19}	9.1094×10^{-31}	5.4858×10^{-4}
proton	p	$+1.6022 \times 10^{-19}$	1.6726×10^{-27}	1.0073
neutron	n	0	1.6749×10^{-27}	1.0087

Note: The charge is measured in coulombs (C). The final column gives the mass in atomic mass units (u); 1 u = 1.660 54 × 10^{-27} kg ($\frac{1}{12}$ the mass of the ^{12}C atom) (p. 10).

Over the intervening years, it has been shown that protons and neutrons are themselves composed of still smaller particles called quarks. The existence of quarks has helped us understand how the atomic nucleus can stay together despite the presence of positively charged protons in close proximity. However, quarks are very unstable outside the confines of the atomic nucleus and are of more interest to physicists than chemists.

To examine how atoms are constructed, we will consider the simplest possible atom, hydrogen, with the chemical symbol H. A hydrogen atom consists of a single proton in the nucleus, and a single electron. We designate this as ${}_{1}^{1}\mathrm{H}$. We use this terminology for any chemical element *X* as follows:

$${}_{Z}^{A}\mathrm{X}$$

where *A* is the mass number, *Z* is the atomic number and *X* is the **chemical symbol** of the chemical element. The **atomic number (*Z*)** is the number of protons in the nucleus. The **mass number (*A*)** is the number of protons in the nucleus plus the number of neutrons (*N*) in the nucleus.

Note that the atomic number is also equal to the number of electrons in a *neutral* atom (i.e. one in which the number of protons and the number of electrons is the same). A chemical element is defined by its atomic number; all atoms having the same atomic number are atoms of the same element. Therefore, the symbol ${}_{1}^{1}\mathrm{H}$ tells us that an atom of hydrogen contains 1 proton (*Z* = 1), 1 electron and 0 neutrons (*A* = 1).

If we were to analyse a sample of hydrogen atoms, we would find that roughly 1 atom in every 6600 would have approximately twice the mass of a ${}_{1}^{1}\mathrm{H}$ atom. These heavier atoms belong to an isotope of hydrogen called deuterium. **Isotopes** are atoms of an element with the same number of protons (i.e. the

same value of *Z)* but different numbers of neutrons (i.e. different values of *A*). Deuterium atoms are symbolised as $^{2}_{1}H$, meaning that there is 1 proton ($Z = 1$) and 1 neutron ($A = 2$) in the nucleus. The $^{1}_{1}H$ atom is sometimes called protium to distinguish it from deuterium. In chemical terms, deuterium atoms behave essentially identically to hydrogen atoms, but there are some important differences in reactivity when they are bonded to other atoms. In addition, hydrogen also has a third isotope called tritium, $^{3}_{1}H$, which has 1 proton and 2 neutrons in the nucleus. It is the least abundant isotope of hydrogen, with only 1 to 10 atoms of tritium in every 10^{18} atoms of hydrogen. Tritium is **radioactive**, meaning that the nucleus is unstable and undergoes spontaneous decay to give an atom of helium, He, a process we will look at in greater detail in chapter 27. Helium atoms are characterised by having 2 protons in the nucleus ($Z = 2$). Helium has two stable isotopes, $^{3}_{2}He$ and $^{4}_{2}He$, with 1 and 2 neutrons, respectively, in the nucleus. The element with 3 protons in the nucleus, lithium ($Z = 3$), has the stable isotopes $^{6}_{3}Li$ and $^{7}_{3}Li$ with 3 and 4 neutrons, respectively. Any atom of a specified *A* and *Z* is called a **nuclide**. A **radionuclide** is a radioactive nuclide.

WORKED EXAMPLE 1.2

The Composition of Atoms

The following radioactive isotopes have medical applications. Determine the number of protons, neutrons and electrons in each isotope.

(a) $^{165}_{66}Dy$ Dy (used in the treatment of arthritis)

(b) $^{131}_{53}I$ (used to image the thyroid gland)

(c) $^{59}_{26}Fe$ (used in studies of iron metabolism)

Analysis

The number of protons is equal to the atomic number (*Z*), the number of neutrons is found from *Z* and the mass number (*A*), and the number of electrons in a neutral atom must equal the number of protons.

Solution

(a) Dy is the chemical symbol for dysprosium. The subscript 66 is *Z*, which is the number of protons in the nucleus. The superscript 165 is *A*. We find the number of neutrons by subtracting *Z* from *A*: $A - Z = 165 - 66 = 99$ neutrons. Because this is a neutral atom, the number of electrons must equal the number of protons. $^{165}_{66}Dy$ has 66 protons, 99 neutrons and 66 electrons.

(b) I is the symbol for iodine. $Z = 53$ and $A = 131$. *Z* tells us that the nucleus contains 53 protons. Subtracting *Z* from *A*, we find that there are 78 neutrons in this isotope. Finally, the atom is neutral, so there are 53 electrons.

(c) Iron, Fe, has $Z = 26$. A neutral atom of $^{59}_{26}Fe$ has 26 protons, 26 electrons, and $59 - 26 = 33$ neutrons.

Is our answer reasonable?

In all cases, the number of protons is equal to the number of electrons, as required for neutral atoms. We have followed the rules for calculating the number of neutrons and have carried

out the calculations properly. Our answers should therefore be correct.

PRACTICE EXERCISE 1.2

The following radioactive isotopes have medical applications. Determine the number of protons and neutrons in each.

(a) $^{177}_{71}\mathrm{Lu}$ (used as an imaging and therapeutic agent)

(b) $^{133}_{54}\mathrm{Xe}$ (used in studies of the lungs)

(c) $^{192}_{77}\mathrm{Ir}$ (used in the form of a wire for internal cancer treatment)

Inclusion of the atomic number in this terminology is almost redundant when the chemical symbol is included, so it is common to see a shorthand version that excludes this. Thus, we often write $^{1}_{1}\mathrm{H}$ as simply $^{1}\mathrm{H}$, as we know that all atoms of hydrogen have $Z = 1$. Using the same shorthand version, deuterium would be written as $^{2}\mathrm{H}$ and tritium as $^{3}\mathrm{H}$.

Atomic Mass

We saw in table 1.2 that the $^{12}\mathrm{C}$ isotope is used as the basis by which **atomic mass** is measured. The **atomic mass unit (u)** is the mass ($1.660\ 54 \times 10^{-27}$ kg) equal to $\frac{1}{12}$ the mass of one atom of $^{12}\mathrm{C}$, and the masses of all atoms are measured relative to this. The atomic mass unit is also known as the Dalton (Da), particularly in biochemistry. Using this scale, we find that the mass of a single $^{19}\mathrm{F}$ atom is 18.998 403 2 u and that of a single $^{31}\mathrm{P}$ atom is 30.973 762 u. Because both fluorine and phosphorus have only one naturally occurring isotope, we can be sure that any fluorine atom we chose from a macroscopic sample of fluorine would have a mass of 18.998 403 2 u, while any phosphorus atom chosen from a macroscopic sample of phosphorus would have a mass of 30.973 762 u. We therefore say that the atomic mass of fluorine is 18.998 403 2 u and the atomic mass of phosphorus is 30.973 762 u. However, the majority of elements in the periodic table comprise two or more isotopes, and the mass of a single atom chosen at random from a macroscopic sample of these elements would not be constant — it would depend on which isotope was chosen. We therefore define the atomic mass of these elements as the average mass per atom of a naturally occurring sample of atoms of the element. Consider, for example, bromine, Br. There are two naturally occurring isotopes of Br, namely $^{79}_{35}\mathrm{Br}$ and $^{81}_{35}\mathrm{Br}$, each of which contains 35 protons in the nucleus. Nuclei of the former contain 44 neutrons while those of the latter contain 46. Any naturally occurring sample of bromine will be composed of 50.69% of the $^{79}_{35}\mathrm{Br}$ isotope and 49.31% of the $^{81}_{35}\mathrm{Br}$ isotope. Given the atomic masses of these isotopes ($^{79}_{35}\mathrm{Br} = 78.9183$ u, $^{81}_{35}\mathrm{Br} = 80.9163$ u) we can calculate the average atomic mass of Br by taking the sum of the atomic mass of each isotope multiplied by its abundance as follows.

$$\text{average atomic mass of Br} = (0.5069 \times 78.9183\ \text{u}) + (0.4931 \times 80.9163\ \text{u}) = 79.90\ \text{u}$$

The average atomic mass of Br, 79.90 u, is just less than the average of the masses of the two isotopes (79.9173 u) because the lighter $^{79}_{35}\mathrm{Br}$ isotope is slightly more abundant than the heavier $^{81}_{35}\mathrm{Br}$ isotope.

Figure 1.11 illustrates the range of isotopic compositions found in four elements, one of which is tin, the element with the largest number of stable isotopes.

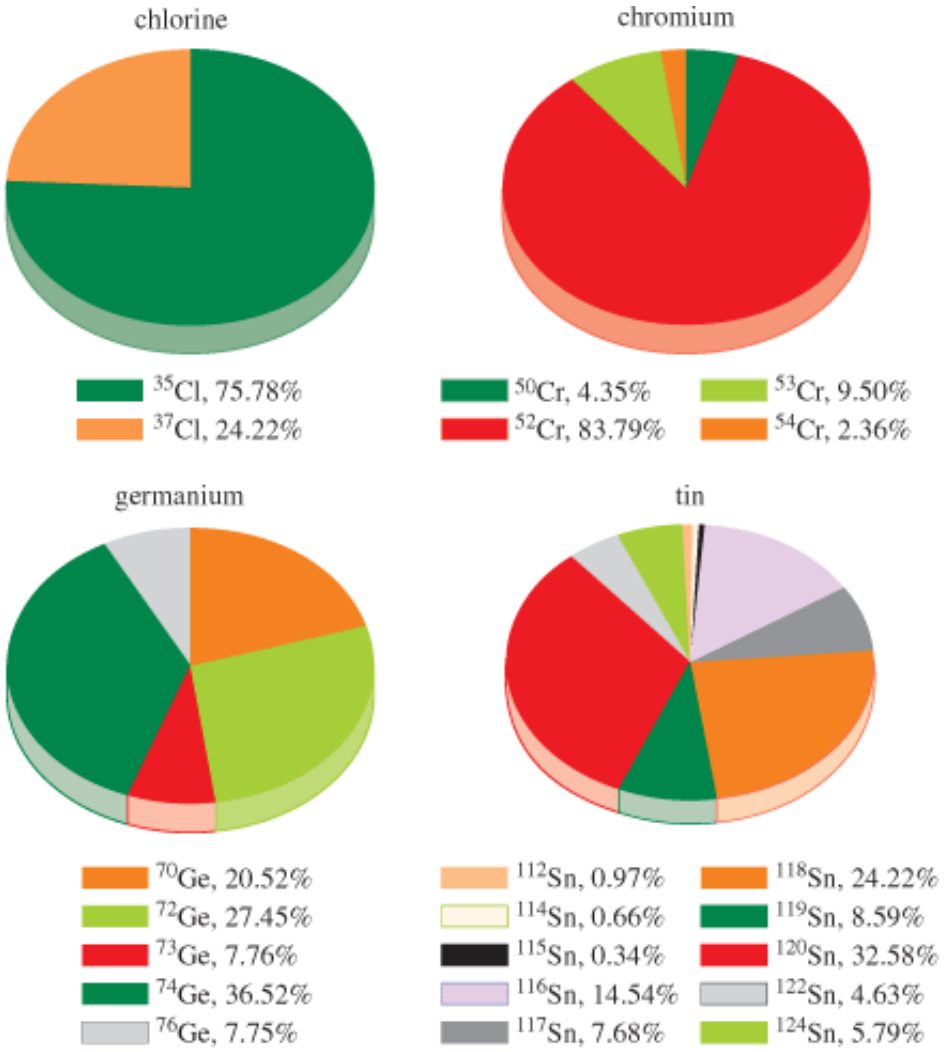


FIGURE 1.11 The natural abundances of the isotopes of chlorine, Cl, chromium, Cr, germanium, Ge, and tin, Sn, illustrate the diversity of isotopic distributions. The mass number and relative abundance of each isotope are indicated.

While the distribution of isotopes in samples of most elements is essentially constant, there are ten elements (H, Li, B, C, N, O, Si, S, Cl and Tl) which show substantial variation in their isotopic compositions, depending on the source of the element. Consider, for example, hydrogen. As we have seen, this element has three isotopes, ^{1}H, ^{2}H and ^{3}H, the last of which we will neglect in this discussion because of its negligible abundance. If we analysed samples of atmospheric methane and natural gas, we would find that the proportion of the ^{2}H isotope in the hydrogen atoms of the former would be greater than that in the latter, and hence the average atomic mass of H in the two samples would be different. Therefore, instead of quoting a single value for the average atomic mass of hydrogen, a range of values of atomic mass is given [1.007 84 u; 1.008 11 u], which corresponds to the lowest and highest values measured in natural samples. Table 1.3 gives the range of atomic mass values for these ten elements, together with the conventional atomic masses which can be used when the source of the sample is unknown.

TABLE 1.3 Atomic Mass Ranges and Conventional Atomic Masses for H, Li, B, C, N, O, Si, S, Cl and Tl

Element name	Symbol	Atomic number	Atomic mass range (u)	Conventional atomic mass (u)
hydrogen	H	1	[1.007 84; 1.008 11]	1.008
lithium	Li	3	[6.938; 6.997]	6.94

boron	B	5	[10.806; 10.821]	10.81
carbon	C	6	[12.0096; 12.0116]	12.011
nitrogen	N	7	[14.006 43; 14.007 28]	14.007
oxygen	O	8	[15.999 03; 15.999 77]	15.999
silicon	Si	14	[28.084; 28.086]	28.085
sulfur	S	16	[32.059; 32.076]	32.06
chlorine	Cl	17	[35.446; 35.457]	35.45
thallium	Tl	81	[204.382; 204.385]	204.38

In this book, we will use the conventional atomic masses listed in table 1.3 in any calculations involving these ten elements.

WORKED EXAMPLE 1.3

Calculating Average Atomic Masses from Isotopic Abundances

Naturally occurring titanium, Ti, is a mixture of five isotopes and has the following isotopic composition:

$$^{46}_{22}\text{Ti}(8.25\%),\ ^{47}_{22}\text{Ti}(7.44\%),\ ^{48}_{22}\text{Ti}(73.72\%),\ ^{49}_{22}\text{Ti}(5.41\%),\ ^{50}_{22}\text{Ti}(5.18\%)$$

The atomic masses of the isotopes are as follows:

$$^{46}_{22}\text{Ti}(45.9526316\ \text{u}),\ ^{47}_{22}\text{Ti}(46.9517631\ \text{u}),\ ^{48}_{22}\text{Ti}(47.9479463\ \text{u}),\ ^{49}_{22}\text{Ti}(48.9478700\ \text{u}),\ ^{50}_{22}\text{Ti}(49.9447912\ \text{u})$$

Use this information to calculate the average atomic mass of titanium.

Analysis

In a sample containing many atoms of titanium, 8.25% of the total mass is contributed by atoms of ^{46}Ti, 7.44% by atoms of ^{47}Ti, 73.72% by atoms of ^{48}Ti, 5.41% by atoms of ^{49}Ti and 5.18% by atoms of ^{50}Ti. This means that, when we calculate the mass of the hypothetical 'average atom' of Ti, we have to weight it according to both the masses of the isotopes and their relative abundance. (Keep in mind, of course, that such an atom does not really exist. This is just a simple way to see how we can calculate the average atomic mass of this element.)

Solution

We will calculate 8.25% of the mass of an atom of ^{46}Ti, 7.44% of an atom of ^{47}Ti, 73.72% of an atom of ^{48}Ti, 5.41% of an atom of ^{49}Ti and 5.18% of an atom of ^{50}Ti. Adding these contributions gives the total mass of the 'average atom'. Therefore:

$$\begin{aligned}\text{average atomic mass of Ti} &= (0.0825 \times 45.952\,631\,6\text{ u}) + (0.0744 \times 46.951\,763\,1\text{ u}) + \\ &\quad (0.7372 \times 47.947\,946\,3\text{ u}) + (0.0541 \times 48.947\,870\,0\text{ u}) + \\ &\quad (0.0518 \times 49.944\,791\,2\text{ u}) \\ &= 47.687\text{u}\end{aligned}$$

Is our answer reasonable?

By far the most abundant isotope is ^{48}Ti, so we would expect the average atomic mass to be close to the mass of this isotope. Our calculated average atomic mass, 47.867 u, is indeed just less than the mass of the ^{48}Ti isotope (47.947 946 3 u), because the lighter ^{46}Ti and ^{47}Ti isotopes are slightly more abundant than the heavier ^{49}Ti and ^{50}Ti isotopes. Hence, we can feel confident our answer is correct.

Chemistry Research

The Open Pool Australian Light Water Reactor

As we have seen in this chapter, some atomic nuclei are radioactive and decay spontaneously to give lighter nuclei. The energy produced in such radioactive decay processes can be harnessed in nuclear reactors to generate electricity. However, the Open Pool Australian Light Water Reactor (OPAL) in Sydney, the only nuclear reactor in Australasia, produces no electricity and is used only for scientific applications under the auspices of the Australian Nuclear Science and Technology Organisation (ANSTO). Some of these applications are outlined below.

The OPAL reactor, pictured in figures 1.12 and 1.13, uses uranium enriched in the isotope $^{235}_{92}\text{U}$ as its nuclear fuel, and consumes about 30 kg of uranium per year. When a $^{235}_{92}\text{U}$ nucleus undergoes radioactive decay, free neutrons are produced. Neutrons interact with matter in specific ways, and analysis of the results of these interactions can provide extensive information about the matter being studied. Beams of neutrons from the OPAL reactor are used as the radiation source in a number of instruments designed to investigate a variety of properties of matter. These instruments include diffractometers designed to investigate the three-dimensional arrangement of atoms (particularly hydrogen atoms) in solids, measure stress in materials, study the magnetic properties of substances, and record the motions of atoms in chemical reactions on the millisecond timescale.

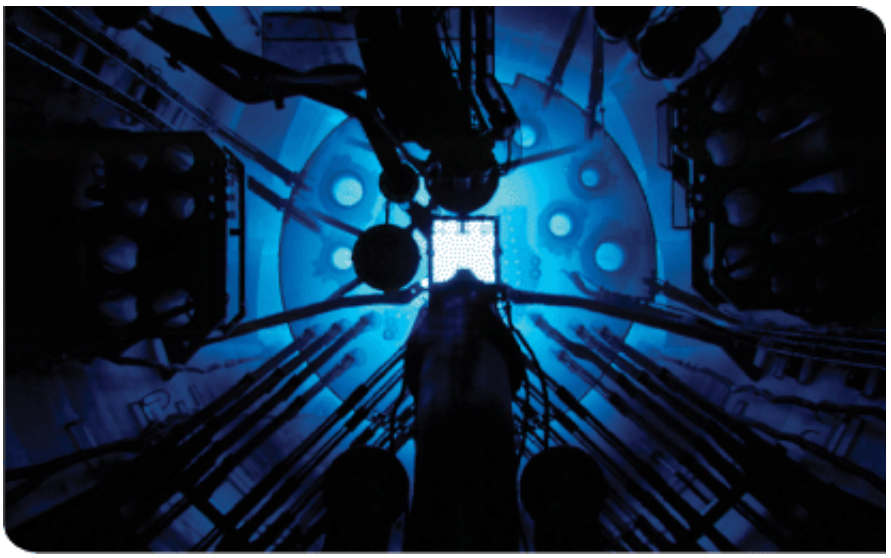


FIGURE 1.12 The blue glow due to Cherenkov radiation. This radiation is emitted when charged particles such as high energy electrons travel at a speed faster than the speed of light in the medium through which they travel (in this case, water).

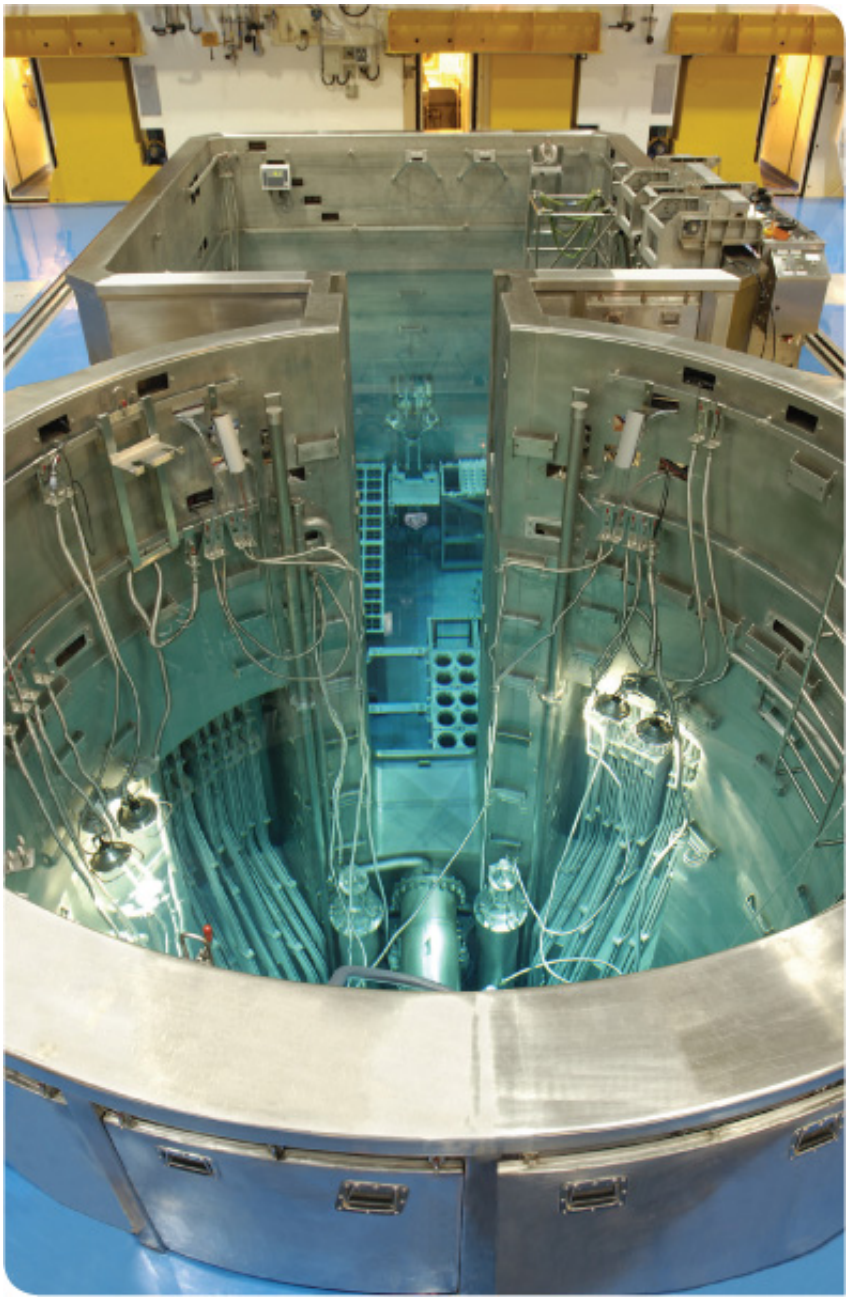


FIGURE 1.13 A view of the OPAL reactor. The reactor core lies at the bottom of the circular

section.

Neutrons can also be used to prepare macroscopic amounts of specific isotopes. As we have seen in worked example 1.2, some radioactive isotopes are useful in medical diagnosis and treatment. However, these often do not occur naturally in usable quantities owing to their short lifetimes. For example, the $^{99m}_{43}Tc$ (Tc = technetium, m = metastable) isotope, which is used in over 80% of nuclear medicine imaging procedures, must be prepared via the decay of the $^{99}_{42}Mo$ (Mo = molybdenum) isotope, which is itself radioactive and has a half life of 66 hours. The latter is prepared in the OPAL reactor by the irradiation of a uranium target with neutrons and, following purification, is then shipped to hospitals throughout Australasia. Other medical isotopes produced by the OPAL reactor are $^{153}_{62}Sm$, $^{90}_{39}Y$, $^{51}_{24}Cr$ and $^{131}_{53}I$.

In addition to the OPAL reactor, ANSTO is also equipped with particle accelerators and cyclotrons, both of which involve elementary particles travelling at very high speeds. The ANTARES (Australian National Tandem Accelerator for Applied Research) particle accelerator has been used to determine, among other things, the age of an important European historical artefact. A crown made of iron and gold at the cathedral in Monza, Italy was thought to be that of Charlemagne (c. 742–814), the first Holy Roman Emperor, but historical documents could only date it to sometime between the late Roman and the Middle Ages, a time span of several hundred years. Fortunately, the precious stones in the crown were attached using a mixture of beeswax and clay, and this allowed the use of radiocarbon dating, a process where the amount of the radioactive isotope $^{14}_{6}C$ in the beeswax could be measured. Analysis of less than 1 mg of the mixture using ANTARES placed the date of the crown's manufacture between the years 700 and 780, a time period that coincides with the life of Charlemagne.

PRACTICE EXERCISE 1.3

Aluminium atoms have a mass that is 2.248 45 times that of an atom of ^{12}C. What is the atomic mass of aluminium?

PRACTICE EXERCISE 1.4

Naturally occurring copper is composed of 69.15% ^{63}Cu and 30.85% ^{65}Cu. Atoms of ^{63}Cu have a mass of 62.9296 u and those of ^{65}Cu have a mass of 64.9278 u. Calculate the average atomic mass of copper.

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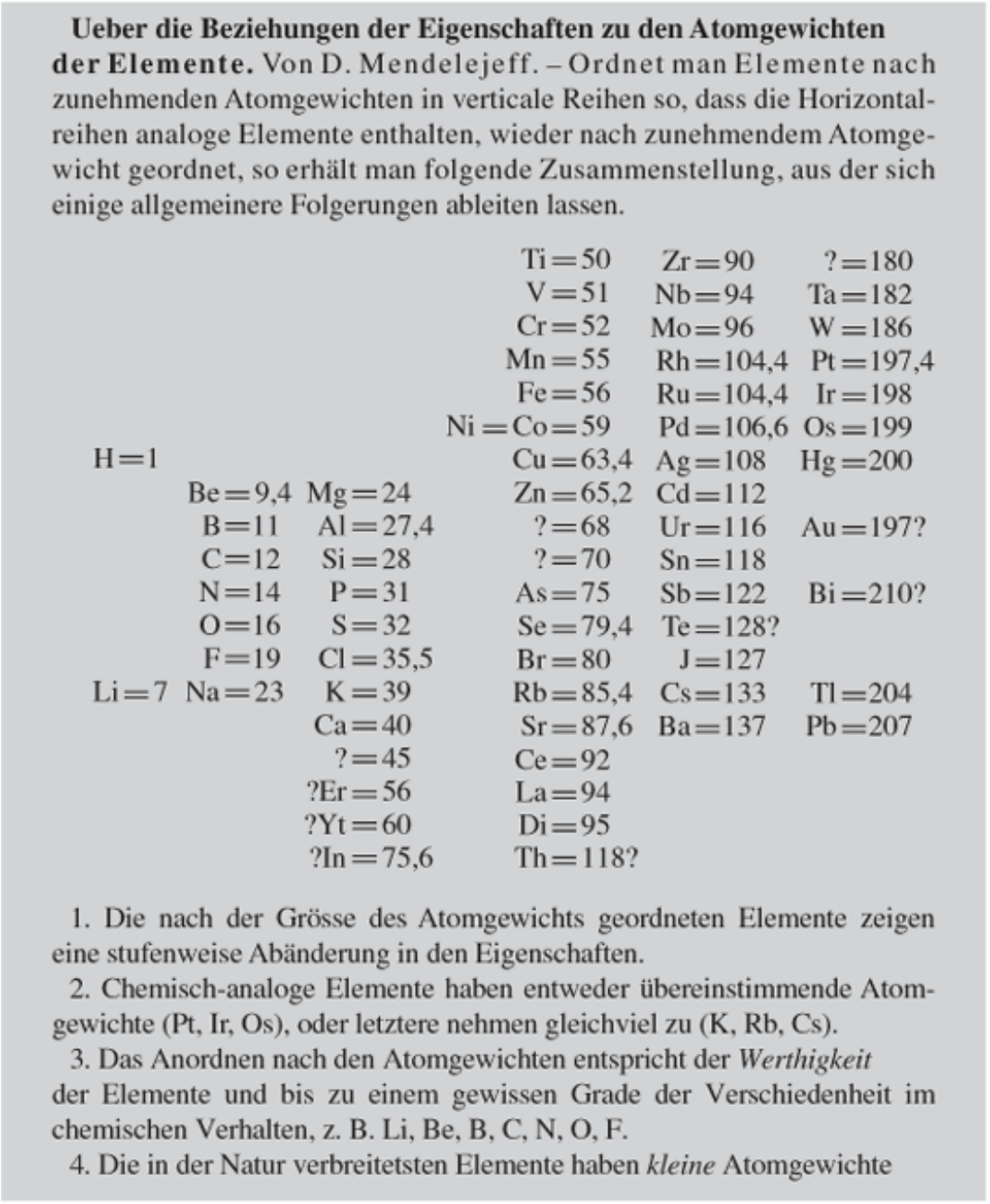
1.4 The Periodic Table of the Elements

We have already seen that the elements H, He and Li can be ordered on the basis of increasing atomic number (Z = 1, 2 and 3, respectively). If we continue such an ordering, we obtain the **periodic table of the elements**. The periodic table we use today is based primarily on the efforts of a Russian chemist, Dmitri Ivanovich Mendeleev (1834–1907, pictured in figure 1.14), and a German physicist, Julius Lothar Meyer (1830–1895). Working independently, these scientists developed similar periodic tables only a few months apart in 1869. Mendeleev is usually given the credit, however, because he published his version first.



FIGURE 1.14 Dmitri Ivanovich Mendeleev developed the periodic table. /SPL/Russell Kightley

The extraordinary thing about the work of Mendeleev and Meyer was that they knew nothing of the structure of the atom, so were unaware of the concept of atomic number, which is the basis of the modern periodic table. What they did know, however, were the atomic masses of many of the elements. Bear in mind also that not all of the elements had been discovered at this time. Mendeleev was preparing a chemistry textbook for his students at the University of St Petersburg and, looking for some pattern among the properties of the elements, he found that, when he arranged them in order of increasing atomic mass, similar chemical properties were repeated over and over at regular intervals. For instance, the elements lithium, Li, sodium, Na, potassium, K, rubidium, Rb, and caesium, Cs, are soft metals that react vigorously with water. Similarly, the elements that immediately follow each of these also constitute a set with similar chemical properties. Thus, beryllium, Be, follows lithium; magnesium, Mg, follows sodium; calcium, Ca, follows potassium; strontium, Sr, follows rubidium; and barium, Ba, follows caesium. All of these elements form compounds with oxygen having a 1 : 1 metal to oxygen ratio. Mendeleev used such observations to construct his periodic table, which is illustrated in figure 1.15.



Ueber die Beziehungen der Eigenschaften zu den Atomgewichten der Elemente. Von D. Mendelejeff. – Ordnet man Elemente nach zunehmenden Atomgewichten in verticale Reihen so, dass die Horizontalreihen analoge Elemente enthalten, wieder nach zunehmendem Atomgewicht geordnet, so erhält man folgende Zusammenstellung, aus der sich einige allgemeinere Folgerungen ableiten lassen.

			Ti = 50	Zr = 90	? = 180	
			V = 51	Nb = 94	Ta = 182	
			Cr = 52	Mo = 96	W = 186	
			Mn = 55	Rh = 104,4	Pt = 197,4	
			Fe = 56	Ru = 104,4	Ir = 198	
			Ni = Co = 59	Pd = 106,6	Os = 199	
H = 1			Cu = 63,4	Ag = 108	Hg = 200	
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112		
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?	
	C = 12	Si = 28	? = 70	Sn = 118		
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?	
	O = 16	S = 32	Se = 79,4	Te = 128?		
	F = 19	Cl = 35,5	Br = 80	J = 127		
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204	
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207	
		? = 45	Ce = 92			
		?Er = 56	La = 94			
		?Yt = 60	Di = 95			
		?In = 75,6	Th = 118?			

1. Die nach der Grösse des Atomgewichts geordneten Elemente zeigen eine stufenweise Abänderung in den Eigenschaften.

2. Chemisch-analoge Elemente haben entweder übereinstimmende Atomgewichte (Pt, Ir, Os), oder letztere nehmen gleichviel zu (K, Rb, Cs).

3. Das Anordnen nach den Atomgewichten entspricht der *Werthigkeit* der Elemente und bis zu einem gewissen Grade der Verschiedenheit im chemischen Verhalten, z. B. Li, Be, B, C, N, O, F.

4. Die in der Natur verbreitetsten Elemente haben *kleine* Atomgewichte

FIGURE 1.15 Mendeleev's original periodic table, taken from the German chemistry journal *Zeitschrift für Chemie*, 1869, 12, 405–6.

At first glance, Mendeleev's original table looks little like the ‘modern’ table given in figure 1.16. However, a closer look reveals that the rows and columns have been interchanged. The elements in Mendeleev's table are arranged in order of increasing atomic mass. When the sequence is broken at the right places and stacked, the elements fall naturally into columns.

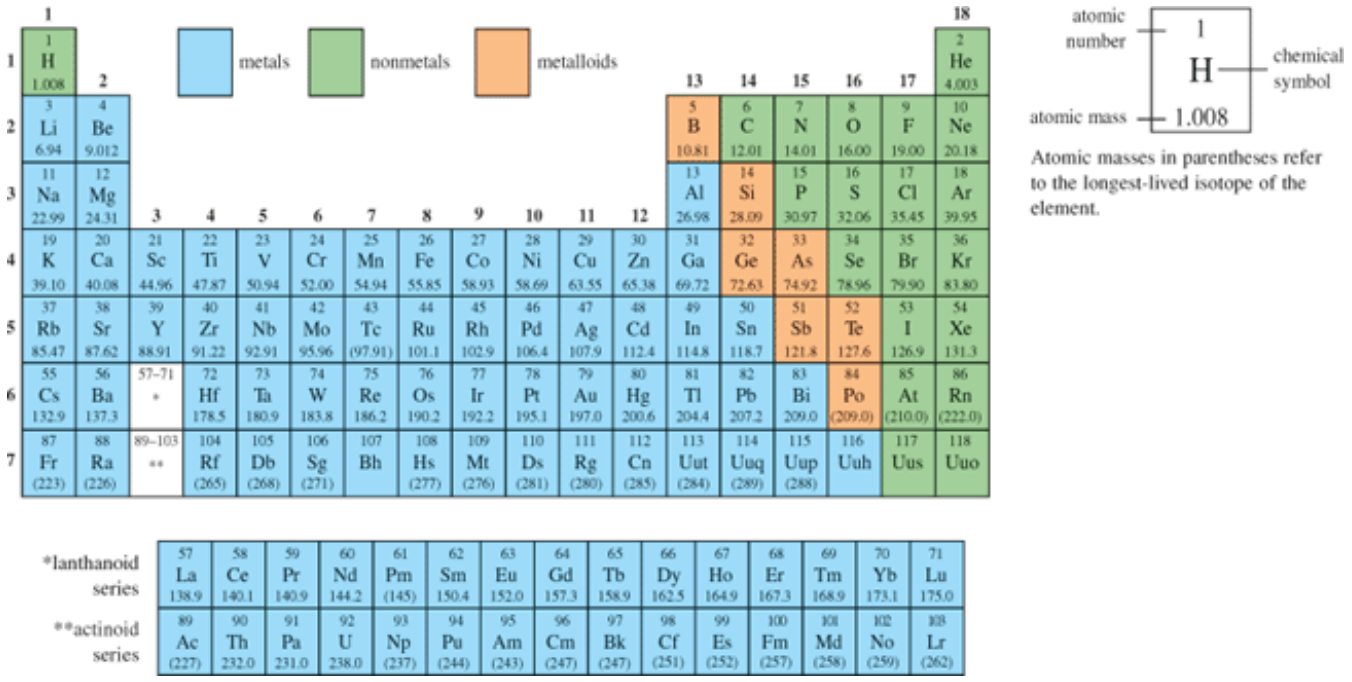


FIGURE 1.16 The periodic table of the elements. At the time of writing, 118 elements were known.

Mendeleev placed elements with similar properties in the same row even when this left occasional gaps in the table. For example, he placed arsenic, As, in the same row as phosphorus because they had similar chemical properties, even though this left gaps in other rows. In a stroke of genius, Mendeleev reasoned, correctly, that the elements that belonged in these gaps had simply not yet been discovered. In fact, on the basis of the location of these gaps, Mendeleev could predict, with astonishing accuracy, the properties of the yet-to-be-found elements, and his predictions helped serve as a guide in the search for them.

The elements tellurium, Te, and iodine, I (note that the German for 'iodine' is *jod*, which has the abbreviation J in Mendeleev's original table), caused Mendeleev some problems. According to the best estimates at that time, the atomic mass of tellurium was greater than that of iodine. Yet, if these elements were placed in the table according to their atomic masses, they would not fall into the proper rows required by their properties. Therefore, Mendeleev switched their order, believing that the atomic mass of tellurium had been incorrectly measured (it had not), and in so doing violated his ordering sequence based on atomic mass.

The table that Mendeleev developed is the basis of the one we use today, but one of the main differences is that Mendeleev's table lacks the elements helium, He, neon, Ne, argon, Ar, krypton, Kr, xenon, Xe, and radon, Rn. In Mendeleev's time, none of these elements had yet been discovered because they are relatively rare and because they have virtually no tendency to undergo chemical reactions. When these elements were finally discovered, beginning in 1894, another problem arose. Two more elements, argon, Ar, and potassium, K, did not fall into the rows required by their properties if they were placed in the table in the order required by their atomic masses. Another switch was necessary and another exception had been found. It became apparent that atomic mass was not the true basis for the periodic repetition of the properties of the elements. With Rutherford's discovery of the structure of the atom, it became apparent that the elements in the periodic table were arranged in order of increasing atomic *number*, not atomic *mass*, and when this was realised it became obvious that Te and I, and Ar and K, were in fact in the correct positions.

The Modern Periodic Table

The periodic table in use today is shown in figure 1.16, and also on the inside front cover of this book. The horizontal rows are called **periods** and are numbered 1 to 7, while the vertical columns are called **groups** and are numbered 1 to 18. The elements are arranged in order of increasing atomic number across each

period, and a new period begins after each group 18 element. The atomic masses are given (generally to four significant figures) below each chemical symbol. While the atomic mass usually increases with atomic number, you can see the exceptions we mentioned previously (Te and I, and Ar and K) as well as Co and Ni. While the isotopic composition and, therefore, the atomic masses of most elements are well established, there are some unstable elements that undergo spontaneous radioactive decay (see chapter 27). Given that the isotopic composition of such elements cannot be known, it is usual to simply quote the mass number of the longest lived isotope of the element, and these are given in parentheses in the periodic table. Note that there are discontinuities in the periodic table between elements 56 and 72, and between elements 88 and 104, and these two sets of elements are given below the table itself. The elements from 57 to 71 are called the **lanthanoids** (or, less commonly, the **rare earth elements**). Elements 89 to 103 are called the **actinoids**. The lanthanoids and actinoids are generally situated below the rest of the periodic table, simply to save space and to make the table easier to read; note that the lanthanoid and actinoid elements are chemically distinct from the rest of the elements in the periodic table, and do not belong to any of the groups 1 to 18. The lanthanoids and actinoids are sometimes called the ***f*-block elements**, and a similar terminology is also used elsewhere in the table; elements in groups 1 and 2 are called the ***s*-block elements**, elements in groups 3 to 12 are called the ***d*-block elements**, and elements in groups 13 to 18 are called the ***p*-block elements**. As we will see, *s*, *p*, *d* and *f* refer to orbitals, particular regions in space in the atom where electrons have a high probability of being found. The *d*-block elements are also called **transition metals**.

Individual groups within the periodic table are also known by particular names, although this practice is less prevalent than in the past. Group 1 elements are called **alkali metals**, group 2 elements are called **alkaline earth metals**, group 15 elements are called **pnictogens**, group 16 elements are called **chalcogens**, group 17 elements are called **halogens** and group 18 elements are called **noble gases**. Of these, only the terms halogens and noble gases are in common usage.

All elements on the periodic table belong to one of three categories — metals, nonmetals and metalloids — and the groupings are shown by the different shadings on the periodic table in figure 1.16. **Metals** are generally good conductors of heat and electricity, are malleable (can be beaten into a thin sheet) and ductile (can be drawn out into a wire), and have the usual metallic lustre. Elements that do not have these characteristics are called **nonmetals**, and the majority of these are gases at room temperature and pressure. The properties of **metalloids** lie somewhere between the metals and nonmetals. The most notable property of these elements is the fact that they tend to be semiconductors, and metalloids such as silicon, Si, and germanium, Ge, have therefore found wide use in silicon chips and transistors. Note that the classification of the recently prepared elements 116, 117 and 118 is somewhat arbitrary, as weighable quantities of these have not yet been obtained.

Naming the Elements

All of the elements in the periodic table have one-, two- or three-letter abbreviations of their names. The abbreviations of many elements are simply the first one or two letters of their names (e.g. carbon, C, oxygen, O, lithium, Li) but there are quite a number of elements for which the derivation of the abbreviation is not quite so obvious: for example, potassium, K, tin, Sn, lead, Pb, and iron, Fe. Such apparent anomalies occur because of the way that the elements were originally named. When a new element is discovered, the discoverer usually gets to suggest a name for the element, which is then ratified by IUPAC, the International Union of Pure and Applied Chemistry.

Of all the elements on the periodic table, C, S, Fe, Cu, As, Ag, Sn, Sb, Au, Hg, Pb and Bi were known to ancient civilisations so the date of their ‘discovery’ is not known. Of these, Fe, Cu, Ag, Sn, Sb, Au, Hg and Pb are abbreviations for the Latin names *ferrum*, *cuprum*, *argentum*, *stannum*, *stibium*, *aurum*, *hydrargyrum* and *plumbum*. The earliest known discovery of an element was that of phosphorus, P. It was isolated in 1669 by Hennig Brand from the distillation of urine (he was apparently trying to make silver or gold — unsuccessfully, of course!) and was named after the Greek word *phosphoros*, meaning ‘bringer of light’, as the element glows in the dark. Elements have been named after countries (germanium, francium, americium,

polonium) and even after the places they were first discovered; the Swedish town of Ytterby has the distinction of having four elements (erbium, Er, ytterbium, Yb, yttrium, Y, and terbium, Tb) named after it, as these were first found in deposits close to the town. Surprisingly few elements have been named after people; at present, only 15 people have been immortalised on the periodic table, and they are listed in table 1.4. It is interesting to note that none of the people listed discovered the element named after them.

TABLE 1.4 People after whom elements have been named

Name	Brief biography	Element named
Vasilii Yefrafovich von Samarski-Bykhovets (1803–1870)	Chief of staff of the Russian Corps of Mining Engineers	samarium, Sm (element 62)
Johan Gadolin (1760–1852)	Finnish chemist; first person to isolate a lanthanoid element	gadolinium, Gd (element 64)
Pierre (1859–1906) and Marie (1867–1934) Curie	Husband and wife scientific team; Pierre French and Marie Polish by birth; jointly won the Nobel Prize in physics in 1903	curium, Cm (element 96)
Albert Einstein (1879–1955)	Most famous scientist of the twentieth century, if not all time; German by birth; won the Nobel Prize in physics in 1921	einsteinium, Es (element 99)
Enrico Fermi (1901–1954)	Italian physicist; made great advances in the study of nuclear reactions; won the Nobel Prize in physics in 1938	fermium, Fm (element 100)
Dmitri Mendeleev (1834–1907)	Russian chemist; renowned for the development of the periodic table	mendelevium, Md (element 101)
Alfred Nobel (1833–1896)	Swedish inventor of dynamite and patron of the Nobel Prizes	nobelium, No (element 102)
Ernest Lawrence (1901–1958)	American inventor of the cyclotron; won the Nobel Prize in physics in 1939	lawrencium, Lr (element 103)
Ernest Rutherford (1871–1937)	New Zealand physicist/chemist; made seminal contributions to understanding the structure of the atom; won the Nobel Prize in chemistry in 1908	rutherfordium, Rf (element 104)
Glenn Seaborg (1912–1999)	American chemist; first prepared many of the elements beyond uranium in the periodic table; won the Nobel Prize in chemistry in 1951	seaborgium, Sg (element 106)
Niels Bohr (1885–1962)	Danish physicist; studied electronic energy levels within atoms, which aided our understanding of the atom; won the Nobel Prize in physics in 1922	bohrium, Bh (element 107)
Lise Meitner (1878–1968)	Austrian physicist; made fundamental discoveries concerning nuclear fission; controversially never awarded a Nobel Prize	meitnerium, Mt (element 109)
Wilhelm Röntgen (1845–1923)	German physicist; discoverer of X-rays; winner of the inaugural Nobel Prize in physics in 1901	röntgenium, Rg (element 111)
Nicolaus Copernicus (1473–1543)	Polish astronomer; proposed that the Sun, rather than the Earth, was the centre of the solar system	copernicium, Cn (element

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1.5 Electrons in Atoms

While we have touched briefly on the concept of electrons, we have to this point concentrated primarily on the nucleus of the atom and the way in which the number of protons in the nucleus determines the chemical identity of the atom. However, many of the chemical properties of an atom and, most importantly, its chemical reactivity are determined not by the nucleus but by the electrons.

One of the most interesting things about electrons is that we cannot really say *exactly* where they are at any particular time, so we usually talk about their *most probable* locations. Electrons occupy regions of space called **orbitals** in atoms. Each orbital has a characteristic electron distribution and energy. For example, the lowest energy situation for a hydrogen atom, the **ground state**, occurs when the single electron occupies an orbital in which its most probable distance from the nucleus is 5.29×10^{-11} m. This orbital has a spherical electron distribution. If the ground state hydrogen atom absorbs a specific amount of energy, the electron can be promoted to a higher energy orbital to form an **excited state** in which the electron lies, on average, further from the nucleus. Such a process is called an **electronic transition**, and the electron distribution in the higher energy orbital is dumbbell shaped. Similarly, the electron in an excitedstate hydrogen atom can move to a lower energy orbital through the emission of energy, often in the form of light. Indeed, as we will see in chapter 4, such processes are the basis behind both neon and sodium vapour lights. Orbitals have definite energies, so the energy of any electron is dictated by the energy of the orbital it occupies; therefore, an electron in an atom can have only certain well-defined energies. This is a fundamental principle of the science of quantum mechanics called **quantisation**, a phenomenon first proposed by the German physicist Max Planck (1858–1947, Nobel Prize in physics, 1918) in 1900. We will learn more about the quantisation of energy in chapter 4.

Electrons have a single negative charge, and the overall charge on any chemical species is determined by the number of electrons relative to the number of protons; for example, the peroxide ion, O_2^{2-}, has a 2- charge because there are two more electrons than protons in the ion. Similarly, the Li^+ ion contains three protons and two electrons, so it has a single positive charge. In addition to their negative charge, all electrons have an intrinsic property called **spin**. This can have one of two values, which are commonly called ‘spin up’ and ‘spin down’ and are often depicted as follows:

↑ (spin up)

↓ (spin down)

Each orbital within an atom can contain a maximum of two electrons, one of which must be spin up and the other spin down.

Chemists are interested in electrons because they constitute the chemical bonds that hold atoms together in molecules. Covalent chemical bonds usually consist of one, two or three pairs of electrons shared between atoms, each pair containing electrons of opposite spin. For a molecule to undergo a chemical reaction, these bonds must usually be broken and new ones made; this requires a reorganisation of the electron pairs between the reactant and product molecules, and the ease with which this can be done determines how fast the reaction occurs. Reactions in which one or more electrons are transferred between chemical species are also known; such reactions, known as **redox reactions**, are important in a huge number of chemical and biochemical processes; in fact, as you are reading this, iron ions and oxygen molecules are busy exchanging electrons in your blood to transport oxygen around your body.

Because of their importance in both chemical structure and chemical reactivity, electrons occupy a central place in chemistry. In the remaining chapters of this book, we will learn more of the properties of atoms and molecules that are predominantly dictated by electrons.

We have learned much about the atom in the years since Rutherford's seminal experiment. Indeed, we

have detailed only the very basics of atomic structure in the preceding pages; later chapters will outline some of the amazing complexity of the atom. For the moment, it is sufficient for you to appreciate that the atom is composed of a positively charged central nucleus containing protons and neutrons, which is surrounded by negatively charged electrons that can undergo transitions only between well-defined energy levels. And with only 118 different types of these building blocks, we can construct the universe.

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SUMMARY

Atoms, Molecules, Ions, Elements and Compounds

Atoms are a fundamental building block of all matter. Uncharged collections of atoms bonded together in a definite structure are called molecules. These are held together by covalent bonds that share electrons between adjacent atoms. Ions are charged chemical species that may be derived from both atoms and molecules. Cations are positively charged, while anions are negatively charged. Elements comprise only a single type of atom, while compounds are made up of two or more chemical elements. All of these different chemical entities can be involved as reactants in chemical reactions, in which they are transformed to products.

The Atomic Theory

All matter is composed of atoms. The existence of atoms was proposed on the basis of:

- the law of conservation of mass. Mass is conserved in chemical reactions.
- the law of definite proportions. Elements are combined in the same proportions by mass in any particular compound.
- the law of multiple proportions. When two elements form more than one compound, the different masses of one element that combine with the same mass of the other element are in the ratio of small whole numbers.

Dalton's atomic theory was the first to propose the existence of atoms on the basis of scientific observations. The basic tenets of his theory are:

1. Matter consists of tiny particles called atoms.
2. Atoms are indestructible. In chemical reactions, the atoms rearrange but they do not themselves break apart.
3. In any sample of a pure element, all the atoms are identical in mass and other properties.
4. The atoms of different elements differ in mass and other properties.
5. When atoms of different elements combine to form a given compound, the constituent atoms in the compound are always present in the same fixed numerical ratio.

Dalton's theory allows us to use chemical equations, in which reactants and products are separated by an arrow, to describe chemical reactions. Such equations are balanced when they contain the same number of each type of atom on each side of the arrow.

Modern apparatus enables us to ‘see’ individual atoms, and atomic theory is now atomic fact.

The Structure of the Atom

Although Dalton proposed the atom to be indivisible, experiments in the late nineteenth century showed this was not the case. The negatively charged electron was the first subatomic particle to be discovered, while Rutherford's gold foil experiment, in which a thin gold sheet was bombarded with alpha particles, gave evidence for a small, positively charged nucleus. The positive charge is due to subatomic particles called protons, and the number of these in the nucleus determines the identity of the atom in question. The third component of the atom, the neutron, was predicted by Rutherford and found by Chadwick. The atom thus comprises three subatomic particles, the electron, proton and neutron, the latter two collectively being called nucleons. Each type of atom is designated by a chemical symbol, which is determined by its atomic number (Z), the number of protons in the nucleus. The mass number (A) is equal to the number of protons plus the number of neutrons in the nucleus. The terminology used to depict an atom of any element X is ${}^{A}_{Z}X$. All atoms with the same Z are of the same element; however, atoms of the same element can differ in the number of neutrons in the nucleus, and this gives rise to

isotopes. Isotopes can be either radioactive (i.e. they decay spontaneously) or stable. A radioactive nucleus is called a radionuclide, while a nuclide is the name given to any atomic nucleus. We can measure atomic mass in atomic mass units (u), where 1 u = 1.660 54 × 10^{-27} kg, and is equal to $\frac{1}{12}$ of the mass of one atom of ^{12}C. The atomic mass of any sample of atoms is the weighted average of the masses of the isotopes present in the sample.

The Periodic Table of the Elements

The periodic table of the elements contains the 118 known elements arranged in order of increasing atomic number, and was developed by both Mendeleev and Meyer. The horizontal rows are called *periods* and the vertical columns *groups*. Elements in the same group tend to have similar chemical properties. The periodic table is divided into sections according to the electron configuration of the elements, namely the *s*-block elements, the *p*-block elements, the *d*-block elements and the *f*-block elements. The *f*-block elements are divided into the lanthanoids (also sometimes called the rare earth elements) and the actinoids, while the *d*-block elements are also called the transition metals. The elements in certain groups in the periodic table have special names: group 1 elements are called alkali metals, group 2 elements are called alkaline earth metals, group 15 elements are called pnictogens, group 16 elements are called chalcogens, group 17 elements are called halogens and group 18 elements are called noble gases. The elements of the periodic table can be classified as metals, nonmetals, or metalloids.

Electrons in Atoms

Electrons occupy regions of space called orbitals. The lowest energy arrangement of electrons in the orbitals of an atom is called the ground state. Electrons can be promoted to higher energy orbitals by absorption of energy to give excited states; conversely, electrons in higher energy orbitals can move to lower energy orbitals with the emission of energy, often as light. Such processes are called electronic transitions. The energies of electrons in atoms are determined by the energies of the orbitals within the atom, so electrons in atoms can have only certain well-defined energies. This is called quantisation, a fundamental principle of quantum mechanics. Electrons have a single negative charge, and one of two possible spins. An orbital in an atom can hold a maximum of two electrons, which must be of opposite spin. Covalent bonds comprise one, two or three pairs of electrons. Chemical reactions often involve reorganising these electrons in bond-making and bond-breaking processes. Redox reactions involve the transfer of one or more electrons between chemical species.

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KEY CONCEPTS AND EQUATIONS

The law of conservation of mass *(section 1.2)*

The total mass of reactants present before a reaction starts equals the total mass of products after the reaction is finished. We can use this law to check whether we have accounted for all the substances formed in a reaction.

The law of definite proportions *(section 1.2)*

If we know the mass ratio of the elements in one sample of a compound, the ratio will be the same in a different sample of the same compound.

The law of multiple proportions *(section 1.2)*

In different compounds containing the same two elements, the different masses of one element that combine with the same mass of the other element are in a ratio of small whole numbers.

Atomic mass *(section 1.3)*

This is used to determine the mass of any atom relative to that of the ^{12}C isotope.

Periodic table of the elements *(section 1.4)*

This is a table of the chemical elements arranged in order of increasing atomic number. We can use the periodic table to figure out whether a particular element is a metal, nonmetal or metalloid, predict its chemical reactivity, calculate its number of protons and electrons, obtain its atomic mass and so on. In fact, all of chemistry is contained within the periodic table.

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REVIEW QUESTIONS

Atoms, Molecules, Ions, Elements and Compounds

1.1 Define the following terms: atom, covalent bond, ion, cation, anion, element, compound, reactant, chemical reaction, product.

The Atomic Theory

1.2 Name and state the three laws of chemical combination discussed in this chapter.

1.3 Which postulate of Dalton's atomic theory is based on the law of conservation of mass? Which is based on the law of definite proportions?

1.4 Which of the laws of chemical combination is used to define the term ‘compound’?

1.5 In your own words, describe how Dalton's atomic theory explains the law of conservation of mass and the law of definite proportions.

The Structure of the Atom

1.6 Write the symbol for the isotope that forms the basis of the atomic mass scale. What is the mass of this atom expressed in atomic mass units?

1.7 What are the names, symbols, electric charges and masses (expressed in u) of the three chemically important subatomic particles introduced in this chapter?

1.8 Where in an atom is nearly all of its mass concentrated? Explain your answer in terms of the particles that contribute to this mass.

1.9 What is a nucleon? Which ones have we studied in this chapter?

1.10 Define the terms ‘atomic number’ and ‘mass number’.

1.11 In terms of the structures of atoms, how are isotopes of the same element alike? How do they differ?

1.12 Consider the symbol ${}^{A}_{Z}X$, where X stands for the chemical symbol for an element. What information is given by (a) A and (b) Z?

1.13 Write the symbols of the isotopes that contain the following. (Use the table of atomic numbers printed inside the front cover, as needed.)

(a) an isotope of iodine having atoms with 78 neutrons

(b) an isotope of strontium having atoms with 52 neutrons

(c) an isotope of caesium having atoms with 82 neutrons

(d) an isotope of fluorine having atoms with 9 neutrons

The Periodic Table of the Elements

1.14 What is the chemical symbol for each of the following elements?

(a) chlorine,

(b) sulfur,

(c) iron,

(d) silver,

(e) sodium,

(f) phosphorus,

(g) iodine,

(h) copper,

(i) mercury,

(j) calcium

1.15 What is the name of each of the following elements?

(a) K,
(b) Zn,
(c) Si,
(d) Sn,
(e) Mn,
(f) Mg,
(g) Ni, (h) Al,
(h) C,
(i) N

1.16 On what basis did Mendeleev construct his periodic table? On what basis are the elements arranged in the modern periodic table?

1.17 In the periodic table, what is a ‘period’? What is a ‘group’?

1.18 Why did Mendeleev leave gaps in his periodic table?

1.19 Which is better related to the chemistry of an element: its mass number or its atomic number? Give a brief explanation in terms of the basis for the periodic table.

1.20 On the basis of their positions in the periodic table, why is it not surprising that ^{90}Sr, a dangerous radioactive isotope of strontium, replaces calcium in newly formed bones?

1.21 In the refining of copper, sizable amounts of silver and gold are recovered. Why is this not surprising?

1.22 Why would you reasonably expect cadmium to be a contaminant in zinc but not in silver?

1.23 Based on discussions in this chapter, explain why it is unlikely that scientists will discover a new element, never before observed, having an atomic mass of approximately 73.

1.24 In each of the following sets of elements, state which fits the description in parentheses.

(a) Ce, Hg, Si, O, I (halogen)
(b) Pb, W, Ca, Cs, P (transition metal)
(c) Xe, Se, H, Sr, Zr (noble gas)
(d) Th, Sm, Ba, F, Sb (lanthanoid element)
(e) Ho, Mn, Pu, At, Na (actinoid element)

1.25 Which property of metals allows them to be drawn into wire?

1.26 Gold can be hammered into sheets so thin that some light can pass through them. Which property of gold allows such thin sheets to be made?

1.27 Which nonmetals occur as monatomic gases (gases that exist as single atoms)?

1.28 Which two elements exist as liquids at room temperature and pressure?

1.29 Which physical property of metalloids distinguishes them from metals and nonmetals?

1.30 Sketch the shape of the periodic table and mark off those areas where we find

(a) metals,
(b) nonmetals and
(c) metalloids.

Electrons in Atoms

1.31 What is an orbital?

1.32 When electrons of opposite spins occupy an orbital, we say that their spins are paired. Molecules with odd numbers of electrons, therefore, cannot have all of the electron spins paired, and we say that they have unpaired spins. Which of the following molecules *must* have unpaired spins: N_2, F_2, CO, NO, NO_2?

1.33 What is the difference between an atom in its ground state and an atom in its excited state, given that the numbers of protons, neutrons and electrons in both situations are the same?

1.34 Quantisation is very important on the atomic scale but, in the large scale of our everyday lives, we barely notice it. Why do you think this might be so?

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REVIEW PROBLEMS

1.35 Laughing gas is a compound formed from nitrogen and oxygen in which there is 1.75 g of nitrogen for every 1.00 g of oxygen. The compositions of several nitrogen–oxygen compounds follow. Which of these is laughing gas?

(a) 6.35 g nitrogen, 7.26 g oxygen

(b) 4.63 g nitrogen, 10.58 g oxygen

(c) 8.84 g nitrogen, 5.05 g oxygen

(d) 9.62 g nitrogen, 16.5 g oxygen

(e) 14.3 g nitrogen, 40.9 g oxygen

1.36 One of the substances used to melt ice on footpaths and roads in cold climates is calcium chloride. In this compound, calcium and chlorine are combined in a ratio of 1.00 g of calcium to 1.77 g of chlorine. Which of the following calcium–chlorine mixtures will produce calcium chloride with no calcium or chlorine left over after the reaction is complete?

(a) 3.65 g calcium, 4.13 g chlorine

(b) 0.856 g calcium, 1.56 g chlorine

(c) 2.45 g calcium, 4.57 g chlorine

(d) 1.35 g calcium, 2.39 g chlorine

(e) 5.64 g calcium, 9.12 g chlorine

1.37 Ammonia is composed of hydrogen and nitrogen in a ratio of 9.33 g of nitrogen to 2.00 g of hydrogen. If a sample of ammonia contains 6.28 g of hydrogen, what mass of nitrogen does it contain?

1.38 A compound of phosphorus and chlorine used in the manufacture of a flame retardant treatment for fabrics contains 1.20 g of phosphorus for every 4.12 g of chlorine. Suppose a sample of this compound contains 6.22 g of chlorine. What mass of phosphorus does it contain?

1.39 Refer to the data about ammonia in question 1.37. If 4.56 g of nitrogen combined completely with hydrogen to form ammonia, what mass of ammonia would be formed?

1.40 Refer to the data about the phosphorus–chlorine compound in question 1.38. If 12.5 g of phosphorus combined completely with chlorine to form this compound, what mass of the compound would be formed?

1.41 Molecules of a certain compound of nitrogen and oxygen contain one atom each of N and O. In this compound, there is 1.143 g of oxygen for each 1.000 g of nitrogen. Molecules of a different compound of nitrogen and oxygen contain one atom of N and two atoms of O. What mass of oxygen would be combined with each 1.000 g of nitrogen in the second compound?

1.42 Tin forms two compounds with chlorine. In one of them (compound 1), there are two Cl atoms for each Sn atom; in the other (compound 2), there are four Cl atoms for each Sn atom. When combined with the same mass of tin, what would be the ratio of the masses of chlorine in the two compounds? In compound 1, 0.597 g of chlorine is combined with each 1.000 g of tin. What mass of chlorine would be combined with 1.000 g of tin in compound 2?

1.43 The mass corresponding to 1 atomic mass unit is $1.660\ 54 \times 10^{-24}$ g. Use this value to calculate the mass in grams of 1 atom of ^{12}C.

1.44 Use the mass corresponding to the atomic mass unit given in question 1.43 to calculate the mass of 1 atom of sodium.

1.45 The chemical substance in natural gas is a compound called methane. Its molecules are composed of carbon and hydrogen and each molecule contains four atoms of hydrogen and one atom of carbon. In this compound, 0.335 97 g of hydrogen is combined with 1.0000 g of ^{12}C. Use this

information to calculate the atomic mass of the element hydrogen.

1.46 Element *X* forms a compound with oxygen in which there are two atoms of *X* for every three atoms of O. In this compound, 1.125 g of *X* is combined with 1.000 g of oxygen. Use the average atomic mass of oxygen to calculate the average atomic mass of *X*. Use your calculated atomic mass to identify element *X*.

1.47 If an atom of ^{12}C had been assigned a relative mass of 24.0000 u, determine the average atomic mass of hydrogen relative to this mass.

1.48 An atom of ^{109}Ag has a mass that is 9.0754 times that of a ^{12}C atom. What is the atomic mass of this isotope of silver expressed in atomic mass units?

1.49 Naturally occurring magnesium is composed of 78.99% of ^{24}Mg (with an atomic mass of 23.9850 u), 10.00% of ^{25}Mg (with an atomic mass of 24.9858 u) and 11.01% of ^{26}Mg (with an atomic mass of 25.9826 u). Use this information to calculate the average atomic mass of magnesium.

1.50 Give the numbers of neutrons, protons and electrons in the atoms of each of the following isotopes. (Use the periodic table printed inside the front cover, as needed.)

(a) ^{226}Ra

(b) ^{14}C

(c) $^{206}_{82}Pb$

(d) $^{23}_{11}Na$

1.51 Give the numbers of electrons, protons and neutrons in the atoms of each of the following isotopes. (Consult the periodic table printed inside the front cover as necessary.)

(a) ^{137}Cs

(b) ^{131}I

(c) $^{238}_{92}U$

(d) $^{197}_{79}Au$

1.52 From the elements Ne, Cs, Sr, Br, Co, Pu, In and O, choose one that fits each of the following descriptions.

(a) a group 2 metal

(b) an element with properties similar to those of aluminium

(c) a transition metal

(d) a noble gas

(e) an actinoid

1.53 Write the names and chemical symbols for three examples of each of the following:

(a) halogens,

(b) alkali metals,

(c) actinoids and

(d) noble gases.

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ADDITIONAL EXERCISES

1.54 An atom of an element has 25 protons in its nucleus.

(a) Is the element a metal, a nonmetal or a metalloid?

(b) On the basis of the average atomic mass, write the symbol for the element's most abundant isotope.

(c) How many neutrons are in the isotope you described in (b)?

(d) How many electrons are in an atom of this element?

(e) How many times heavier than ^{12}C is the average atom of this element?

1.55 Elements *X* and *Y* form a compound in which there is one atom of *X* for every four atoms of *Y*. When these elements react, it is found that 1.00 g of *X* combines with 5.07 g of *Y*. When 1.00 g of *X* combines with 1.14 g of O, it forms a compound containing two atoms of O for each atom of *X*. Calculate the atomic mass of *Y*.

1.56 An iron nail is composed of four isotopes with the percentage abundances and atomic masses given in the following table. Calculate the average atomic mass of iron.

Isotope	Percentage abundance	Atomic mass (u)
^{54}Fe	5.80	53.9396
^{56}Fe	91.72	55.9349
^{57}Fe	2.20	56.9354
^{58}Fe	0.28	57.9333

1.57 Rust contains an iron–oxygen compound in which there are three oxygen atoms for each two iron atoms. In this compound, the iron to oxygen mass ratio is 2.325 : 1.000. Another compound of iron and oxygen contains these elements in the ratio of 2.616 : 1.000. What is the ratio of iron to oxygen atoms in the second iron–oxygen compound?

1.58 One atomic mass unit corresponds to a mass of $1.660\ 54 \times 10^{-24}$ g. Calculate the mass, in grams, of one atom of magnesium. What is the mass of one atom of iron, expressed in grams? Use these two answers to determine how many atoms of Mg are in 24.305 g of magnesium and how many atoms of Fe are in 55.847 g of iron. Compare your answers. What conclusions can you draw from the results of these calculations? Without actually performing any calculations, how many atoms do you think would be in 40.078 g of calcium?

1.59 The diameter of a typical atom is 10^{-10} m, and the diameter of a typical nucleus is 10^{-15} m. Calculate the typical atomic and nuclear volumes and determine what fraction of the volume of a typical atom is occupied by its nucleus.

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KEY TERMS

actinoids
alkali metals
alkaline earth metals
alpha particle
anion
atomic mass
atomic mass unit (u)
atomic number (*Z*)
atom
cation
chalcogens
chemical equation
chemical reaction
chemical symbol
compound
covalent bond
d-block elements
Dalton's atomic theory
electronic transition
electron
element
excited state
f-block elements
ground state
group
halogens
ion
isotopes
lanthanoids
law of conservation of mass
law of definite proportions
law of multiple proportions
mass number (*A*)
matter
metalloids
metals
molecule
neutron
noble gases
nonmetals
nucleon
nucleus
nuclide
orbital
p-block elements
periodic table of the elements
period
pnictogens
product
proton
quantisation
radioactive
radionuclide
rare earth elements
reactant
redox reaction
s-block elements
spin
subatomic particles
transition metals

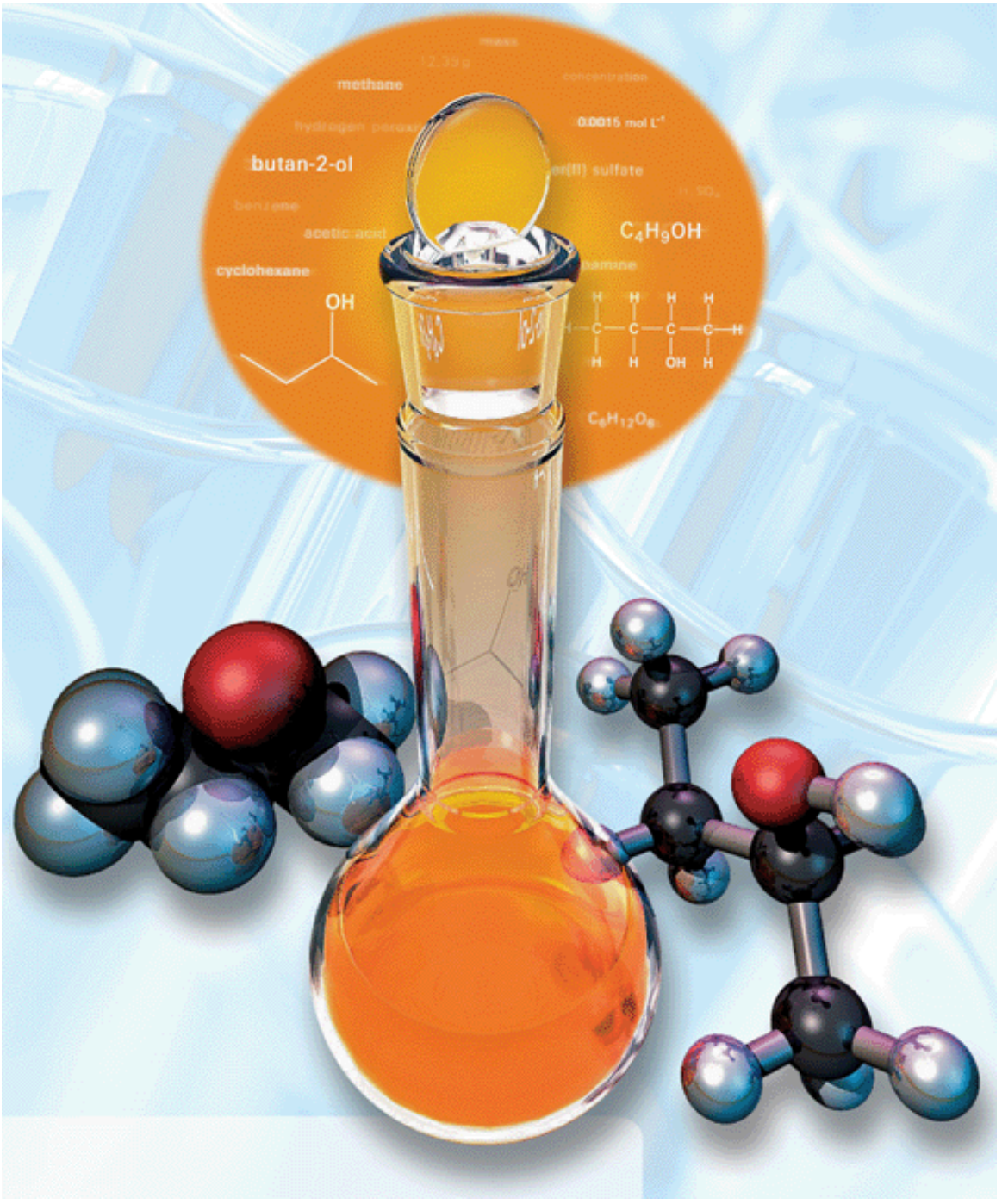
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CHAPTER

2 The Language of Chemistry

Chemistry, like any specialist discipline, has a language all its own. The language of chemistry is not merely about words; it is also about symbols, diagrams, formulae, abbreviations, equations and pictures. A working knowledge of this language is needed to be able to describe and depict chemical elements, compounds and processes, and to communicate and appreciate many of the important concepts of this science. In this chapter we will concentrate on three important areas within the broad field of the language of chemistry:

- measurement and units
- representations of molecules
- nomenclature, the way in which we name chemical species.



KEY TOPICS

2.1 Measurement
2.2 Representations of molecules
2.3 Nomenclature

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2.1 Measurement

Chemistry is a science of measurement. Whenever we weigh a certain mass of a particular substance, evaluate the rate of a chemical reaction or determine the cell potential of an electro-chemical cell, we are making measurements. Measurements always have a unit and always have an associated uncertainty. A measurement that is missing either of these is meaningless.

SI Units

On 23 September 1999, NASA, the National Aeronautics and Space Administration of the USA, lost contact with its *Mars Climate Orbiter* spacecraft (figure 2.1) as it was about to enter orbit around Mars. The orbiter eventually crashed into the planet. The loss was attributed to an error that resulted from an incorrect use of units; one team of scientists working on the project used imperial units (feet, pounds) while others, working in a different location, used SI units (metres, kilograms) in calculating the thrust necessary to place the spacecraft into orbit around Mars. Similarly, on 23 July 1983, Air Canada flight 143, a Boeing 767 with 69 people on board, ran out of fuel at 12 000 m because the fuel had been measured in incorrect units. Thankfully, the pilots were able to glide to a successful landing.

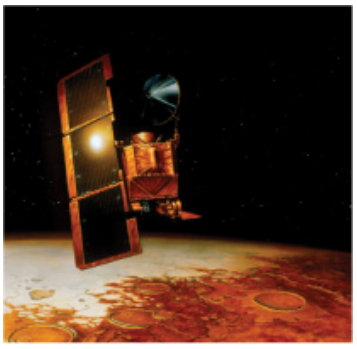


FIGURE 2.1 NASA's *Mars Climate Orbiter* crashed into Mars after calculations were made using inconsistent units.

These two examples illustrate the significance of units in our modern world. A **unit** is a specific standard quantity of a particular property, against which all other quantities of that property can be measured. For example, we can measure all lengths with respect to the length of 1 metre, and metre is therefore a unit of length. Humans have recognised the importance of units of measurement for thousands of years. One of the earliest documented units of measurement was the *cubit*, a unit of length used in ancient Egypt equal to the distance between the tip of the middle finger and the elbow. In fact, many units used by the ancient Egyptians were based on parts of the human body, such as the digit, the palm, the hand and the span. Obviously people come in all different shapes and sizes, so this system was far from satisfactory. Over time, a jumble of measuring systems and standards developed. For example, it is believed that in around the year 1100, England's King Henry I defined the *yard* as the distance from the end of his nose to the tip of his thumb, while 200 years later King Edward II decreed that three barleycorns laid end to end constituted an *inch*. It was in France, following the French Revolution in 1789, that a serious attempt was first made to develop an international system of units. On 22 June 1799, two pieces of platinum, one weighing exactly 1 kilogram and the other exactly 1 metre in length, were deposited in the Archives de la République in Paris, marking the introduction of what is commonly known as the metric system and what scientists call **SI (Système International) units**. The SI has a set of base units for seven measured quantities. These are given in table 2.1 along with their definitions (notice that the definition of the metre has changed since 1799; the metre is now expressed more precisely, in terms unimaginable 200 years ago).

TABLE 2.1 The Seven SI Base Units

Measurement	Unit	Symbol	Derivation
length	metre	m	The metre is the length of the path travelled by light in a vacuum during a time interval of $\frac{1}{299\,792\,458}$ of a second.
mass	kilogram	kg	The kilogram is equal to the mass of the international prototype of the kilogram.
time	second	s	The second is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the ^{133}Cs atom.
temperature	kelvin	K	The kelvin is the fraction $\frac{1}{273.16}$ of the thermodynamic temperature of the triple point of water.
amount of substance	mole	mol	The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilograms of ^{12}C. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles or specified groups of such particles.

electric current	ampere	A	The ampere is the constant current which, if maintained in two straight parallel conductors of infinite length, of negligible cross-section and placed 1 metre apart in a vacuum, would produce, between these conductors, a force of 2×10^{-7} newtons per metre of length.
luminous intensity	candela	Cd	The candela is the luminous intensity, in a given direction, of a monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of $\frac{1}{683}$ watt per steradian.

A working knowledge of the units and symbols given in table 2.1 is essential in chemistry. However, the precise definitions are generally complicated, and it is not necessary to memorise their derivations, which are given for interest only. It should be noted that, at the time of writing, proposals have been made to redefine both the mole and the kilogram. The international prototype of the kilogram (which is kept in a vault at the International Bureau of Weights and Measures near Paris) has been found to have lost about 50 μg over time, and a definition which does not involve a physical object that is subject to change is thought to be preferable. Similarly, a definition of the mole that does not involve mass has been proposed. Such redefinitions will make no difference to the use of SI units in everyday life, and will have only a miniscule impact on all but the most precise scientific measurements.

We are all familiar with the SI units for length (**metre**, m), mass (**kilogram**, kg) and time (**second**, s). The SI unit of temperature (**kelvin**, K) has absolute zero (-273.15°C), the coldest possible temperature, as its zero point. Temperature is more commonly measured in degrees Celsius — a temperature in Celsius may be converted to degrees kelvin by adding 273.15. This means that the freezing point of water, 0°C, is equal to 273.15 K, while the boiling point of water, 100°C, is 373.15 K. Note that a temperature *difference* of 1 kelvin (we do not say 1 degree kelvin) is the same as a temperature difference of 1 degree Celsius.

The SI unit of amount of substance, a concept that will be discussed in chapter 3, is the **mole** (mol), while the unit of electrical current, the **ampere**, will be discussed when we study electro-chemistry in chapter 12. The SI unit of luminous intensity (the brightness of the radiation emitted by phosphorescent and fluorescent compounds) is the **candela**.

The SI units for *any* physical quantity can be built from these seven base units. For example, there is no SI base unit for area, but we know that to calculate the area of a rectangular room we multiply its length by its width (i.e. its length in one dimension by its length in the other). Therefore, the SI unit for area is derived by multiplying the unit for length (m) by the unit for length (m) to give m^2 (metre squared, or square metre). Table 2.2 lists several derived SI units that are important in chemistry.

TABLE 2.2 SI Derived Units Commonly Used in Chemistry

Measurement	Expression in terms of simpler quantities	Unit	Expression in terms of SI base units
area	length × width[(a)]	square metre	m^2
volume	length × width × height[(a)]	cubic metre	m^3
speed, velocity	distance[(b)]/time	metre per second	$m\ s^{-1}$
acceleration	velocity/time	metre per second squared	$m\ s^{-2}$
density	mass/volume	kilogram per cubic metre	$kg\ m^{-3}$
specific volume	volume/mass	cubic metre per kilogram	$m^3\ kg^{-1}$
force	mass × acceleration	newton, N	$1\ N = 1\ kg\ m\ s^{-2}$
pressure	force/area	pascal, Pa	$1Pa = 1N\,m^{-2} = 1\,kg\,m^{-1}s^{-2}$
energy	force × distance[(b)]	joule, J	$1J = 1N\,m = 1\,kg\,m^2s^{-2}$
power	energy/time	watt, W	$1W = 1J\,s^{-1} = 1\,kg\,m^2s^{-3}$
electric charge	electric current × time	coulomb, C	$1\ C = 1\ A\ s$
electric potential	energy/electric charge	volt, V	$1V = 1J\,C^{-1} = 1\,kg\,m^2s^{-3}A^{-1}$

(a) Width and height are simply length in different directions.
(b) Distance is another name for length.

The units for area and volume, square metre and cubic metre, respectively, are probably familiar to you, as are their symbols, m^2 and m^3. However, while you are also probably familiar with the unit of velocity, metre per second, you may perhaps wonder how the symbol m s^{-1} is obtained. To obtain a velocity, we divide length by time, and we obtain the unit for velocity by dividing the unit of length (m) by the unit of time (s). We can write the symbol for the resulting unit in two ways: as m/s, or, as we shall do throughout this book, as m s^{-1}. Recall that x^{-1} is simply another way of writing $\frac{1}{x}$, and so, when we write m s^{-1}, this is the same as $\mathrm{m} \times \frac{1}{\mathrm{s}} = \mathrm{m/s}$. Similarly, we obtain an acceleration by dividing velocity by time, and the unit is then derived from the unit of velocity (m s^{-1}) divided by the unit of time (s). The unit is therefore $\frac{\mathrm{m\,s^{-1}}}{\mathrm{s}} = \mathrm{m\,s^{-2}}$ (metre per second squared), where s^{-2} is the same as $\frac{1}{s^2}$. This illustrates a very important concept that is used throughout this book when we perform calculations: *units undergo the same kinds of mathematical operations as the numbers to which they are attached*. We demonstrate this in worked example 2.1.

WORKED EXAMPLE 2.1

Deriving SI units

Heat capacity, which we will meet in chapter 8, is a measure of the heat required to raise the temperature of a particular substance by 1 K. We can obtain heat capacity values by dividing the heat provided by the temperature change obtained. What is the derived SI unit of heat capacity?

Analysis

As we obtain heat capacity values by dividing heat by temperature change, we will obtain the unit for heat capacity by dividing the units of heat by the units of temperature change.

Solution

The SI unit of heat is the joule (J) and the SI unit of temperature, and therefore temperature change, is the kelvin (K). Therefore, the unit of heat capacity is:

$$\frac{\mathrm{J}}{\mathrm{k}} = \mathrm{J\,k^{-1}} \text{(read as joules per kelvin)}$$

PRACTICE EXERCISE 2.1

The kinetic energy of an object of mass *m* moving at velocity *u* is $\frac{1}{2}mu^2$. What is the derived SI unit of kinetic energy?

Sometimes it is inconvenient to use SI base or derived units. For example, we would not want to use metres to measure the tiny length of an atomic radius or the enormous distance to the nearest star. The SI system addresses this problem by the use of prefixes that divide or multiply the unit by a particular power of ten. For example, the prefix *centi* means the following unit is divided by 100, while the prefix *kilo* signifies that the following unit is multiplied by 1000. Table 2.3 lists the most common prefixes.

TABLE 2.3 Common Prefixes for SI Units

Prefix	Symbol	Factor
tera	T	10^{12}
giga	G	10^{9}
mega	M	10^{6}
kilo	k	10^{3}
deci	d	10^{-1}
centi	c	10^{-2}
milli	m	10^{-3}

micro	μ	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}
femto	f	10^{-15}

Each prefix has an associated symbol, which is placed immediately before the base unit. Therefore, km refers to kilometre, a unit of 10^{3} m, while cm (centimetre) is a unit of 10^{-2} m.

WORKED EXAMPLE 2.2

Using SI prefixes

Objects that are smaller than about 2×10^{-7} m cannot be seen under an optical microscope. Could we use an optical microscope to observe a virus that is 20 nm long?

Analysis

We need to convert 20 nm to metres, and compare it with 2×10^{-7} m. The SI symbol n stands for *nano* and means 10^{-9}, so we will use this conversion factor.

Solution

We know from table 2.3 that 1 nm = 1×10^{-9} m, and therefore 20 nm = 20×10^{-9} m = 2×10^{-8} m. This is less than 2×10^{-7} m and hence we will not be able to see this virus using an optical microscope.

Is our answer reasonable?

We can check our result by converting the size of the smallest visible object (2×10^{-7} m) to nanometres so that it can be compared directly with the size of the virus; 2×10^{-7} m is equal to 200×10^{-9} m, or 200 nm. The virus is 20 nm long; the smallest object that can be seen under the microscope is 200 nm, so again we conclude that the virus will not be visible.

PRACTICE EXERCISE 2.2

1. Give the abbreviation for:
    a. microgram
    b. micrometre
    c. nanosecond.
2. How many metres are in:
    a. 1 nm
    b. 1 cm
    c. 1 pm?
3. What symbol is used to represent:
    a. 10^{-2} g
    b. 10^{6} m
    c. 10^{-6} s?

Non-SI units

Although SI units have been adopted in nearly all countries (USA, Myanmar and Liberia being the only exceptions), there are many

non-SI units in common usage throughout the world. For example, we saw on p. 25 that temperatures are much more likely to be measured in degrees Celsius (or degrees Fahrenheit in the USA, Myanmar and Liberia) than in the SI unit kelvin. Even chemists are not immune to this; we often use the litre, a unit of volume equal to 1000 cm^3, rather than the more correct (but inconveniently large) m^3. The millilitre (1 cm^3) is also often used. Various non-SI units of pressure (atmosphere, millimetre of mercury, torr, bar), rather than the SI unit pascal, are still regularly seen in the chemical literature. As long as use of non-SI units persists, it will occasionally be necessary for you to be able to convert between non-SI and SI units. To do this, we need to know the conversion factor between the units. Then we can obtain an equation to convert between the two. This is illustrated in worked example 2.3.

WORKED EXAMPLE 2.3

Unit conversions

The laws of cricket state that a cricket pitch is 22 yards in length. How long is a cricket pitch in metres given that 1 metre = 1.0936 yards?

Analysis

We are told that 1 metre corresponds to 1.0936 yards; in other words, there are 1.0936 yards in every metre or, to put it yet another way, 1.0936 yards per metre. Therefore, the conversion factor, in terms of yards per metre, is $\frac{1.0936\ \text{yard}}{1\ \text{metre}} = 1.0936\ \text{yard metre}^{-1}$.

However, we are asked to convert from yard to metre, and therefore need the conversion factor in terms of metres per yard (metre $yard^{-1}$). We obtain this knowing that:

$$\frac{1\text{metre}}{1.0936\ \text{yard}} = 0.9144\ \text{metre yard}^{-1}$$

We can now solve the problem by multiplying this conversion factor by 22 yards.

Solution

22 yard × 0.9144 metre $yard^{-1}$ = 20.12 metre

Is our answer reasonable?

We know that 1 metre is slightly longer than 1 yard, so we would expect our numerical answer to be slightly less than 22, which it is. Notice also, as we will see on pp. 28–9, that the units in our solution are consistent; yard × metre $yard^{-1}$ = metre.

PRACTICE EXERCISE 2.3

Use the given conversion factors to carry out the following conversions involving pressure units.

1. Convert 0.3 bar to pascal (1 pascal = 1 × 10^{-5} bar).
2. Convert 451 millimetres of mercury to pascal (1 pascal = 7.50 × 10^{-3} millimetres of mercury).
3. Convert 3.81 atmospheres to pascal (1 pascal = 9.87 × 10^{-6} atmosphere).

Notice that the method of unit conversion described on p. 27 can also be used for conversion between SI units. For example, suppose we wanted to express 418 cm^3 in m^3; we would need the conversion factor in terms of m^3 cm^{-3}. From the unit prefix ‘c’, we know that:

$$\begin{aligned} 1\ \text{cm} &= 1\times10^{-2}\text{m} \\ \text{Therefore, } 1\ \text{cm}^2 &= (1\times10^{-2}\text{m})^2 = 1\times10^{-4}\text{m}^2 \\ \text{and } 1\ \text{cm}^3 &= (1\times10^{-2}\text{m})^3 = 1\times10^{-6}\text{m}^3 \end{aligned}$$

The conversion factor is therefore $\frac{1\times10^{-6}\text{m}^3}{\text{cm}^3} = 1\times10^{-6}\text{m}^3\text{cm}^{-3}$, and we carry out the conversion as follows:

$$418\ \text{cm}^3 \times 1\times10^{-6}\text{m}^3\text{cm}^{-3} = 418\times10^{-6}\text{m}^3$$

Dimensional Analysis

One of the questions most commonly asked by students is 'What equations do I need to learn for the final exam?' If you read this book from cover to cover (or indeed, if you just go to the glossary of equations at the end of the book), you will find a large number of equations, all of which are important to the subject of chemistry in one sense or another, and you might think that it is necessary for you to learn them all by heart. You'll be happy to know that this is not the case.

Dimensional analysis involves using the units of a physical quantity to derive the equation used to determine its value. We first encountered this on p. 26 when we stated that '*units undergo the same kinds of mathematical operations as the numbers to which they are attached*'. We then went on to illustrate this in worked example 2.1 (p. 26) when we determined the units of heat capacity (J K^{-1}) through knowledge of the fact that heat capacity is equal to heat (J) divided by temperature change (K). We will now look at this principle more closely, using the stoichiometric equations $M = \frac{m}{n}$ and $c = \frac{n}{V}$, which will be introduced in chapter 3. These are two of the most used equations in chemistry and, without doubt, these equations are the two most often written incorrectly. Yet, all you need to know to determine the correct forms of these equations are the units of molar mass (M), g mol^{-1}, and concentration (c), mol L^{-1}.

The unit of molar mass, g mol^{-1}, is obtained by dividing a physical quantity having the unit gram by a physical quantity having the unit mole. These physical quantities are mass (m) and amount (n), respectively. Knowing this allows us to write the equation relating mass, amount, and molar mass as follows:

$$\text{molar mass unit}(\text{g mol}^{-1}) = \frac{\text{gram}}{\text{mole}}$$

Therefore, $\text{molar mass} = \frac{\text{physical quantity measured in gram}}{\text{physical quantity measured in mole}} = \frac{\text{mass}}{\text{amount}} = \frac{m}{n}$

And there you have it — the equation is given by the units. The correct units of molar mass (g mol^{-1}) are obtained *only* if we divide mass (g) by amount (mol). *No other combination of mass and amount will give the correct units of molar mass*.

A similar situation occurs in the case of concentration. The unit of concentration is mol L^{-1}, and is therefore obtained by dividing a physical quantity having the unit mole by a physical quantity having the unit litre. We know that mole is the unit of amount (n) and litre is the unit of volume (V). Therefore, we can write:

$$\text{concentration units}(\text{mol L}^{-1}) = \frac{\text{mole}}{\text{litre}}$$

Therefore, $\text{concentration} = \frac{\text{physical quantity measured in mole}}{\text{physical quantity measured in litre}} = \frac{\text{amount}}{\text{volume}} = \frac{n}{V}$

Again, no other combination of amount and volume will give the correct units of concentration.

Dimensional analysis assists you not only in remembering the correct form of an equation, but also in ensuring you have rearranged an equation correctly. Consider, for example, rearranging the above equation for concentration, to make n the subject. The correct rearrangement, obtained by multiplying both sides of the equation by V, gives

$$n = c \times V$$

and we can easily check this because we know that the units on both sides of the equation must be the same. On the left-hand side, we have units of mol and on the right-hand side we have units of mol L^{-1} × L = mol. Therefore, we can be confident that we have rearranged the equation correctly.

If we had arranged the variables incorrectly, e.g. $n = \frac{c}{V}$ or $n = \frac{V}{c}$, we could quickly see from the units that we had made a mistake; $\frac{V}{c}$ gives units of mol L^{-1}/L = mol L^{-2}, while $\frac{V}{c}$ gives units of L/mol L^{-1} = L^2 mol^{-1}. Neither can be correct as they do not give the units of mol.

This is always a good check whenever you rearrange an equation; *if the units are not the same on both sides of the rearranged equation, you have made a mistake.*

There are situations where dimensional analysis might, at first glance, appear not to work. Consider, for example, the ideal gas equation, $pV = nRT$, which we will encounter in chapter 6. Given that pressure (p) is measured in Pa, volume (V) in m^3, amount (n) in mol and temperature (T) in K, and the gas constant (R) has units of J mol^{-1} K^{-1}, we can work out the units on both sides of the equation:

The units of pV (left-hand side) are Pa × m^3 = Pa m^3.

The units of nRT (right-hand side) are mol × J mol^{-1} K^{-1} × K = J.

This does not appear to be correct, as it looks as though we have different units on each side of the equation. However, remember that both Pa and J are derived units; from table 2.2 (p. 25) we can see that 1 J = 1 kg m^2 s^{-2} and 1 Pa = 1 kg m^{-1} s^{-2}. Therefore

$$\text{pa}\,\text{m}^3 = \text{kg}\,\text{m}^{-1}\text{s}^{-2} \times \text{m}^3 = \text{kg}\,\text{m}^2\text{s}^{-2} = \text{J}$$

and we can see that the units on both sides of the equation are, in fact, the same.

Dimensional analysis is not limited to these relatively simple equations. It works for *any* equation. This is because the numbers and the units on both sides of an equation must be the same. As worked example 2.4 shows, dimensional analysis can also be used to determine the correct form of an equation if you know the units of all the constituent components.

WORKED EXAMPLE 2.4

Dimensional Analysis

An aqueous sugar solution will boil at a temperature slightly greater than 100 °C, depending on how much sugar the solution contains. The magnitude of this boiling point elevation (ΔT) can be calculated from some combination of the molal boiling point elevation constant (K_b) and the molality (b) of the solution. Given that the units of b are mol kg^{-1} and those of K_b are K mol^{-1} kg, what equation should be used to calculate ΔT when this is measured in K?

Analysis

We need to combine the units of b and K_b to give units of K in our final answer. There are three possibilities:

$$\Delta T = \frac{K_b}{b}$$

$$\Delta T = \frac{b}{K_b}$$

$$\Delta T = K_b b$$

We need to determine the final units for ΔT that result from each of these three possibilities. The correct equation will give final units of K.

Solution

We insert the appropriate units into each of the three expressions above.

$$\frac{K_b}{b} \text{ has units of } \frac{\text{K}\,\text{mol}^{-1}\text{kg}}{\text{mol}\,\text{kg}^{-1}} = \text{K}\,\text{mol}^{-2}\text{kg}^2$$

$$\frac{b}{K_b} \text{ has units of } \frac{\text{mol}\,\text{kg}^{-1}}{\text{K}\,\text{mol}^{-1}\,\text{kg}} = \text{K}^{-1}\text{mol}^2\text{kg}^{-2}$$

$$K_b b \text{ has units of } \text{K}\,\text{mol}^{-1}\text{kg} \times \text{molkg}^{-1} = \text{K}$$

Therefore, the correct equation to calculate the boiling point elevation is $\Delta T = K_b b$.

Is our answer reasonable?

Given that there is only one way of combining the units of K_b and b to give units of K, we can be confident our answer is correct.

We will learn more about boiling point elevation in chapter 10.

PRACTICE EXERCISE 2.4

Deduce the correct form of each of the following equations by considering the units of all the components of the equation.

(a) Obtain an equation for mass (*m*, g) in terms of molar mass (*M*, g mol^{-1}) and amount (*n*, mol).

(b) Obtain an equation for the gas constant (*R*, J mol^{-1} K^{-1}) in terms of pressure (*p*, Pa), volume (*V*, m^3), amount (*n*, mol) and temperature (*T*, K).

(c) Obtain an equation for the speed of light (*c*, m s^{-1}) in terms of energy (*E*, J), Planck's constant (*h*, J s) and wavelength (λ, m).

Uncertainties and Significant Figures

Every measurement has an associated uncertainty, which results from the limitations of the methods we use to make the measurement. Consider, for example, a quantity that you probably know well: your weight. If you used an analogue set of bathroom scales which can weigh to the nearest kilogram to weigh yourself, you might find that your weight lies almost exactly halfway between the divisions corresponding to 71 kg and 72 kg. Do you quote your weight as 71 kg or 72 kg? There is obviously some uncertainty over the last figure in the measurement. You therefore invest in a more expensive set of digital scales which can weigh to the nearest 0.1 kilogram; using these, you find you weigh 71.6 kg. However, if you wait long enough, you notice that the display fluctuates between 71.5 kg and 71.7 kg. Again, the last figure in the answer is uncertain. You could keep buying scales that weigh to ever smaller fractions of a kilogram, but *you would always find that there would be some uncertainty in the final figure of the measurement.* We can illustrate this concept further by considering the two thermometers in figure 2.2, which display the same temperature.

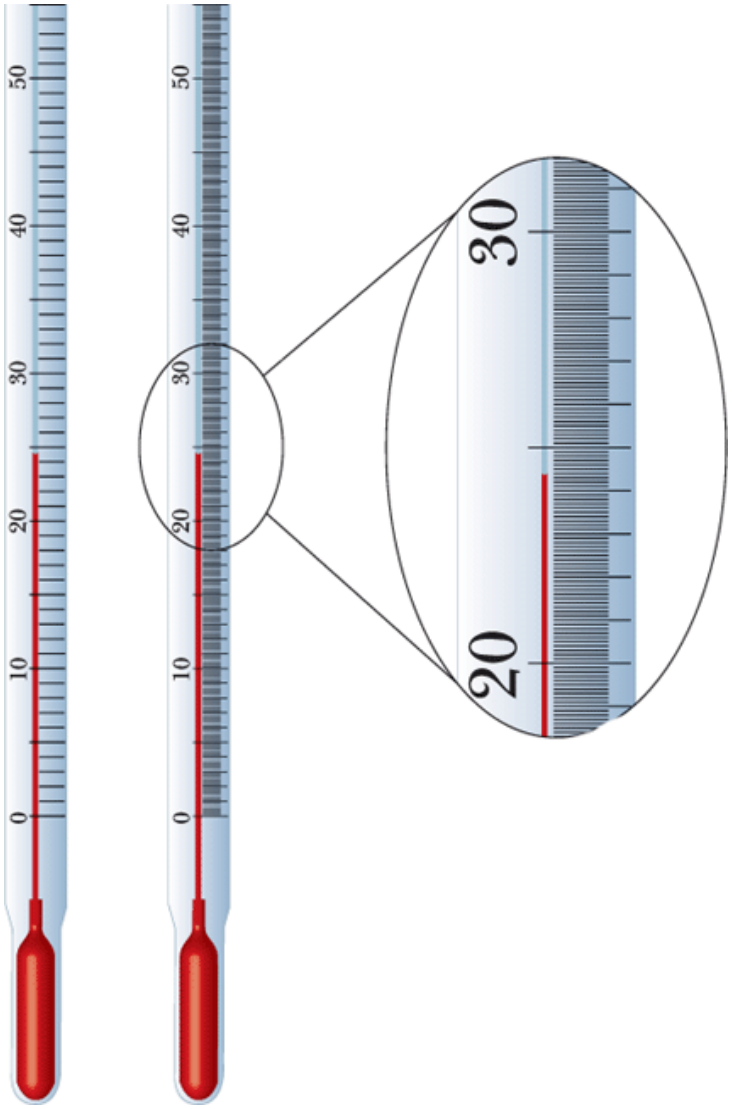


FIGURE 2.2 Thermometers with different scales give readings with different precision. The thermometer on the left has divisions that are 1 °C apart, allowing the temperature to be estimated to the nearest 0.1 °C. The thermometer on the right has divisions every 0.1 °C, therefore permitting estimation of the temperature to 0.01 °C.

The divisions on the left thermometer are 1 °C apart and it is therefore certain, barring any imperfections in the manufacture of the thermometer, that the temperature is greater than 24 °C and less than 25 °C. It can be estimated that the top of the fluid column falls about 0.3 of the way between the div isions for 24 °C and 25 °C, so the measurement can be recorded as 24.3 °C. However, we cannot say that the temperature is exactly 24.3 °C, as the last figure is only an estimate, and the left thermometer might be read as 24.2 °C by one observer and 24.4 °C by another. The thermometer on the right is graduated in divisions of 0.1 °C and may therefore be read to a greater precision than the other thermometer. Reading the thermometer on the right, it is now certain, again assuming no flaws in the thermometer, that the temperature lies between 24.3 °C and 24.4 °C, and another figure in the measurement can be estimated by noting that the top of the fluid lies about 0.2 of the way between the divisions. Therefore, the temperature according to the thermometer on the right would be stated as 24.32 °C. By convention in science, all figures in a measurement up to and including the first estimated figure are recorded. The figures recorded according to this convention are called **significant figures**. The thermometer on the right can be read to a greater precision, and the measurement made contains a correspondingly larger number (4) of significant figures. The number of significant figures in a measurement is equal to the number of digits known for certain, plus one that is estimated. Therefore, *there will always be uncertainty in the last significant figure of any measurement.* In the above example, the final figures of both 24.3 °C and 24.32 °C are uncertain.

It is usually easy to determine the number of significant figures in a number — simply count the figures. However, ambiguities may arise when zeros are present; for example, does the number 0.0023 contain two (23), four (0023) or five (0.0023) significant figures? Such problems can be avoided by writing numbers in **scientific notation**, which immediately shows how many significant figures are present. Scientific notation expresses numbers in terms of powers of ten; for example, the number 15 becomes 1.5×10^{1} in scientific notation, 362 becomes 3.62×10^{2}, and so on. In scientific notation, 0.0023 is written as 2.3×10^{-3}, and it can be seen that the number contains only two significant figures. Similarly, the more precise number 0.002 30 would be written as 2.30×10^{-3}, and this then has three significant figures. Note that the number of significant figures in a measurement is the same regardless of the units. For example, a length of 2.3×10^{-3} m can be expressed in millimetres (2.3 mm) or nanometres (2.3×10^{6} nm), but in each case the values must have the same number of significant figures, as the precision of the measurement does not depend on the units in which it is expressed.

WORKED EXAMPLE 2.5

Significant Figures

Determine the number of significant figures in the following numbers.

(a) 0.004 136

(b) 0.1060

(c) 10.01

Analysis

We need to write the above numbers in scientific notation. We can then determine the number of significant figures from the number of figures in the scientific notation.

Solution

The numbers written in scientific notation are as follows.

(a) 4.136×10^{-3}

(b) 1.060×10^{-1}

(c) 1.001×10^{1}

Therefore, all three numbers have four significant figures.

Is our answer reasonable?

The ambiguity in significant figures comes with zeros. Are they significant, or are they placeholders? In the number 0.004 136, all the zeros are placeholders, and writing this in scientific notation (4.136×10^{-3}) makes this clear — none of the zeros appear in the scientific notation of this number, so they cannot be significant. The other two numbers contain zeros that *are* significant, because they appear in the scientific notation. Taking these rules into account, our answer is reasonable.

PRACTICE EXERCISE 2.5

How many significant figures do the following numbers contain?

(a) 1.000 405

(b) 0.001 000

(c) 1 000 010.0

The uncertainty in any measurement generally depends on the precision of the instrument used to make that measurement. For example, a 20 mL pipette may have an uncertainty of ±0.05 mL (± means ‘plus or minus’). We would therefore quote the pipette as measuring 20.00 ± 0.05 mL (see figure 2.3).

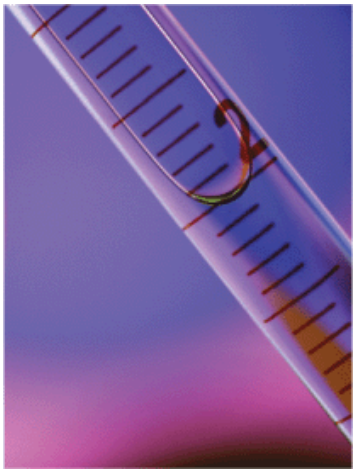


FIGURE 2.3 The 0.1 mL graduations on this pipette imply an uncertainty of ±0.05 mL.

This means that the pipette delivers between 19.95 mL and 20.05 mL whenever it is used. This type of uncertainty is called an **absolute uncertainty**; in other words, the uncertainty has the same units as the quantity being measured. We can also quote the **percentage uncertainty** for an instrument. In this case, we would calculate the percentage uncertainty for the pipette as follows:

$$\begin{aligned}\text{percentage uncertainty} &= \frac{\text{absolute uncertainty}}{\text{measured quantity}} \times 100\% \\ &= \frac{0.05\ \text{mL}}{20.00\ \text{mL}} \times 100\% \\ &= 0.25\%\end{aligned}$$

As we will see below, percentage uncertainties are important when we are doing calculations involving either multiplication or division.

It should be noted that there are two types of uncertainties in any measurement. Random uncertainties refer to the reproducibility of a measurement, and are generally taken account of in the quoted uncertainty of the apparatus used to make the measurement. These are what give rise to the total uncertainty that we report at the end of a calculation (see below). Systematic uncertainties usually result from deficiencies in the measuring equipment or from human error, for example, when using a pipette which delivers only 19.00 mL rather than the stated 20.00 mL, or using a pH meter which has been incorrectly calibrated. These uncertainties can be eliminated through careful experimental technique.

Uncertainties and Significant Figures in Calculations

We have shown above how to determine the number of significant figures in an individual number. But when we use numbers in a calculation, how many significant figures does the answer contain? And how do uncertainties in numerical measurements translate to an uncertainty in the final answer when these measurements are used in calculations? More often than not, you will be relying on your calculator to carry out calculations; this will generally give an answer containing many more significant figures than are justified and will tell you nothing about the uncertainty in that answer. You therefore need to make use of some rules to appreciate what sort of precision you should give in your final answer.

To determine the appropriate number of significant figures in the answer of a calculation, the following rules apply:

- When a numerical measurement is multiplied by a constant, the number of significant figures in the answer will be the same as that in the numerical measurement.
- When two or more numerical measurements are multiplied or divided, the number of signifi-cant figures in the answer should not be greater than the number of significant figures in the least precise measurement.
- When two or more numerical measurements are added or subtracted, the answer should have the same number of decimal places as the measurement with the fewest number of decimal places.

We can illustrate these rules as follows. If we calculate:

$$\frac{3.14 \times 2.751}{0.64}$$

on a ten-digit calculator, the answer is 13.497 093 75, a number with ten figures. But how many of these figures are significant? The numbers in the numerator (top line) contain three and four signifi-cant figures respectively, while the denominator (bottom line) contains two significant figures (the 0 at the start of the number is not significant) and so it makes no sense to have an answer that is many orders of magnitude more precise than any of the numbers from which it is derived. The rule at the bottom of the previous page for multiplication and division states that we can have only as many significant figures in our final answer as there are in the least precise measurement. Therefore, in this example, we can express our answer to only two significant figures, so our final answer becomes:

$$\frac{3.14 \times 2.751}{0.64} = 13$$

If we calculate the sum:

$$\begin{array}{r} 3.247 \\ 41.36 \\ +125.2 \\ \hline 169.8 \end{array}$$

a calculator will give the answer as 169.807. However, looking at the layout of the sum above, we see that there are no figures beneath the 7 of 3.247 or the 6 of 41.36; in other words, the first figure after the decimal point is the only one that is known for all three numbers. Adding an unknown figure to the 6 or 7 will give an answer that is also unknown, so for this sum we are not justified in writing figures in the second and third places after the decimal point. The first figure after the decimal point is the only one that is known for all three numbers and, therefore, we round the answer to the first decimal place, giving 169.8.

Different rules apply when working with logarithms, as we will do extensively in chapter 11 when considering pH.

- The logarithm of a number can have the same number of figures to the right-hand side of the decimal point as there are significant figures in the number.

For example, the number 0.003 21 has three significant figures (this becomes more obvious when it is written in scientific notation as 3.21×10^{-3}). Using a calculator to determine the logarithm gives –2.493 494 967 6. This should then be quoted as -2.493.

The reverse is also true; given a logarithm, you determine the correct number of significant figures in the antilogarithm from the number of figures to the right of the decimal point. Hence, using a calculator, we find that the antilogarithm of -4.18 is $6.606\ 934\ 48 \times 10^{-5}$. This should be quoted to two significant figures, namely 6.6×10^{-5}.

The above rules for logarithms apply to both common ($\log_{10}$) and natural (ln or $\log_e$) logarithms.

While significant figures and uncertainties are related, the rules for determining the uncertainty in the answer of a calculation are somewhat different from those for significant figures on the previous page. They are as follows:

- When two or more numerical measurements are added or subtracted, the uncertainty in the final answer is the sum of the absolute uncertainties in the measurements.
- When two or more numerical measurements are multiplied or divided, the uncertainty in the final answer is the sum of the percentage uncertainties in the measurements.

It is usual to quote the final uncertainty as an absolute uncertainty, so it is necessary to be able to convert from a percentage to an absolute uncertainty.

We will illustrate these rules in worked example 2.6.

WORKED EXAMPLE 2.6

Calculating uncertainties

As we will see in section 2.2, many simple salts are obtained as hydrates from aqueous solution; that is, they crystallise with a definite number of water molecules (sometimes called water of crystallisation). Such salts have the general formula $M_aX_b{\cdot}cH_2O$, where a, b and c are generally integers. The water of crystallisation can often be removed by heating, to give the anhydrous salt M_aX_b.

In an experiment, 2.400 g of $CoSO_4{\cdot}7H_2O$ was heated to remove the water of crystallisation until no further mass loss was observed. At this point, the mass of anhydrous $CoSO_4$ obtained was 1.323 g. Use these figures to calculate the percentage, by mass, of H_2O in $CoSO_4{\cdot}7H_2O$, and give the uncertainty in your final answer. Note that the balance used to weigh the samples has an absolute uncertainty of ±0.001 g.

Analysis

We are given the mass of the hydrated and anhydrous salts, so the mass difference between these must correspond to the mass of water in the hydrated salt. We then divide this by the mass of the hydrated salt and multiply by 100 to obtain the percentage by mass of water. We must also determine the uncertainty in the final answer. This will derive from the uncertainties in the weighings.

Solution

We will first calculate the percentage by mass of water in the hydrated salt, and then determine the uncertainty in the answer.

$$\begin{aligned}\text{Mass of water in the hydrated salt} &= \text{mass of hydrated salt} - \text{mass of anhydrous salt}\\ &= 2.400\text{g} - 1.323\text{g}\\ &= 1.077\text{g}\end{aligned}$$

$$\begin{aligned}\text{Percentage by mass of water in the hydrated salt} &= \frac{\text{mass of water}}{\text{mass of hydrated salt}} \times 100\\ &= \frac{1.077\text{g}}{2.400\text{g}} \times 100\\ &= 44.88\%\end{aligned}$$

Note that, because each mass has four significant figures, we can quote the answer at this stage to four significant figures.

Now we will carry out the uncertainty analysis. We stated on the previous page that the balance used has an absolute uncertainty of ±0.001 g, so you might think that each measured mass has this uncertainty. In fact, the uncertainty in each measured mass is ±0.002 g. This is because every measurement we make using the balance is in fact the difference between two readings; the final balance reading, and the initial (zero) balance reading, both of which have an absolute uncertainty of ±0.001 g. Because we are essentially subtracting two values, we must add their absolute uncertainties, for example:

$$\begin{aligned}\text{Mass of hydrated salt} &= \text{final balance reading} - \text{initial balance reading}\\ &= (2.400 \pm 0.001)\text{g} - (0.000 \pm 0.001)\text{g}\\ &= (2.400 \pm 0.002)\text{g}\end{aligned}$$

We can now determine the uncertainty in the mass of water in the hydrated salt.

$$\begin{aligned}\text{Mass of water in the hydrated salt} &= (2.400 \pm 0.002)\text{g} - (1.323 \pm 0.002)\text{g}\\ &= (1.077 \pm 0.004)\text{g}\end{aligned}$$

Again, because we are subtracting two measurements, we add their absolute uncertainties.

Because the next step in the calculation, the determination of the percentage by mass of water in the hydrated salt, involves a division, we must convert the absolute uncertainties in both the mass of the hydrated salt and the mass of water in the hydrated salt to percentage uncertainties, and then add them together.

$$\text{Percentage uncertainty} = \frac{\text{absolute uncertainty}}{\text{measured quantity}} \times 100$$

$$\text{Percentage uncertainty in mass of hydrated salt} = \frac{0.002\text{ g}}{2.400\text{ g}} \times 100 = 0.08\%$$

$$\text{Percentage uncertainty in mass of water in the hydrated salt} = \frac{0.004\text{ g}}{1.077\text{ g}} \times 100 = 0.37\%$$

Note that we have retained two significant figures in the percentage uncertainty in the mass of water. It is often advisable to carry extra figures in the uncertainty throughout the calculation and then round to a single figure at the end.

$$\begin{aligned}\text{Percentage by mass of water in the hydrated salt} &= \frac{1.077\text{ g}(0.37\%)}{2.400\text{ g}(0.08\%)} \times 100\\ &= 44.88\%\ (0.45\%)\end{aligned}$$

Now we must convert our calculated percentage uncertainty to an absolute uncertainty. We do this as follows.

$$\begin{aligned}\text{Absolute uncertainty} &= \frac{\text{percentage uncertainty} \times \text{result of calculation}}{100}\\ &= \frac{0.45 \times 44.88\%}{100} = 0.20\%\ (\text{This is an absolute uncertainty in a percentage, so it has the same unit.})\end{aligned}$$

Therefore, our final answer looks as though it is (44.88 ± 0.20)%. However, some thought will show us that this is not quite correct. It is usual to quote uncertainties to a single significant figure; this is because our answer is generally uncertain only in its final figure. So we would then amend our answer above to (44.88 ± 0.2)%. However, this still poses problems as the uncertainty refers not to the final figure but to the first figure after the decimal point. As we have shown that ±0.2 is the minimum uncertainty in our answer, this then dictates the number of significant figures to which the answer can be given; in other words, the second figure after the decimal point in the answer is not significant, given the magnitude of the uncertainty.

Thus, our final answer, including the uncertainty, is (44.9 ± 0.2)%.

Is our answer reasonable?

The mass loss (1.077 g) in going from $CoSO_4 \cdot 7H_2O$ to $CoSO_4$ is solely due to the water molecules in the former. This

mass is a little under half the total mass of $CoSO_4 \cdot 7H_2O$ and thus we would expect that water should make up just under 50% of the total mass of $CoSO_4 \cdot 7H_2O$. Our numerical answer (44.9%) is therefore likely to be correct. Checking that our uncertainty is reasonable is somewhat more difficult. However, we know that the total uncertainty results from two weighings, and that each of these has an uncertainty of much less than 1%. Therefore, our final uncertainty of ±0.2% appears reasonable.

PRACTICE EXERCISE 2.6

Give the answers of the following calculations to the correct number of significant figures.

(a) 4.196 + 8.3492 + 14.73

(b) 5.36 × 1.259

(c) 6.38 × (2.514 + 5.4)

(d) the total mass of two beakers of water, each of which weighs 37.50 g

(e) log(2.185 × 5.48)

(f) $\frac{5.39}{14.1} \times (268 + 64.1)$

PRACTICE EXERCISE 2.7

Perform the following calculations involving measurements. Give the answers to the correct number of significant figures, and use the appropriate units.

(a) 21.0233 g + 21.0 g

(b) 32.02 mL - 2.0 mL

(c) 54.183 g - 0.0278 g

(d) 10.0 g + 1.03 g + 0.243 g

(e) $\frac{10.0324\ \text{g}}{11.7\ \text{mL}}$

(f) 1.03 m × 2.074 m × 3.9 m

PRACTICE EXERCISE 2.8

A student wanted to prepare 100 mL of a 1.000 g L^{-1} solution of NaCl and devised the following method. The student weighed 0.100 g of solid NaCl on a balance and transferred this to a 100 mL volumetric flask. Sufficient water was then added, with stirring, to give a final volume of 100 mL according to the mark on the volumetric flask.

Given that the uncertainties in the balance and volumetric flask were ±0.001 g and ±1 mL, respectively, calculate the final uncertainty in the concentration of the NaCl solution. Did the student succeed in preparing a 1.000 g L^{-1} solution? If not, what was the concentration, including the uncertainty, of the solution?

The word ‘precise’ has been used in this section, without being defined. It is important to appreciate the difference between accuracy and precision when making measurements. A measurement's **accuracy** refers to how close the value is to the correct value, while **precision** signifies how reproducible a particular measurement is when made a number of times and, therefore, how many significant figures it can be quoted to. The two concepts are illustrated in figure 2.4.

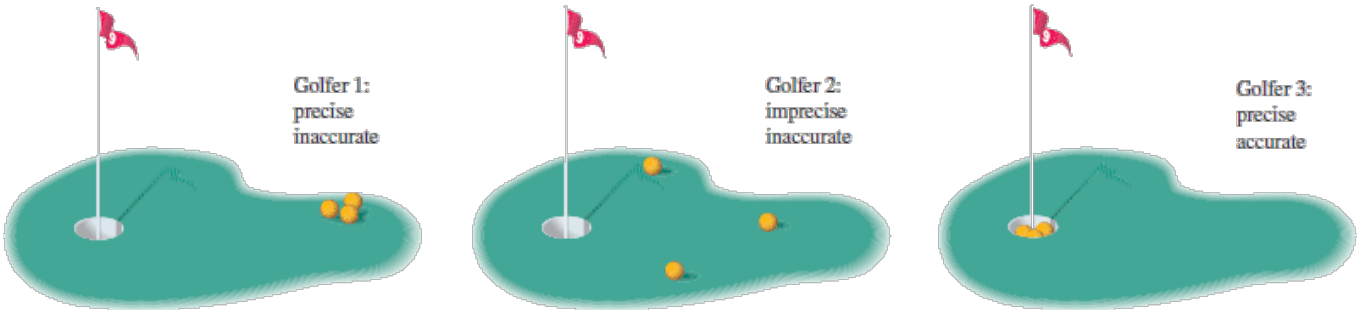


FIGURE 2.4 The difference between precision and accuracy in the game of golf. Golfer 1 hits shots that are precise (because they are tightly grouped), but the accuracy is poor as the balls are not near the target (the 'true' value). Golfer 2 needs help. The shots are neither precise nor accurate. Golfer 3 wins with shots that are precise (tightly grouped) and accurate (in the hole).

PRACTICE EXERCISE 2.9

Four workers weigh a 10.000 g mass three times on several different kitchen scales and obtain the following results.

Worker A: 10.022 g, 9.976 g, 10.008 g

Worker B: 9.836 g, 10.033 g, 9.723 g

Worker C: 10.230 g, 10.231 g, 10.232 g

Worker D: 9.632 g, 9.835 g, 9.926 g

Which set of data has the best precision? Which has the best accuracy?

Chemical Connections

The National Measurement Institute

The National Measurement Institute (NMI) is the organisation responsible for providing unit and measurement standards and services in Australia. It has four main sections:

- legal metrology and business services
- physical metrology
- analytical services
- chemical and biological metrology.

We mentioned earlier in this chapter that the primary standard of mass is the international prototype of the kilogram, which is a platinum–iridium cylinder held at the International Bureau of Weights and Measures. The NMI holds 'Copy No. 44' (figure 2.5) of the international prototype of the kilogram. It serves as the Australian standard of mass and the NMI uses it to calibrate a set of 1 kg stainless steel standards. Those standards are then used to calibrate standards with masses from 0.5 mg to 20 kg, which are used for all calibration work on mass and the measurement of various other quantities.

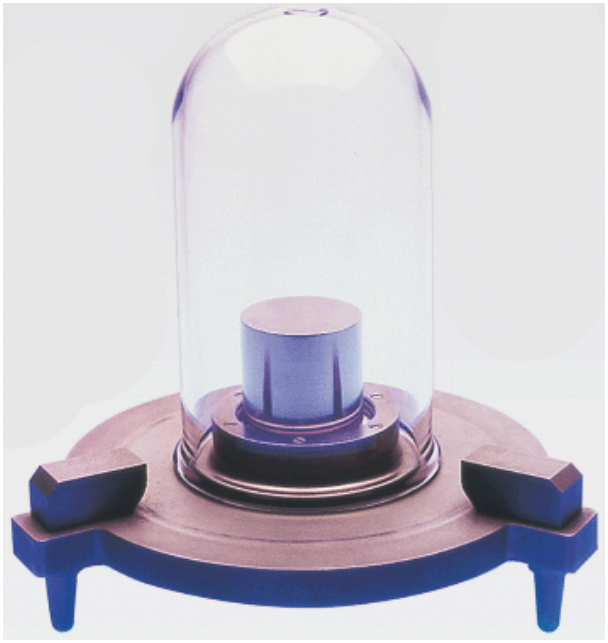


FIGURE 2.5 Australia's Copy No. 44 of the international prototype of the kilogram. This is made of a 90% platinum - 10% iridium alloy.

While measurement might seem a somewhat esoteric field, it is of great importance in many disciplines, including chemistry and business. For example, one of the key aims of the NMI is to promote uniform measurement policy and practice to help international trade. One area in which the NMI has been active is the wine industry.

Australia exports hundreds of millions of litres of wine each year. A wine connoisseur will tell you that taste, bouquet and colour are the qualities that characterise a wine (figure 2.6). A metrologist (someone who specialises in measurement) might talk more about the levels of chemical residues, contaminants and preservatives. In addition to health and quality concerns, many international markets have strict regulations on acceptable levels of ethanol, sulfites and heavy metals in wines. Exporters must comply with these regulations to ensure they can sell their wines into those markets.



FIGURE 2.6 Chemical analysis can quantify what a wine expert detects using the senses.

NMI provides the wine industry with analytical chemistry services to determine pesticide, insecticide and herbicide residues, foreign matter, alcohol content and other important information. The techniques used have been validated against those used in other countries to ensure the measurements are accepted by export markets.

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2.2 Representations of Molecules

The language of chemistry is not only about the meaning of words, but also about how we can represent chemical species using particular combinations of letters, numbers, symbols and pictures (see figure 2.7). In this section we will describe some of the many different ways in which we can depict molecules, as well as the bond-making and bond-breaking processes that occur in chemical reactions.

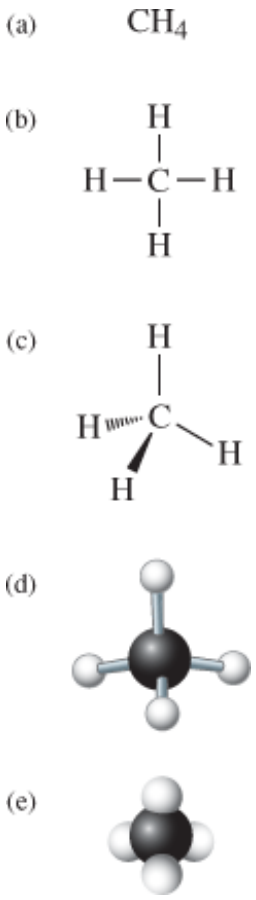


FIGURE 2.7 Different ways of representing the chemical species methane:
(a) chemical formula,
(b) structural formula,
(c) 3-D structural formula,
(d) ball-and-stick model and
(e) space-filling model.

Chemical Formulae

The simplest way to describe the composition of any substance is to write its **chemical formula**. This shows the number of each type of atom present in a substance. A chemical formula contains elemental symbols to represent atoms and subscripted numbers to indicate the number of atoms of each type. It may be as simple as water, H_2O, or as complicated as $C_{30}H_{34}AuBClF_3N_6O_2P_2PtW$, the compound which currently holds the record for containing the most elements. As we have seen in chapter 1, each chemical element is described by a one-, two- or three-letter symbol, and these form the basis for all chemical formulae. The simplest chemical formulae describe pure elements and are usually just their elemental symbols as listed on the periodic table; for example, helium is He, silicon is Si and copper is Cu. Such formulae imply that the bulk elements are composed of either individual atoms which do not interact (such as He) or 'infinite' three-dimensional arrays of bonded atoms (such as Si and Cu). However, this is not the case for some elements and we must write more complex chemical formulae for these. For example, seven elements (hydrogen, nitrogen, oxygen, fluorine, chlorine, bromine and iodine) occur naturally neither as individual atoms nor as

three-dimensional arrays but as molecules containing two atoms (diatomic molecules). To signify this, their chemical formulae are written as H_2, N_2, O_2, F_2, Cl_2, Br_2 and I_2 respectively. Some other elements occur as larger molecules; a phosphorus molecule contains four P atoms and a sulfur molecule contains eight S atoms so their chemical formulae are P_4 and S_8 respectively. A chemical formula that refers to a discrete molecule is often called a **molecular formula** as it describes the types and numbers of atoms present in the molecule. Note that a subscripted numeral refers either only to the atom immediately preceding it, or, if it follows a group of atoms enclosed in parentheses, to the entire group of enclosed atoms. For example, the chemical formula $B(OH)_3$ shows that the compound contains one boron atom, three oxygen atoms and three hydrogen atoms.

Chemical compounds contain more than one element. Therefore, there is potentially more than one way to write the formula of any compound. For example, hydrogen chloride is a diatomic molecule with one atom each of hydrogen and chlorine. Its chemical formula might therefore be written as HCl or ClH. To avoid possible confusion, chemists have standardised the writing of chemical formulae. For **binary compounds** (compounds containing only two elements) the following guidelines apply:

1. With the exception of hydrogen, the element further to the left in the periodic table appears first. Examples are KCl, PCl_3, Al_2S_3 and Fe_3O_4.
2. If hydrogen is present, it appears last except when the other element is from group 16 or 17 of the periodic table. For example, we write hydrogen last in LiH, NH_3, B_2H_6 and CH_4, but first in H_2O_2, H_2S, HCl and HI.
3. If both elements are from the same group of the periodic table, the lower one appears first, for example SiC and BrF_3.
4. If the compound is ionic, we write the cation (the positively charged ion) first, followed by the anion (the negatively charged ion). Examples are NaBr and $MgCl_2$.

Writing chemical formulae for compounds containing more than two elements requires some knowledge of the bonding within the compound. As we will discuss in greater detail in chapter 5, chemical compounds can be divided broadly into two classes — ionic compounds and covalent compounds — which are distinguished by the type of bonding. Ionic compounds are composed solely of ions, and the attractive forces between ions of opposite charge result in the formation of ‘infinite’ three-dimensional lattices. On the other hand, covalent compounds are characterised by bonding involving the sharing of electrons between adjacent atoms. To write the chemical formula of an ionic compound containing more than two elements, we again write the cation followed by the anion. For example, the formula of sodium nitrate, which contains positively charged sodium ions, Na^+, and negatively charged nitrate ions, NO_3^-, is $NaNO_3$. Note that the ordering of the elements in the NO_3^- ion conforms to the rules given above. Note also that we must always ensure that the total charge on the ionic compound is zero, so the number of Na^+ and NO_3^- ions must be the same, and we never include the individual ionic charges in the overall formula. Writing the chemical formula for calcium nitrate is a little more complicated. The formula of the calcium ion is Ca^{2+}, while that of the nitrate ion is NO_3^-. We can see that, to achieve an overall charge of zero, we will require one Ca^{2+} ion and two NO_3^- ions, and it is with the latter that a potential problem arises. We signify the presence of two NO_3^- ions, as we do for any ion, by using a subscripted ‘2’ immediately following the ion. However, you can see that, if we do this, we will have two subscripted numbers immediately adjacent to each other, thereby leading to possible confusion. In cases such as this, we enclose the ion in parentheses, and place the subscripted ‘2’ outside the parentheses. Putting the cation first, we therefore write the chemical formula as $Ca(NO_3)_2$. As stated on the previous page, it is understood that the subscripted ‘2’ refers to the entire group of atoms within the parentheses; that is, the chemical formula implies one Ca^{2+} ion and two NO_3^- ions.

To illustrate the difference between the use of subscripted numbers and numbers of normal case, consider the following chemical reaction, which describes solid $Ca(NO_3)_2$ dissolving in water to form its constituent ions.

$$Ca(NO_3)_2(s) \rightarrow Ca^{2+}(aq) + 2NO_3(aq)$$

Note that subscripts are used only when we are referring to the number of constituent atoms or ions *within an element or compound*; in other words, they appear in chemical formulae only. Conversely, normal case numbers are used as coefficients to describe the number of atoms, ions or molecules present *in a particular chemical reaction*. This will be covered in much greater detail in chapter 3.

PRACTICE EXERCISE 2.10

Write the chemical formulae for the compounds resulting from all possible combinations of the following cations and anions (16 compounds in total).

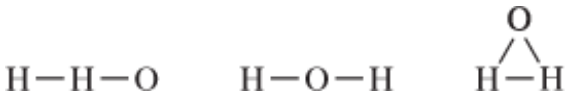
Cations: NH_4^+, K^+, Ca^{2+}, Al^{3+} Anions: Br^-, ClO_4^-, CO_3^{2-}, PO_4^{3-}

If calcium nitrate, a white crystalline solid, is exposed to moist air, it absorbs water and forms a **hydrate**. This hydrate is also a white crystalline solid but it has the chemical formula $Ca(NO_3)_2{\cdot}4H_2O$. This process can be reversed by heating the hydrate under vacuum to remove the water molecules, which results in the formation of **anhydrous** $Ca(NO_3)_2$ (anhydrous means that the compound contains no water molecules). The formation of hydrates is relatively common among ionic compounds, and it is usual to write the water molecules in such compounds at the end of the chemical formula.

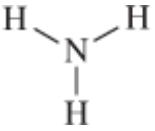
The majority of covalent compounds are carbon-based organic compounds, the chemical formulae of which are often written with carbon first, followed by hydrogen and then the remaining elements in alphabetical order (e.g. C_2H_6O, C_4H_9BrO, CH_3Cl). The major shortcoming of a chemical formula is that it tells us little or nothing about the *structure* of the compound in question. To obtain this information, we require structural formulae.

Structural Formulae

Chemists are interested in the way in which atoms are bonded together to form molecules. While molecular formulae are useful in telling us the chemical makeup of molecules, they only rarely give us any idea of which atom is bonded to which. For example, the molecular formula of water is always written as H_2O, but this tells us nothing about how the atoms are arranged in the molecule. We cannot tell from the molecular formula alone which of the three possible arrangements of atoms below is the correct one for H_2O.



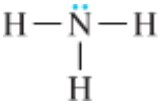
Structural formulae attempt to show the way in which the atoms in a molecule are bonded together, thereby giving us some structural information. The chemical symbols are still used for each element present, but now the constituent atoms are placed in the order in which they are bonded together and the bonds between neighbouring atoms are represented as lines. A single line represents a single bond, which, as we will see in chapter 5, consists of a pair of electrons. Consider for example the ammonia molecule, NH_3. We can show the way in which the four atoms are bonded together in this molecule by drawing the structural formula as follows.



From this depiction, it is obvious that the nitrogen atom is bonded to three H atoms by single bonds. It is also common to see ammonia depicted as:



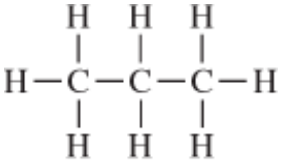
which gives us the same structural information as the previous diagram (the N atom is bonded to three H atoms by single bonds), but shows the molecule apparently adopting a slightly different geometry. This illustrates an important point about structural formulae: *structural formulae do not necessarily show the correct geometry of a compound*, simply because it is difficult to accurately represent three-dimensional molecules in two dimensions. While both of the depictions on the previous page correctly show all of the bonds in the molecule, neither is strictly correct from a structural point of view as they do not show the actual three-dimensional arrangement of the atoms. Both of them also neglect the fact that there is a pair of electrons on the N atom which does not participate in bonding. This is termed a lone pair of electrons. While such electrons are often ignored in depictions of molecules (their presence is usually implied by the chemical formula), they can have significant structural consequences. Where necessary, they can be shown as follows.



In later chapters, you will find it can be important to show lone pairs on atoms, especially when you draw organic reaction mechanisms, which show the movement of electrons in bond-making and bond-breaking processes. Even with the inclusion of the lone pair, this is still not an accurate depiction of the ammonia molecule in a three-dimensional sense, but it shows the correct connections between the constituent atoms of the molecule. We will see later how to introduce three-dimensional elements into structural formulae.

It is in the world of organic chemistry that structural formulae are particularly useful. While many covalent inorganic compounds tend to be small molecules in which a single central atom is joined to 2, 3, 4, 5 or 6 surrounding atoms, organic molecules tend to exist as rings and chains, and have a huge variety of possible geometries. This is due to the unusual propensity of carbon atoms to bond to themselves, a property called **catenation**, which can lead to the formation of massive molecules. Each carbon atom in a molecule can form bonds to as many as four other carbon atoms, which means that even relatively small organic molecules have many different possible ways in which the constituent atoms can be bonded together. Structural formulae allow us to depict these possibilities.

Carbon is a tetravalent element, meaning that it prefers to form a total of four bonds within a molecule. These bonds may be single, double or triple. This means that there are four different ways that a carbon atom can form a total of four bonds: four single bonds, two double bonds, a double bond and two single bonds, or a triple bond and a single bond. Hydrogen, on the other hand, is monovalent, meaning that it usually forms only one single bond to another atom and, in an organic molecule, this is most often to a carbon atom. This can be illustrated by the propane molecule, which has the chemical formula C_3H_8. Given that each C atom must form four bonds and each hydrogen atom must form one, there is only one possible way of attaching all the elements; this is shown in a structural formula below.



propane, C_3H_8

We can see from this that the three carbon atoms of a propane molecule link to form a chain in which each carbon at the end of the chain (called a **terminal carbon**) is singly bonded to three hydrogen atoms, and the inner carbon is singly bonded to two hydrogen atoms. Notice that the structural formula of propane contains more information than the chemical formula. Both formulae identify the number of atoms (three C atoms

and eight H atoms), but the structural formula also shows how the atoms are connected.

The propane molecule contains only C—C and C—H single bonds. It is also possible to have double bonds and triple bonds in organic molecules, which we designate by two and three lines respectively, as shown in figure 2.8.

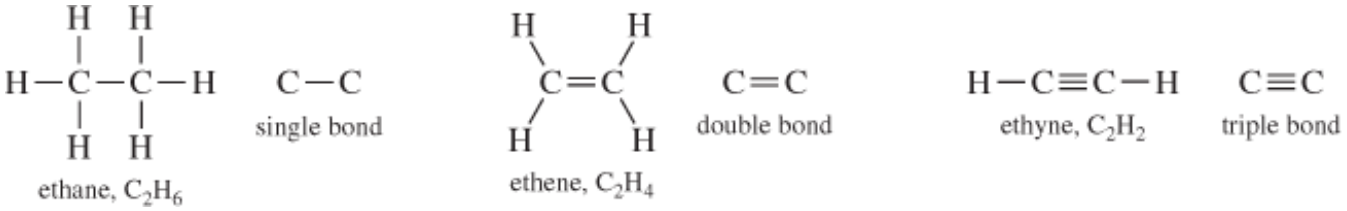


FIGURE 2.8 Depictions of single, double and triple bonds between carbon atoms.

Structural formulae can remove ambiguities inherent in chemical formulae. For example, the ethanol and dimethyl ether molecules have the same chemical formula, C_2H_6O. However, the structural formulae depicted in figure 2.9 clearly show the differences in the way the atoms are connected within the molecules.

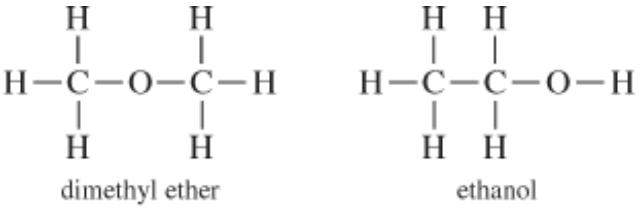
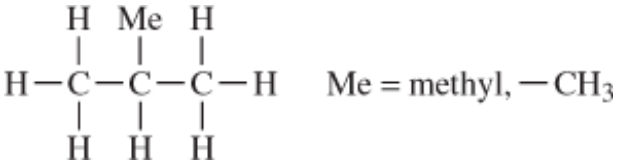


FIGURE 2.9 Structural formulae of dimethyl ether and ethanol. Both molecules have the same chemical formula, C_2H_6O.

Molecules such as these that have the same chemical formula but different chemical structures are called **isomers**. Structural formulae are a convenient way to distinguish between isomers.

Two types of shorthand structural formulae are commonly used. The constituent atoms in **condensed structural formulae** are arranged in bonded groups, and the actual bonds are not drawn. For example, we would write the condensed structural formulae of dimethyl ether and ethanol as CH_3OCH_3 and CH_3CH_2OH respectively, which essentially gives us the same structural information as the structural formulae, but with a significant saving of space. Note that the condensed structural formulae attempt to show the order in which the atoms are bonded together, and differ from the chemical formula, which is C_2H_6O in both cases. Condensed structural formulae can also be drawn for more complex molecules such as 2-methylpropane, C_4H_{10}.



The condensed structural formula of this molecule can be written as $CH_3CH(CH_3)CH_3$, $(CH_3)_2CHCH_3$ or $(CH_3)_3CH$, all of which are equivalent. In these cases, any —CH_3 group in parentheses is understood to be bonded to the middle carbon of the longest carbon chain.

We can also use **line structures**, in which C atoms are not drawn explicitly, to depict molecules. Line structures are constructed according to the following guidelines:

1. All bonds except C—H bonds are shown as lines.
2. C—H bonds and H atoms attached to carbon are not shown in the line structure.
3. Single bonds are shown as one line; double bonds are shown as two lines; triple bonds are shown as three lines.

4. Carbon atoms are not labelled. All other atoms are labelled with their elemental symbols. Following these guidelines, we would then write the line structure of propane, C_3H_8, as:

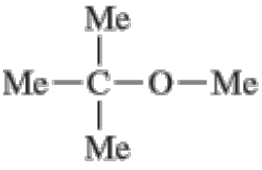


In this diagram a carbon atom is implied at each end of the chain and at the kink in the chain. The carbon atoms are singly bonded to each other and, as there are no other elemental symbols in the structure, it is assumed that each carbon atom bonds to the appropriate number of hydrogen atoms so that it forms a total of four bonds. This means the terminal carbon atoms will bond to three hydrogen atoms and the central carbon atom will bond to two hydrogen atoms. We illustrate how to draw line structures further in worked example 2.7.

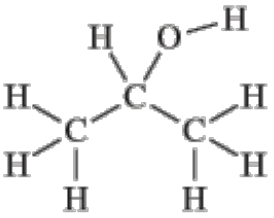
WORKED EXAMPLE 2.7

Drawing line structures

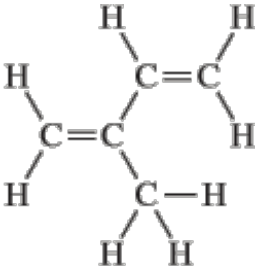
Construct line structures for compounds with the following structural formulae.



methyl *tert*-butyl ether (an antiknock ingredient in petrol)



propan-2-ol (rubbing alcohol)



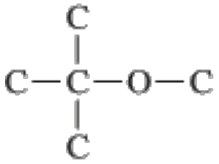
isoprene (sourced from nature to produce rubber)

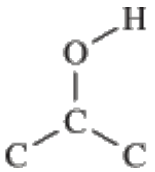
Analysis

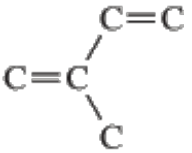
We are asked to convert the structural formulae above to line structures. To do this, we simply apply the guidelines given previously.

Solution

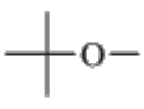
Using guidelines 1 and 2, we remove all C—H bonds and H atoms attached to C atoms from the structure, thereby leaving the carbon-based framework of each molecule (remember that Me = —CH_3). Guideline 3 states that double bonds remain as two lines. This gives us the following:

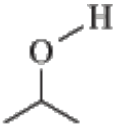


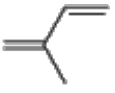




The final guideline tells us to remove the labels for all C atoms. This gives the answer:







Is our answer reasonable?

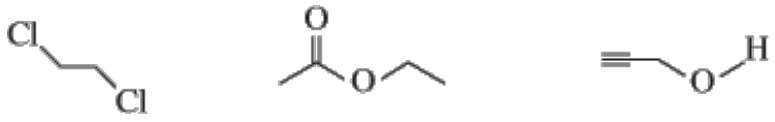
To check that the line structures represent the correct substances, count the number of intersections and line ends, which should equal the number of C atoms in the compound. The first line structure has five, the second has three and the third has five, matching the chemical formulae. Therefore our answers appear correct.

You should be familiar with line structures, and you should be able to convert from a structural formula to a line structure, and from a line structure to a structural formula. To do the latter, keep in mind that carbon atoms are not shown in a line structure, so the first step is to place a C at every line intersection or kink and at the end of every line. Then add singly bonded hydrogen atoms (—H) until every carbon atom has four bonds.

WORKED EXAMPLE 2.8

Converting Line Structures

Draw the structural formulae and determine the chemical formulae of the molecules in the following line structures.

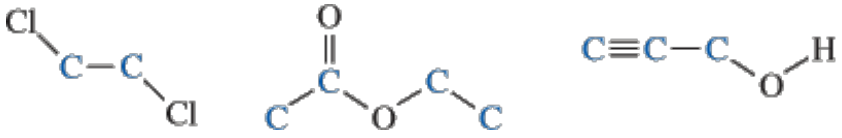


Analysis

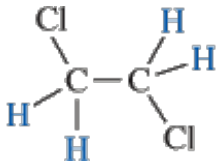
We know that line structures show all structural features except carbon atoms and C—H bonds. We can therefore convert a line structure into a structural formula in two steps. First, place a C at any unlabelled line end and at each line intersection or kink. Second, add hydrogen atoms until each carbon atom has four bonds. The chemical formula is then obtained by counting the number of atoms of each element.

Solution

Begin by placing a C at each intersection, kink and line end.



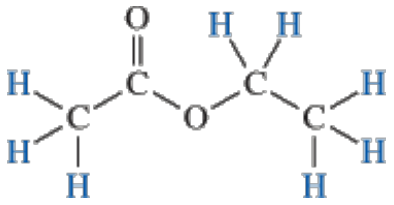
Now add hydrogen atoms until each carbon atom has a total of four bonds. Each carbon atom in the first structure already has two bonds, so each needs two hydrogen atoms. This gives the structural formula:



and the chemical formula $C_2H_4Cl_2$.

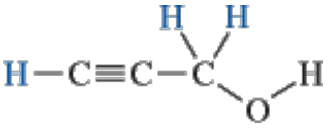
The second structure has four carbon atoms. The two terminal carbon atoms have just one bond, so each needs three hydrogen atoms. The carbon with the double bond to oxygen already has its

complete set of four bonds. The other inner carbon atom has a bond to C and a bond to O, so it needs two hydrogen atoms. This gives the structural formula:



and the chemical formula $C_4H_8O_2$.

The third structure contains a triple bond. The terminal carbon atom needs one hydrogen atom, but the other carbon atom of the triple bond already has four bonds. The next carbon atom has two bonds, one to carbon and one to oxygen. Two hydrogen atoms are needed to give this atom four bonds, and this gives the structural formula:



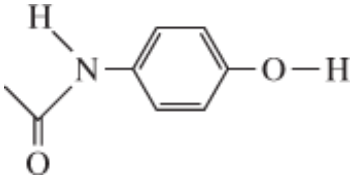
and the chemical formula C_3H_4O.

Is our answer reasonable?

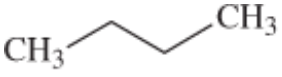
Check the consistencies of the structural formulae by counting the number of bonds associated with each carbon atom. If you have converted the line structure correctly, each carbon atom will have four bonds.

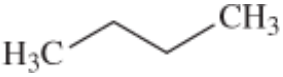
PRACTICE EXERCISE 2.11

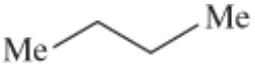
Convert the following line structure into structural and chemical formulae.



While line structures are the basis for the depiction of most molecules in the chemical literature, it is common to see variations on the rules we have outlined previously. For example, we might see butane, C_4H_{10}, written as any of the following:



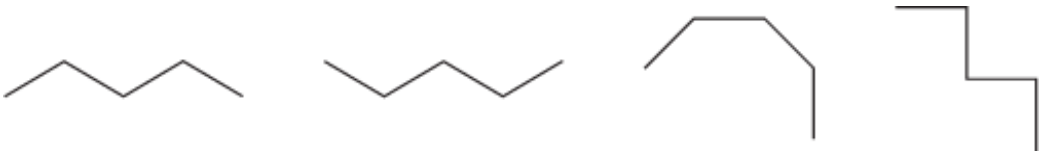




All of these are acceptable alternatives for the ‘strictly correct’ depiction shown below.

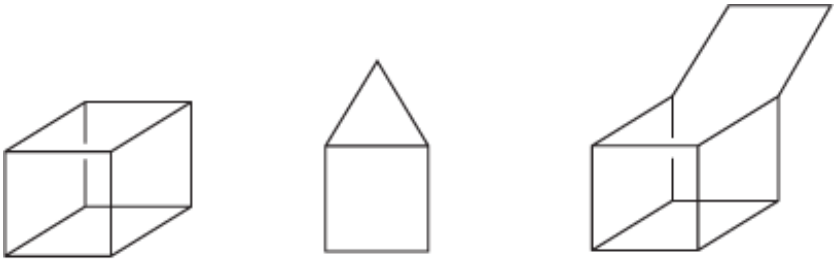


Notice also that in molecules with no double or triple bonds, the carbon chain can be drawn in any orientation. The following equivalent line structures can be drawn for pentane, C_5H_{12}:



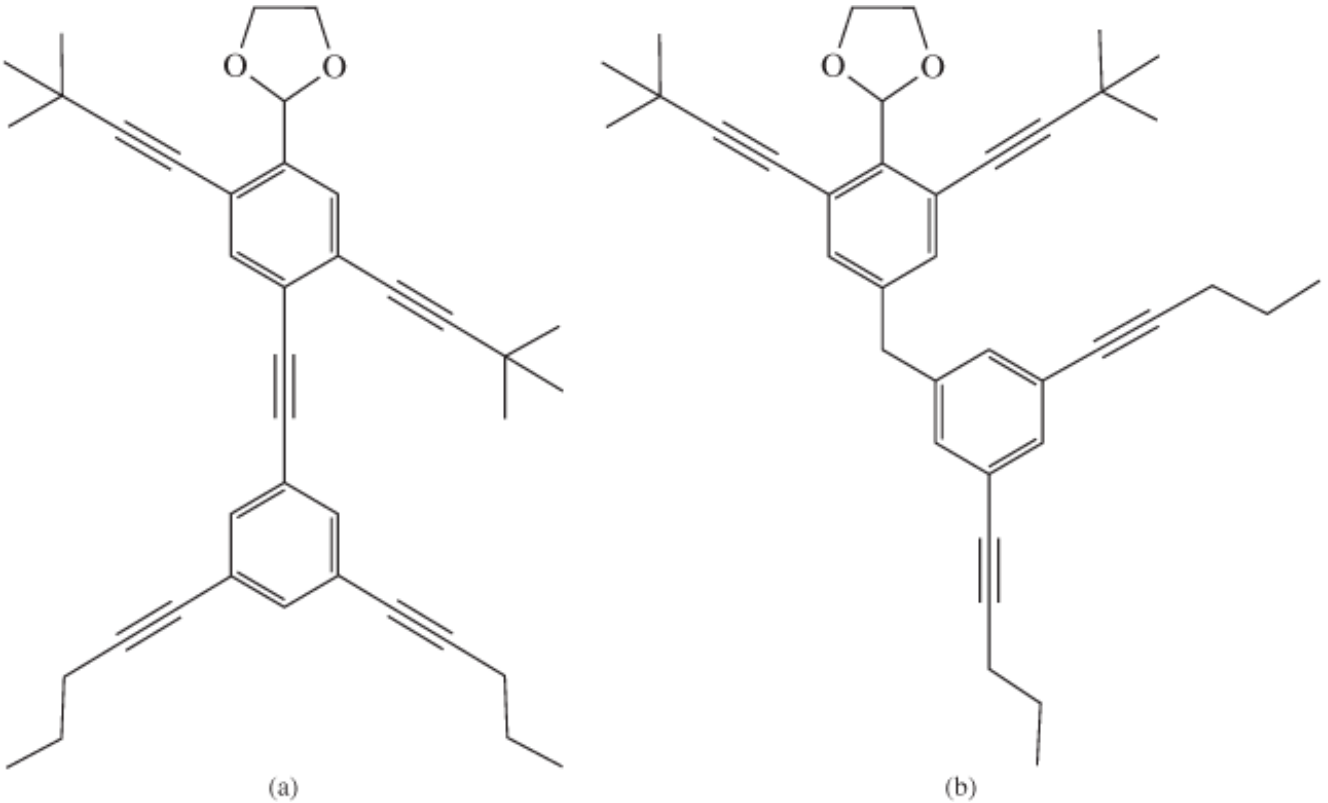
but the first two of these would be most commonly seen.

The depiction of molecules as line structures can give rise to some very interesting shapes, and some of these have served as inspirations for the synthesis of particular molecules. Consider, for example, the molecules below, all of which have been synthesised.



cubane, C_8H_8 housane, C_5H_8 basketane, $C_{10}H_{12}$

Probably the most remarkable example of molecular synthesis inspired by line structures is the series of molecules called Nanoputians, which were reported in 2003 by Dr Stephanie Chanteau and Professor James Tour from Rice University in the USA. These are molecules that, when drawn as line structures, resemble the human form. Two examples of Nanoputians (named after the Lilliputians in Jonathan Swift's *Gulliver's Travels*) are shown in figure 2.10. Had we chosen to describe these with their chemical formulae ($C_{39}H_{42}O_2$ and $C_{38}H_{44}O_2$ for NanoKid and NanoBalletDancer respectively) we would have no idea of the delightful shapes that representations of these molecules display.



(a) (b)

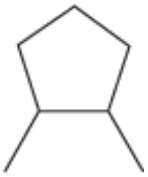
FIGURE 2.10 Line structures of:
(a) NanoKid
(b) NanoBalletDancer.

Three-dimensional Structures

While the structural formulae encountered so far give more structural information than chemical formulae, they do not necessarily give a complete representation of a molecule. For example, none of the molecules shown previously are flat, but you would not know this from looking at the structural formulae. We must therefore attempt to introduce some aspects of three-dimensionality in our representations. There are a number of ways this can be done.

Three-dimensional Structural Formulae

The simplest way of drawing a three-dimensional structure in two dimensions is to use a structural formula or line structure as a base, and then add some perspective. This is illustrated below using the molecule 1,2-dimethylcyclopentane. This is a cyclic molecule consisting of a pentagon of carbon atoms, with —CH_3 groups attached to two adjacent carbons. We can draw the line structure as follows.



However, when this molecule is viewed in three dimensions from side-on, we can immediately see that the flat line structure is not an adequate representation; each carbon atom in the ring has two attached atoms, either two H atoms or a H atom and the C atom of a —CH_3 group, which point either above or below the plane of the ring. This leads to two possible relative arrangements of the —CH_3 groups within the molecule — either both on the same side of the ring, or on opposite sides — and hence two possible isomers named using the prefixes *cis* and *trans* (see figure 2.11).

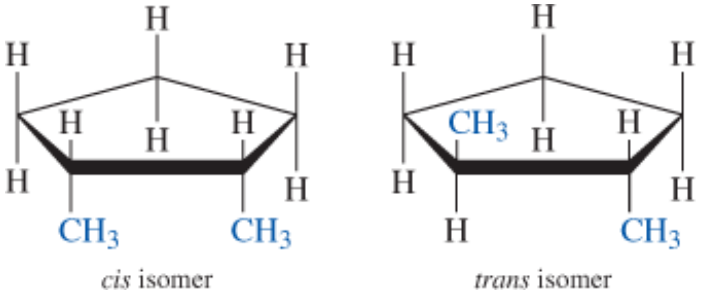
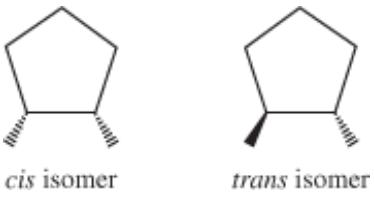


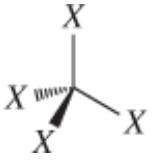
FIGURE 2.11 Representations of the two possible isomers of 1,2-dimethylcyclopentane. The two —CH_3 groups may be arranged so that they are on either the same or opposite sides of the ring. In reality, the cyclopentane rings are not flat but slightly puckered.

The *cis* isomer has both —CH_3 groups on the same side of the ring. (Note that it does not matter whether they are both on the top or bottom side of the ring — the same compound results.) The —CH_3 groups are on opposite sides of the ring in the *trans* isomer. We can show this in our line structure by drawing the bonds to these groups as wedges. A **solid wedge** (▬) represents a bond coming out of the page towards the observer, while a **hashed wedge** (▤) represents a bond going back into the page. A normal line is used for bonds in the plane of the page. Therefore the two isomers can be drawn as line structures as follows:



and it can be easily seen that they are different compounds.

When carbon is bonded to four atoms, those atoms generally adopt a tetrahedral arrangement around the carbon atom, as this arrangement places them as far as possible away from each other. It is conventional to draw the three-dimensional nature of the four bonds around a single carbon atom as follows:



where *X* is any atom. In this representation, one bond goes into the plane of the page, one comes out of the plane of the page, and two lie in the plane of the page. We can show the three-dimensionality of molecules containing more than one carbon atom by joining these individual units together. Such three-dimensional depictions are not limited to organic compounds; we will see in chapter 13 that transition metal complexes can display a wide variety of geometries, and we can use analogous diagrams to portray these. For example, it is common to have six atoms bound to a transition metal ion to give a complex of general formula ML_6. Each L atom sits at the corner of an imaginary octahedron in what is called an octahedral geometry. We would draw such an arrangement as follows.



In this case we have the two ‘vertical’ bonds in the plane of the page, while two bonds go into the plane and two bonds come out of the plane. While it is possible to make remarkably detailed three-dimensional drawings using only a pen and paper, it is easier to use computers to draw somewhat more realistic depictions of molecules.

Ball-and-stick Models

In a **ball-and-stick model**, balls of arbitrary size represent atoms and sticks represent chemical bonds. Figure 2.12 shows a ball-and-stick model of propane. The balls are usually drawn in different colours to distinguish between different elements present in the molecule (see figure 2.13). Such models generally enable the easy visualisation of three- dimensional features of the molecule.

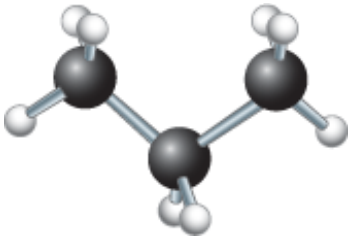


FIGURE 2.12 Ball-and-stick model of propane, C_3H_8.

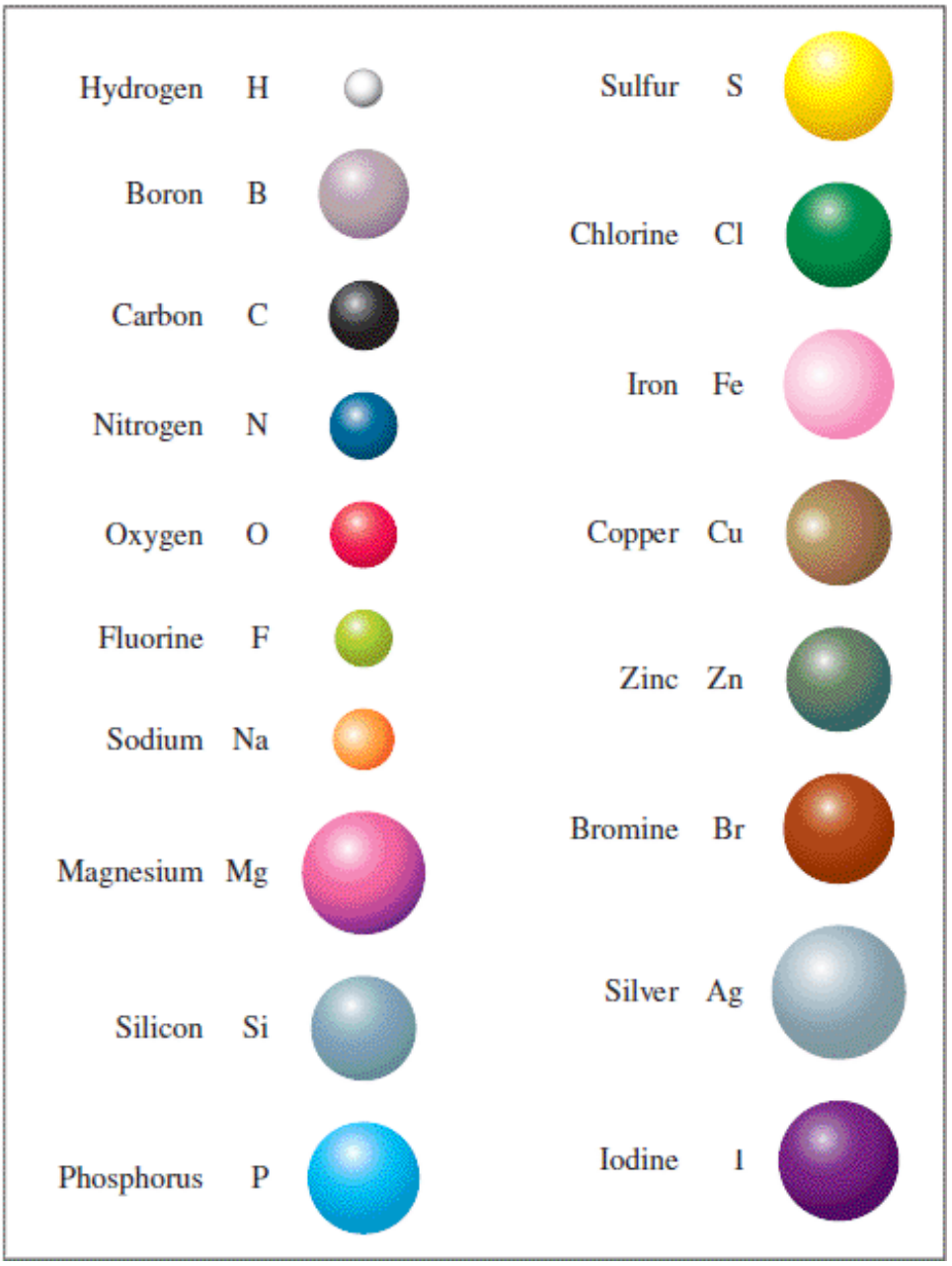

Hydrogen H
Boron B
Carbon C
Nitrogen N
Oxygen O
Fluorine F
Sodium Na
Magnesium Mg
Silicon Si
Phosphorus P
Sulfur S
Chlorine Cl
Iron Fe
Copper Cu
Zinc Zn
Bromine Br
Silver Ag
Iodine I

FIGURE 2.13 The colours and sizes of balls used to represent atoms in this book.

Space-filling Models

While ball-and-stick models are useful, they are far removed from reality — chemical bonds are not sticks, and the size of atoms is by no means arbitrary. A **space-filling model** recognises that a molecule is defined by the space occupied by its electrons, and attempts to represent the relative size of atoms within a molecule by showing the size of each atom's electron cloud. Recall from Rutherford's gold foil experiment (pp. 7–8) that electron clouds make up nearly the entire volume of any atom. Each atom in a space-filling model is shown as a distorted sphere representing the volume occupied by its electrons. These spheres merge into one another to build up the entire molecule. A space-filling model can tell us at a glance whether the electron clouds of atoms in a molecule overlap, and therefore whether those atoms are bonded together or not. Figure 2.14 shows a space-filling model of propane; notice that the spheres of the neighbouring C atoms overlap to a significant extent, implying these atoms are bonded together. The presence of C—H bonds is also obvious from the overlap of the spheres representing C and H. Figure 2.15 shows ball-and-stick and space-filling models of several chemical compounds common in everyday life.

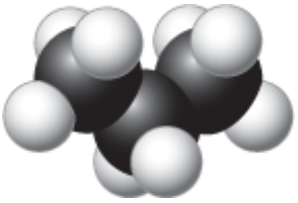


FIGURE 2.14 Space-filling model of propane, C_3H_8.

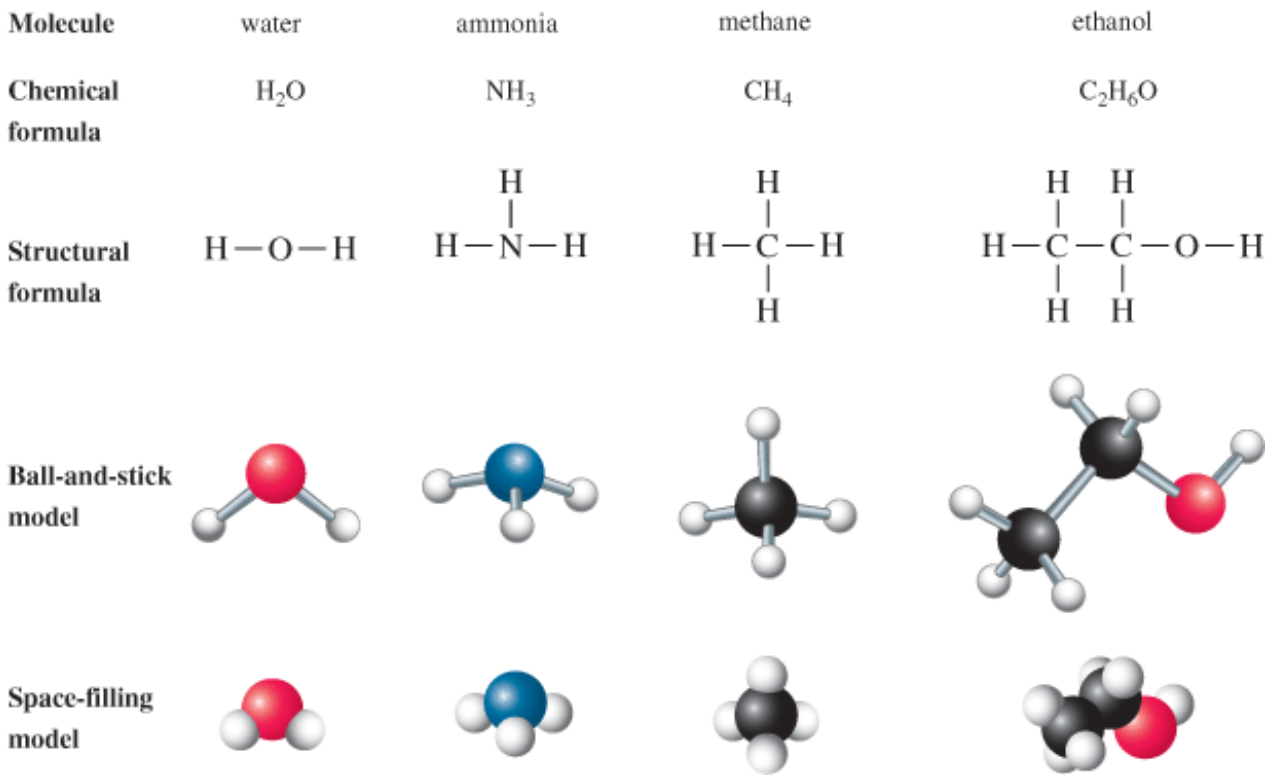


FIGURE 2.15 Different representations of some common compounds.

Other Representations

It is often inconvenient, if not impossible, to show every atom in a large molecule such as a protein or nucleic acid, and it is usual to draw ‘cartoon’ type structures of such molecules. Figure 2.16 shows such a view of haemoglobin, the iron-containing protein that carries oxygen in human blood. Instead of showing each individual atom in the molecule ($C_{2952}H_{4664}N_{812}O_{832}S_8Fe_4$ is the mol ecular formula of one form of the protein), the protein chains are shown as ‘ribbons’ which fold in particular ways depending on their chemical environment.

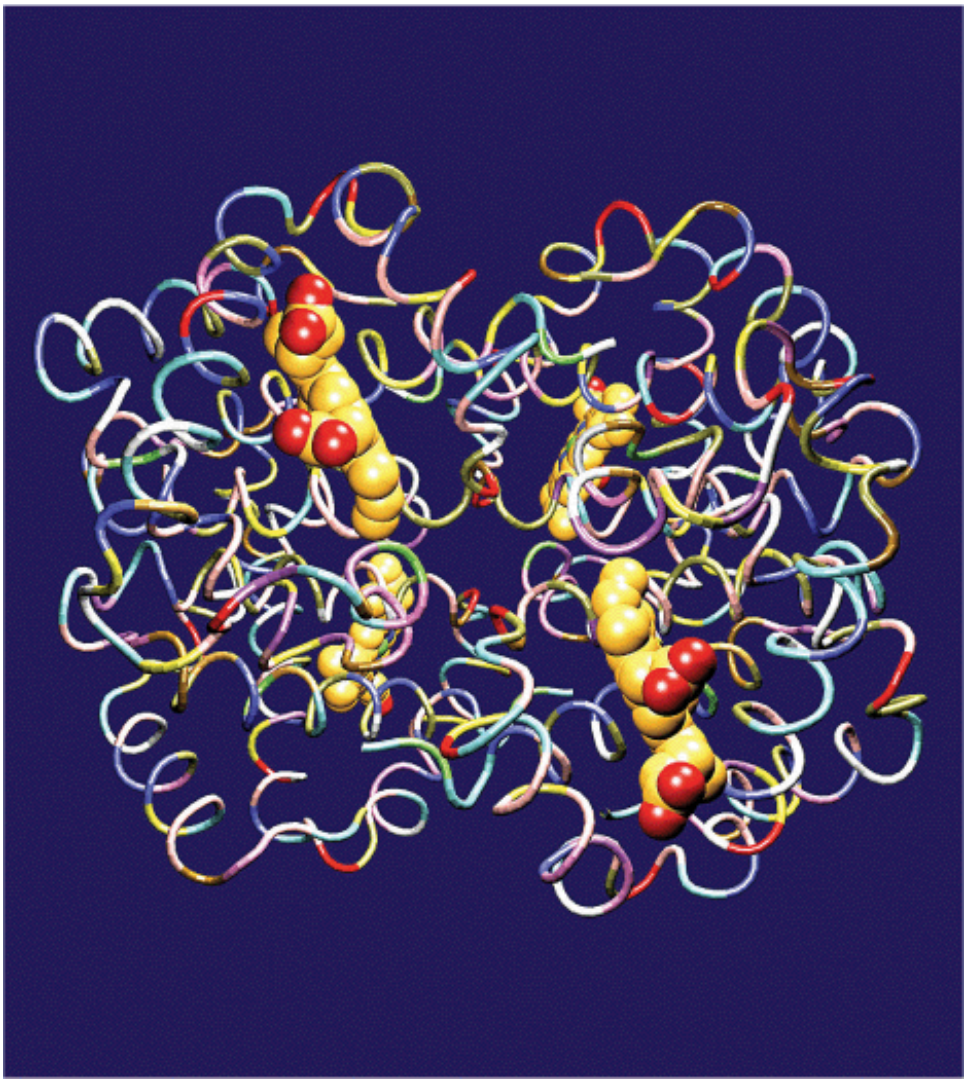


FIGURE 2.16 A representation of the structure of haemoglobin showing four haem groups (coloured spheres). The different coloured ribbons denote different parts of the protein.

Stereoviews are often helpful in visualising large molecules, as they allow the image to be viewed in three dimensions, although viewing them properly requires some practice. An example of a stereoview of DNA is shown in figure 2.17.

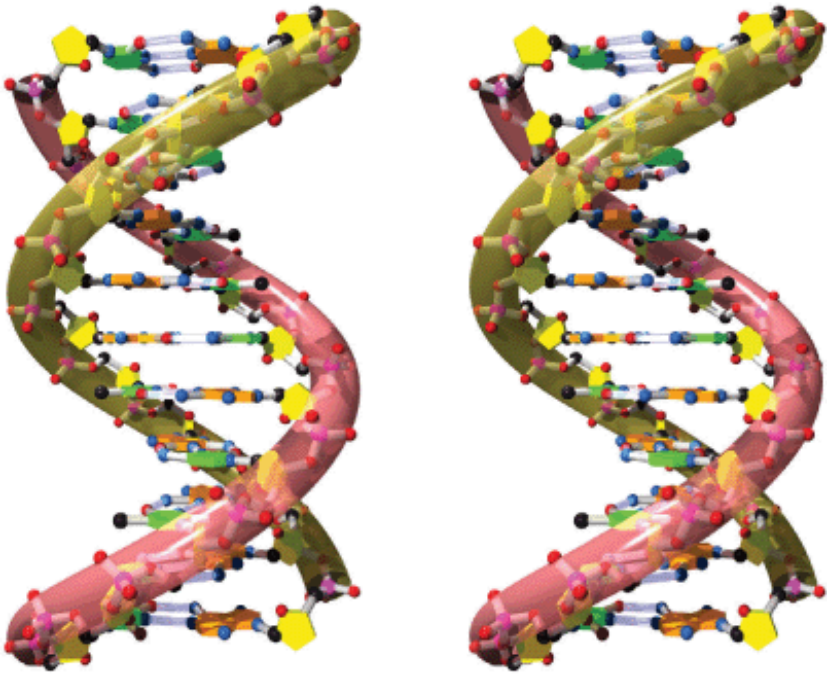


FIGURE 2.17 Stereoview of DNA.

To view stereoviews (which are three-dimensional images), you must be able to ‘go cross-eyed’. You will eventually find that, with lots of practice, a three-dimensional image appears in the middle of the two structures in figure 2.17. If you do not get it the first time, keep trying!

Which of our various depictions is the ‘correct’ one? The answer is ‘none of them’. Atoms are not finite coloured spheres and bonds are not sticks attached to atoms. The representations we use in chemistry are merely attempts to visualise things that, in all probability, are impossible to depict. However, this is not to say that our representations are useless. As we will see throughout this book, we can understand many important facets of molecular structure through studying these representations. But keep in mind at all times that the representations are models; nothing more and nothing less.

Mechanistic Arrows in Chemical Reactions

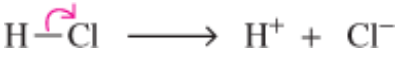
In addition to representing the structures of molecules, we also want to be able to depict the way in which chemical bonds are broken and formed within and between chemical species as chemical reactions occur.

We do this by means of **mechanistic arrows**, which show the movement of electrons in bond-breaking and bond-making processes.

A two-headed mechanistic arrow shows the movement of a pair of electrons. The electrons move from the tail to the head of the arrow, resulting in a number of possible chemical processes, some of which are detailed below.

Bond Breaking

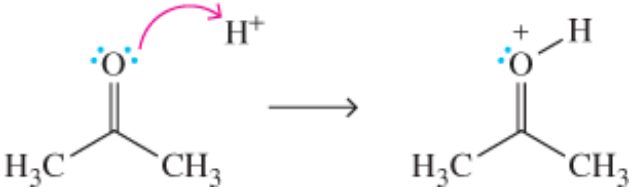
Consider the following bond-breaking process:



In this case, the arrow starts at the middle of the bond. The bond breaks in a **heterolytic** fashion, with both electrons ending up on the Cl atom. This gives rise to the formation of an H^+ cation (proton) and a Cl^- anion.

Bond Making

Consider the following bond-making process:



Here, a bond is formed between the carbonyl O atom and the H^+ ion, with the two electrons in the bond coming from one of the lone pairs of electrons on the carbonyl O atom. This leaves a formal positive charge on the O atom.

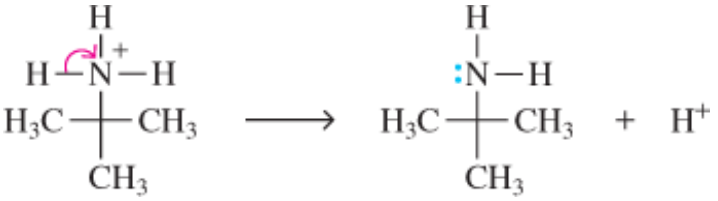
Charge Neutralisation

Consider the following charge-neutralisation process:



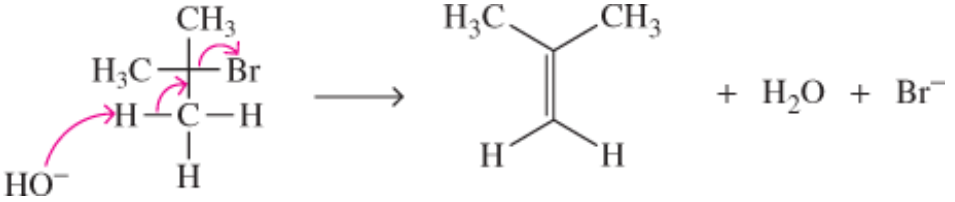
The positively charged carbonyl O atom can be neutralised by taking two electrons from the double bond and locating them on the carbonyl O atom. The arrow starts halfway along the bond and finishes at the O atom. This process leaves the carbonyl C atom positively charged.

In the following charge-neutralisation process



proton loss to give a neutral compound occurs by taking the two electrons from an N—H bond and locating them on the N atom. The tail of the arrow therefore is situated halfway along the N—H bond and the head points to the N atom.

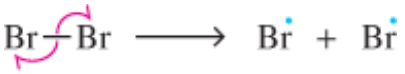
These examples illustrate some important facts about mechanistic arrows. Firstly, the tail of the arrow must be situated at a source of an electron pair: that is, either halfway along a bond or on a lone pair of electrons. Some thought will convince you that this means a mechanistic arrow can never start at either H^+ or an H atom (a very common mistake!). Similarly, the head of the arrow must be situated in a region able to accept a pair of electrons. Thus it would be unlikely, for example, for the head of an arrow to be at a negatively charged atom or ion. It is important to remember that total charge must be conserved in any mechanistic process. Thus, in all the exam ples above, both sides of the equations have the same total charge. It should also be noted that we can use more than one arrow to represent multiple simultaneous bond-making and bond-breaking processes. This is illustrated below.



Here, three processes occur essentially simultaneously.

1. OH^- removes a proton from a CH_3 group, resulting in the formation of H_2O.
2. The pair of electrons which were in the C—H bond move so as to give a C═C double bond.
3. The C—Br bond breaks heterolytically, with both electrons in the bond moving to the Br, to give a Br^- ion.

A single-headed arrow shows the movement of a single electron. Such arrows are usually found only in reactions involving radicals, chemical species which contain one or more unpaired electrons. An example is given below, in which the Br—Br single bond is broken in a **homolytic** fashion, such that each of the bonded atoms receives an electron, giving two bromine radicals.



You will make extensive use of mechanistic arrows in the later chapters of this book, especially in writing organic reaction mechanisms.

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2.3 Nomenclature

Representing molecules as images allows us to impart a great deal of information concerning molecular structure. But molecules can also be named, and there are occasions when this is more convenient than drawing a picture. In the early days of chemistry, the list of known compounds was short, and chemists could memorise the names of all of them. New compounds were often named by their discoverer after their place of origin, physical appearance or properties. Today, more than 50 million compounds are known and millions more are synthesised each year. Chemists consequently need systematic procedures for naming chemical compounds. The International Union of Pure and Applied Chemistry (IUPAC) has established uniform guidelines for naming various types of chemical substances, and chemists increasingly use IUPAC-approved names rather than their common counterparts. In this section we will introduce the rules for **nomenclature**, the system for the naming of compounds. You will encounter many chemical names in subsequent chapters, and the basics that you learn in this section will aid your interpret ation of these names. We will investigate the naming of transition metal complexes in chapter 13. You should be aware that there are some compounds that are better known by their common, unsystematic name, and not their systematic IUPAC name. The best example of this is water, the systematic name of which is oxidane. Unsystematic names for a small number of common compounds are accepted by IUPAC.

Chemistry Research

IUPAC

Associate Professor Richard Hartshorn, University of Canterbury

The International Union of Pure and Applied Chemistry (IUPAC) is the organisation responsible for helping chemists talk to each other about their science. It does this by developing and systematising the nomenclature, symbols and terminology that are required for chemistry. The names and formulae of chemical compounds are central to the language of chemists, and rules are required to tell people how to put them together and work out what they mean. The rules are regularly updated, both to make them simpler, and to provide ways of naming new kinds of molecules that were not envisaged when the rules were first written.

Different sets of rules are required for different kinds of compounds. For example, organic compounds and metal complexes are named in different ways. The different sets of rules appear in IUPAC's ‘colour’ books, including:

- the Red Book (*Nomenclature of Inorganic Chemistry*) (figure 2.18)

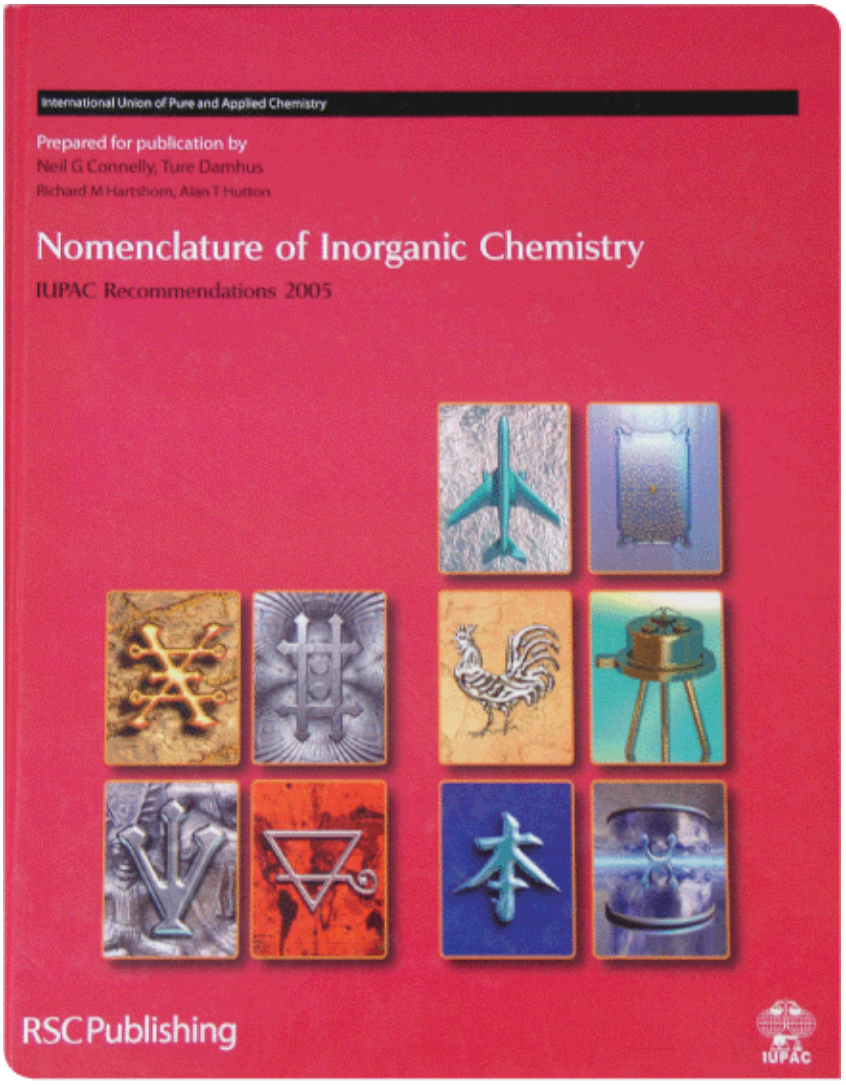


FIGURE 2.18 The Red Book is one of IUPAC's 'rule books' for nomenclature, symbols and terminology.

- the Blue Book (*Nomenclature of Organic Chemistry*)
- the Green Book (*Quantities, Units and Symbols in Physical Chemistry*)
- the Purple Book (*Compendium of Macromolecular Nomenclature*)
- the Gold Book (*Compendium of Chemical Terminology*).

Richard Hartshorn, Associate Professor in the Department of Chemistry at the University of Canterbury, Christchurch, works with IUPAC to develop nomenclature for inorganic compounds — nomenclature rules are not devised solely by chemists from the northern hemisphere!

Hartshorn describes himself as a coordination chemist by inclination and by training. He says he likes making new compounds (pretty colours!) and finding out what reactions can be done on them. In his own words:

> Of course, once compounds have been made, we have to name them. As a coordination chemist, this means knowing how both organic compounds and inorganic compounds are named. Working with IUPAC allows me to have some input into the recommendations for naming compounds.
>
> I got into nomenclature through one of my research projects, which involved preparing and studying complexes of new amino acids. It turned out that the conventional nomenclature that was available was not particularly convenient to highlight the differences and similarities between the various complexes that we had made. The simple answer was to invent something new, and we published an article showing how this nomenclature could be used more generally for any linear or branched chain ligands wrapped around an octahedral centre. The article was seen by some of the people doing nomenclature work with IUPAC. They were on the look-out for anyone showing an interest in nomenclature and its

development, and approached me to see if I was interested in joining their group.

Very soon after that, I found myself part of the small team preparing the revision of the Red Book. It took more than five years' of consultation, and writing and revising the text, in response to comments from nomenclature experts, before the new recommendations were completed and ready for publication. To find it, look up *Nomenclature of Inorganic Chemistry, Recommendations 2005* by NG Connelly, T Damhus, RM Hartshorn and AT Hutton, Royal Society of Chemistry, Cambridge, in your library catalogue. If it is not there, tell your librarian that it should be! I say that because it really should be, not because I have a vested interest — I don't get any royalties!

You can also find it online, through the IUPAC website: www.iupac.org/publications/books/rbook/Red_Book_2005.pdf.

New nomenclature is being developed all the time for new compounds, and sometimes even for old ones. IUPAC is currently developing recommendations for preferred IUPAC names (PINs). Most compounds can be named in more than one systematic way. The PINs recommendations are being developed to help in situations where it is really important that everyone uses the same name (such as in health and safety, patent law, taxation and other regulatory areas). Chemists will still be free to use the current range of systematic nomenclatures, but PINs may be required for particular situations.

Naming Inorganic Compounds

The way in which we name inorganic compounds (i.e. those not composed primarily of carbon and hydrogen) depends to some extent on the exact nature of the compound in question. We will examine the different possible types of inorganic compounds in the following pages. You should appreciate that what follows is, of necessity, an abbreviated version of the IUPAC rules for naming inorganic compounds. The full version may be found at the IUPAC website (www.iupac.org).

Nonmetallic Binary Compounds

The written name of a compound includes the names of the elements it contains and information about the number of atoms of each element present. The elements have to occur in some order, and this is set by the same guidelines as for the chemical formula (see p. 36). Names can contain elemental names, roots derived from elemental names and prefixes indicating the number of atoms of each element. Tables 2.4 and 2.5 list the more important roots and prefixes that appear in the names of nonmetallic binary compounds, compounds that contain only two elements, neither of which are metals.

TABLE 2.4 Common Roots for Naming Compounds

Element	Full name	Root
As	arsenic	arsen-
Br	bromine	brom-
C	carbon	carb-
Cl	chlorine	chlor-
F	fluorine	fluor-
H	hydrogen	hydr-
I	iodine	iod-
N	nitrogen	nitr-
O	oxygen	ox-

P	phosphorus	phosph-
S	sulfur	sulf-

TABLE 2.5 Number Prefixes for Chemical Names

Number	Prefix	Example	Name
1	mono-	CO	carbon monoxide[(a)]
2	di-	SiO_2	silicon dioxide
3	tri-	NI_3	nitrogen triiodide
4	tetra-	$SnCl_4$	tin tetrachloride
5	penta-	PCl_5	phosphorus pentachloride
6	hexa-	SF_6	sulfur hexafluoride
7	hepta-	IF_7	iodine heptafluoride

(a) The final 'o' of the prefix is omitted in this case.

We can summarise the rules for naming nonmetallic binary compounds in four guidelines:

1. The element closer to the left of the periodic table appears first. If both elements are from the same group of the periodic table, the lower one appears first.
2. The element that appears first retains its elemental name.
3. The second element begins with a root derived from its elemental name and ends with the suffix *-ide*. Some common roots are listed in table 2.4.
4. When there is more than one atom of a given element in the formula, the name of the element usually contains a prefix that specifies the number of atoms present. Common prefixes are given in table 2.5.

Numerical prefixes are essential in naming similar binary compounds. For example, nitrogen and oxygen form the six different compounds shown as space-filling models in figure 2.19: NO, nitrogen monoxide; NO_2, nitrogen dioxide; N_2O, dinitrogen oxide; N_2O_3, dinitrogen trioxide; N_2O_4, dinitrogen tetraoxide; and N_2O_5, dinitrogen pentaoxide.

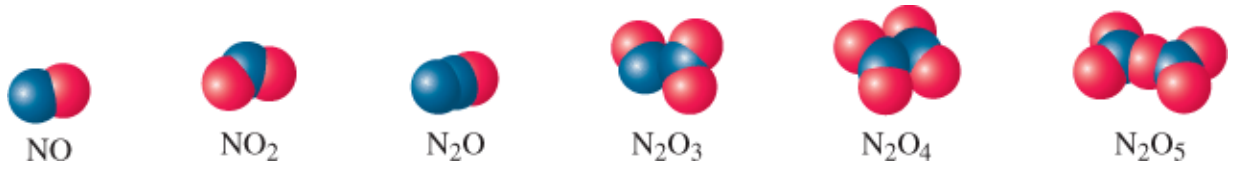


FIGURE 2.19 Space-filling models of the six compounds formed between nitrogen and oxygen.

WORKED EXAMPLE 2.9

Naming binary compounds

Name the following binary compounds: SO_2, CS_2, BCl_3 and BrF_5.

Analysis

None of these compounds contains a metallic element, so we apply the guidelines for non-metallic binary compound nomenclature.

Solution

Name the first element, use a root plus *-ide* for the second element and indicate the number of atoms with prefixes. Therefore, we obtain:

SO_2: sulfur dioxide

CS_2: carbon disulfide

BCl_3: boron trichloride

BrF_5: bromine pentafluoride.

PRACTICE EXERCISE 2.12

Name the compounds that contain:

(a) Four atoms of bromine and one atom of silicon

(b) Three atoms of oxygen and one atom of sulfur

(c) Three atoms of fluorine and one atom of chlorine.

Binary Compounds of Hydrogen

Hydrogen requires special consideration because, as we saw earlier, it may appear first or second in the chemical formula of a compound and, as a result, it may appear first or second in the name. This is particularly evident in the diatomic molecules that hydrogen forms with elements from groups 1 and 17, which are named according to the guidelines on the previous page. For example, LiH is lithium hydride, and HF is hydrogen fluoride. With elements from groups 2 and 16, hydrogen forms compounds containing two atoms of hydrogen. Except for oxygen, there is only one commonly occurring binary compound for each of these elements, so the prefix *di-* is omitted. Examples are H_2S, hydrogen sulfide, and CaH_2, calcium hydride. Oxygen forms two binary compounds with hydrogen. These have unsystematic names: one is water, H_2O (systematic name oxidane), and the other is hydrogen peroxide, H_2O_2 (systematic name dioxidane). Binary compounds of hydrogen with elements from groups 13, 14 and 15 have unsystematic names in common use; B_2H_6 is diborane, CH_4 is methane, SiH_4 is silane, NH_3 is ammonia (systematic name azane) and PH_3 is phosphine (systematic name phosphane). In fact, carbon, boron and silicon form many different binary compounds with hydrogen, and only the simplest of these are listed here.

Ionic Compounds

Binary compounds which contain metal ions are often ionic, consisting of a cation and an anion (see chapter 1, p. 2). We name binary ionic compounds with the cation first and the anion, which takes the suffix *-ide*, last. For example, NaCl is named sodium chloride, while KI is named potassium iodide. Compounds such as CaF_2, in which the numbers of cations and anions are not the same, do not require the actual number of cations and anions to be specified. Thus CaF_2 is named calcium fluoride, not calcium difluoride. The reason for this is that calcium is a group 2 element, and will therefore form only a 2+ cation. This will always combine with two 1- anions to form a neutral ionic compound, and therefore we need not specify *di*fluoride. Using the same reasoning, we can see that Na_2S and MgI_2 are named sodium sulfide and magnesium iodide respectively. Ionic compounds containing polyatomic ions such as NH_4^+, NO_3^- and SO_4^{2-} are again named with the cation followed by the anion, but you will need to learn both the names and the charges of the common polyatomic ions to be able to name, and write chemical formulae for, compounds containing these ions. Table 2.6 lists the more common polyatomic ions.

TABLE 2.6 Names and chemical formulae of some common polyatomic ions

Formula	Name
Cations	
NH_4^+	ammonium
H_3O^+	hydronium (oxonium)
Hg_2^{2+}	dimercury (2+)
Diatomic anions	
OH^-	hydroxide
CN^-	cyanide
Anions with carbon	
CO_3^{2-}	carbonate
HCO_3^-	hydrogencarbonate (bicarbonate)
CH_3COO^-	acetate
$C_2O_4^{2-}$	oxalate
Oxoanions	
SO_4^{2-}	sulfate
SO_3^{2-}	sulfite
NO_3^-	nitrate
NO_2^-	nitrite
PO_4^{3-}	phosphate
MnO_4^-	permanganate
CrO_4^{2-}	chromate
$Cr_2O_7^{2-}$	dichromate
ClO_4^-	perchlorate
ClO_3^-	chlorate
ClO_2^-	chlorite
ClO^-	hypochlorite

You can see from this table that there are a significant number of anions containing a central atom surrounded by oxygen atoms. Such ions are called **oxoanions**, and their names can be deduced using the following rules:

1. The name has a root taken from the name of the central atom (for example, carbonate, CO_3^{2-}, and nitrite, NO_2^-).
2. When an element forms two different oxoanions, the one with fewer oxygen atoms ends in-*ite*, and the other ends in-*ate* (for example, SO_3^{2-}, sulfite, and SO_4^{2-}, sulfate).
3. Chlorine, bromine and iodine each form four different oxoanions that are distinguished by prefixes and suffixes. The nomenclature of these ions is illustrated for bromine, but it applies to chlorine and iodine as well:

BrO^-, hypobromite; BrO_2^-, bromite; BrO_3^-, bromate; and BrO_4^-, perbromate.

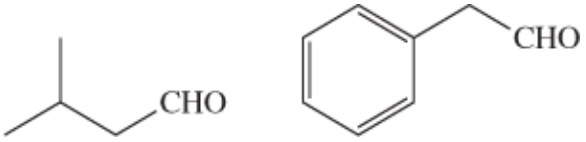
4. A polyatomic anion with a charge more negative than 1- may add H^+ to give another anion. These anions are named from the parent anion by adding the word hydrogen. For example, HCO_3^- is hydrogencarbonate, HPO_4^{2-} is hydrogenphosphate and $H_2PO_4^-$ is dihydrogenphosphate.

Naming Organic Compounds

Organic compounds are composed primarily of carbon and hydrogen atoms, and the naming system used is based on the number of carbon atoms in the particular molecule. Not surprisingly, there are an enormous number of rules for naming organic compounds and at this stage we will restrict ourselves to the basics. Indeed, computer programs are now able to generate names from nearly any structural diagram, providing a helpful supplement to knowledge of the rules of IUPAC nomenclature.

Functional Groups

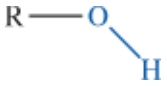
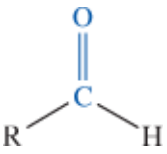
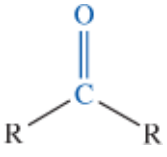
The concept of functional groups underpins all of organic chemistry and makes it the systematic discipline that it is. A **functional group** is simply a group of one or more atoms within a molecule, bonded together in a particular fashion, and is usually the point of reaction within a molecule. Organic molecules are also named primarily according to the functional group or groups they contain. The power of the functional group concept is that molecules containing the same functional group tend to behave in chemically similar ways, and this allows us to predict their reactivity towards particular reagents with some confidence. For example, although the two molecules below look quite different, they both contain the aldehyde functional group, —CHO.

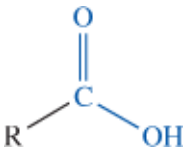


We can therefore predict that both molecules will undergo a reaction called oxidation, in which the —CHO group is converted to a —COOH (carboxylic acid) functional group. Similarly, both compounds will react with species called reducing agents, which will convert the —CHO group to a $—CH_2OH$ (primary alcohol) group. (We will learn a lot more about the specific reactions involved later in this textbook.)

It therefore makes sense to name organic compounds according to their functional groups, and we will learn how this is done on the following pages. But first, the common functional groups that you will encounter are outlined in table 2.7. Note that R is a commonly used symbol to denote either a H atom, or an alkyl group (table 2.9, p. 55). You should be able to identify the presence of each of these functional groups in any molecule.

TABLE 2.7 Common Functional Groups

Functional group	Name of group	Found in	R =
	hydroxyl	alcohols	C
	carbonyl	aldehydes	C or H
	carbonyl	ketones	C



carboxyl	carboxylic acids	C or H

Alcohols

The —OH (hydroxyl) group is present in all alcohols. It is attached to a carbon atom, which itself may be attached to one, two or three other carbon atoms (the exception is methanol, CH_3OH, which contains only one carbon atom). Alcohols are classified as primary (1°), secondary (2°) or tertiary (3°) according to this number, as shown in figure 2.20.

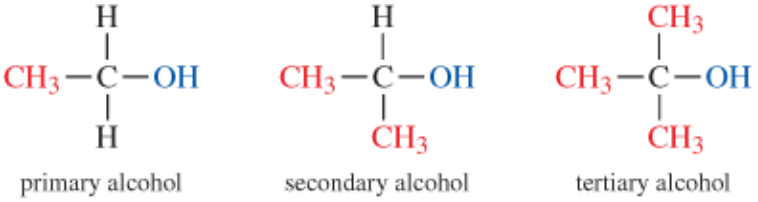


FIGURE 2.20 Structural formulae of primary, secondary and tertiary alcohols.

We can also classify carbon atoms within molecules according to this scheme. Thus a carbon atom attached to one carbon atom (as in a primary alcohol) is called a **primary carbon atom**, a carbon atom attached to two carbon atoms (as in a secondary alcohol) is called a **secondary carbon atom**, and a carbon atom attached to three carbon atoms (as in a tertiary alcohol) is called a **tertiary carbon atom**.

WORKED EXAMPLE 2.10

Writing possible structures for alcohols

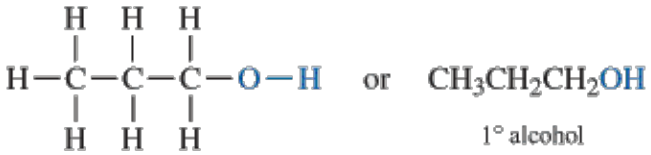
Write condensed structural formulae for the two alcohols with the molecular formula C_3H_8O. Classify each as primary, secondary or tertiary.

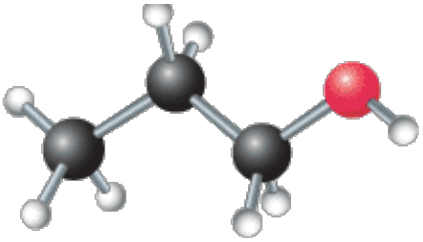
Analysis

We know that alcohols contain the —OH group. We must therefore draw the two possible structures of the formula C_3H_8O which contain an —OH group, remembering that each carbon atom in the molecule must have four bonds. In problems like this, it is generally easiest to draw the structural formula, and then convert it to the condensed form.

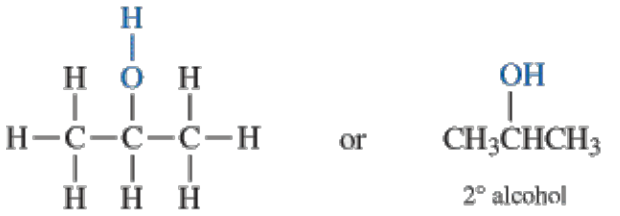
Solution

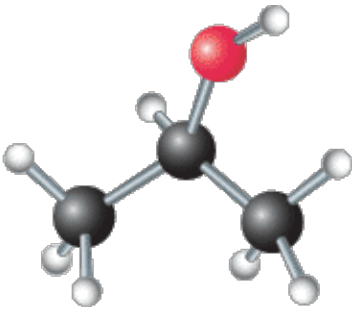
We have a three-carbon chain in the molecule, and so the —OH group can be attached only to either the terminal carbon (it does not matter which one; the same compound results regardless of which end we attach the functional group to) or the central carbon. Therefore, we begin by drawing the carbon chain, then attach the —OH group in the two possible positions, and fill in the hydrogen atoms. Doing this gives us the following two compounds.





The compound above is a primary alcohol as the —OH group is attached to a carbon atom directly bonded to only one other carbon.





In contrast to the first structure, the above compound is a secondary alcohol, the central carbon in the chain being bonded to two other carbon atoms.

PRACTICE EXERCISE 2.13

Write condensed structural formulae for the four alcohols with the molecular formula $C_4H_{10}O$. Classify each as primary, secondary or tertiary.

Aldehydes and Ketones

Aldehydes and ketones both contain the same functional group, the carbonyl group (C═O), but they differ in the way that the carbonyl group is bonded to the rest of the molecule. Aldehydes *always* have the carbon atom of the carbonyl group bonded to at least one hydrogen atom, and this means that the carbonyl group of an aldehyde must always be at the *end* of a carbon chain. Conversely, the carbon atom of the carbonyl group in ketones is *always* bonded to two other carbon atoms, and therefore can never be at the end of a carbon chain. We can write the aldehyde either explicitly as:



or as RCHO in a condensed structural formula. The differences between aldehydes and ketones are shown in figure 2.21.

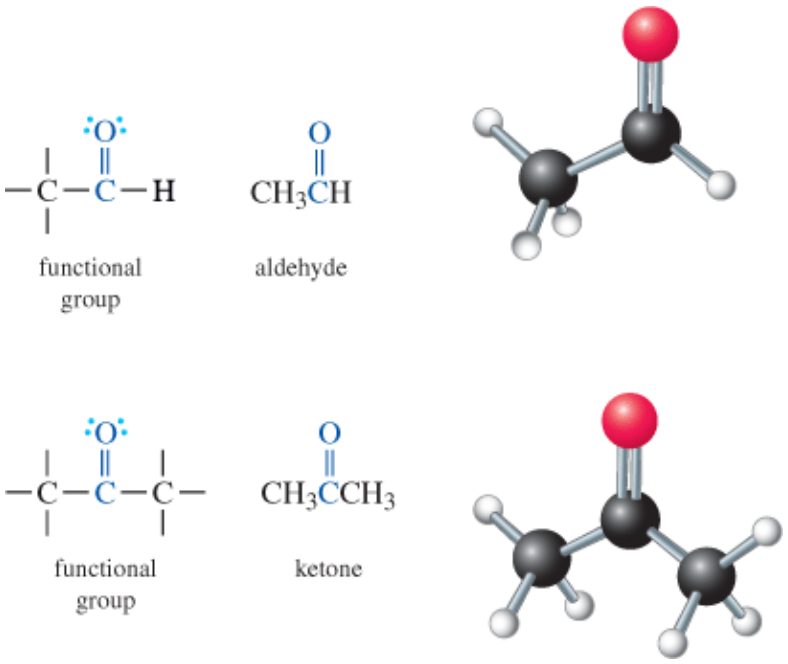


FIGURE 2.21 Structural formulae and ball-and-stick models of an aldehyde and a ketone.

WORKED EXAMPLE 2.11

Writing possible structures for aldehydes

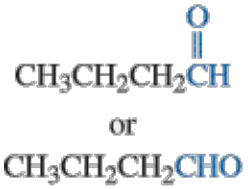
Write condensed structural formulae for the two aldehydes with the chemical formula C_4H_8O.

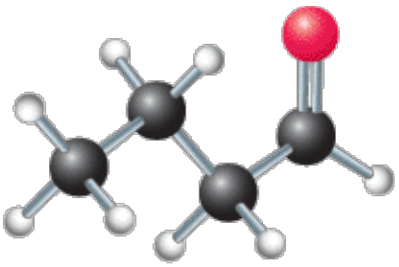
Analysis

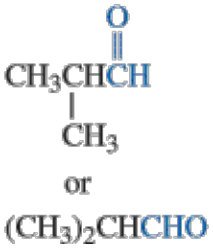
We know that the functional group in aldehydes can be only at the end of a carbon chain. In this case, we have four carbon atoms, and there are two possible ways of connecting these so that the —CHO group lies at the end of a chain.

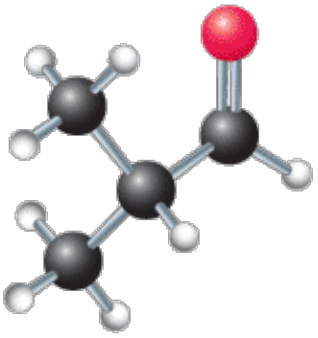
Solution

Begin by writing the —CHO group and then attaching the remaining three carbon atoms. We can connect the four carbon atoms in a straight chain or a branched chain. The two possibilities are shown below.









PRACTICE EXERCISE 2.14

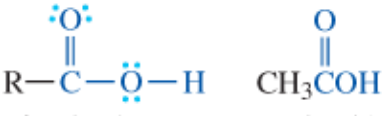
Write condensed structural formulae for the three ketones with the molecular formula $C_5H_{10}O$.

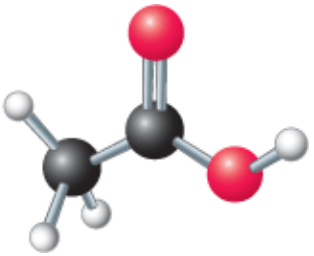
Carboxylic Acids

The functional group found in all carboxylic acids is the carboxyl group, —COOH. We can write this explicitly as:



or, more commonly, as RCOOH. As the carbon atom of a carboxyl group can bond to only one other atom, carboxyl groups are *always* found at the end of a carbon chain.





WORKED EXAMPLE 2.12

Writing possible structures for carboxylic acids

Write a condensed structural formula for the carboxylic acid with the molecular formula $C_3H_6O_2$.

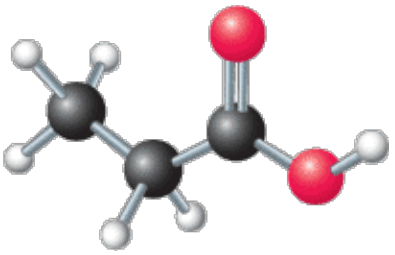
Analysis

There is only one possible compound we can draw here. It must contain a three-carbon chain with a —COOH group on the end.

Solution

Begin by drawing the —COOH group and then attach the remaining carbon atoms. Finish by adding hydrogen atoms so that all the carbon atoms have four bonds. This gives us the compound shown on the next page.





PRACTICE EXERCISE 2.15

Write condensed structural formulae for the two carboxylic acids that have the molecular formula $C_4H_8O_2$.

The Nomenclature of Alkanes

The names of some organic compounds have already been used in this chapter, but we have not yet learned how these names are derived. Organic compounds, as mentioned previously, are named according to their functional group. The first step in naming most organic compounds is to identify the functional group that they contain. However, we will begin by looking at a series of compounds that are not considered to contain any functional group at all: the alkanes.

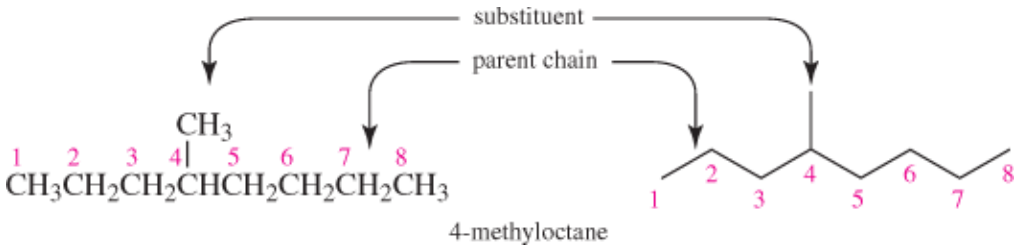
Alkanes are molecules that contain only carbon and hydrogen and in which carbon atoms are joined by single bonds only. Alkanes can be divided into two classes, depending on the overall geometry of the carbon atoms. Alkanes in which the carbon atoms are joined in chains are called **acyclic alkanes** and have the general formula C_nH_{2n+2}. The carbon atoms in alkanes can also be joined together to form one or more rings, and such compounds are called **cycloalkanes**. All alkanes belong to a group of organic compounds called **hydrocarbons**, which are molecules composed solely of carbon and hydrogen. Alkanes are sometimes called **saturated hydrocarbons**, to denote the fact that all the carbon–carbon bonds are single. As there are no functional groups in alkanes, we name them according to the length of the longest carbon chain. There are two parts to the name of an alkane: a prefix, indicating the number of carbon atoms in the chain, and the ending–*ane*. The prefixes for carbon chain lengths up to 10 carbon atoms are shown in table 2.8.

TABLE 2.8 Prefixes Used in the IUPAC System for Chain Lengths of 1 to 10 Carbon Atoms

Prefix	Number of carbon atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6

hept-	7
oct-	8
non-	9
dec-	10

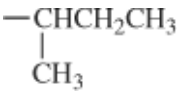
The simplest alkane is methane, which contains one carbon atom and has the formula CH_4. Note that the suffix and prefix are not hyphenated, but are written together as one word. The alkane with six carbon atoms in a straight chain ($CH_3CH_2CH_2CH_2CH_2CH_3$) is likewise called hexane. Names for the straight-chain alkanes are straightforward, but things become more complex for alkanes in which the carbon chain is branched. In order to name such alkanes, identify the longest straight carbon chain (the **parent chain**), and then treat any groups which branch off this chain as **substituents**. The IUPAC name of an alkane with a branched chain consists of a root name that indicates the longest chain of carbon atoms in the compound, substituent names that indicate the groups bonded to the parent chain, and numbers that indicate the carbon atom to which the substituents are attached. This is illustrated below for 4-methyloctane, C_9H_{20}, in which the longest carbon chain contains eight carbon atoms (hence *octane*) and the —CH_3 (methyl) group bonded to C(4) is a substituent (hence *4-methyl*).

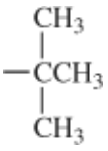


The substituents in alkanes are named according to the alkane from which they are derived. For example, a —CH_3 substituent is derived from methane, CH_4, through the removal of one H atom. Similarly, a —C_2H_5 substituent is derived from ethane, C_2H_6, by removal of one H atom. A substituent derived from an alkane by the removal of one H atom is called an **alkyl group** and is commonly represented by the symbol R. Alkyl groups are named by dropping the *-ane* from the name of the parent alkane and adding the suffix *-yl*. Therefore, a —CH_3 substituent is called *methyl*, and a —C_2H_5 substituent *ethyl*. Table 2.9 gives names and structural formulae for eight of the most common alkyl groups. Note that, when alkyl substituents contain three or more carbon atoms, there is more than one possible arrangement of the carbon atoms in the substituent. We differentiate between these possibilities using the prefixes iso, *sec*- and *tert*-. Iso implies the presence of a —$CH(CH_3)_2$ group at the end of the substituent carbon chain (the only possibility for a three-atom chain), while the prefixes *sec*- and *tert*- imply that the substituent is bonded to the longest carbon chain via a secondary or tertiary carbon atom, respectively. When *sec*- and *tert*- are part of a name, they are always italicised and hyphenated. However, iso, as used in both isopropyl and isobutyl, is not treated as a prefix like *sec*- and *tert*-, and is neither italicised nor hyphenated.

TABLE 2.9 Names, formulae and abbreviations of the most common alkyl groups

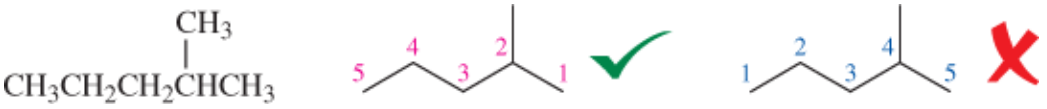
Name	Condensed structural formula	Abbreviation
methyl	—CH_3	Me
ethyl	—CH_2CH_3	Et
propyl	—$CH_2CH_2CH_3$	Pr
isopropyl	—$CHCH_3$ (with CH_3 below)	i-Pr
butyl	—$CH_2CH_2CH_2CH_3$	Bu
isobutyl	—CH_2CHCH_3 (with CH_3 below)	i-Bu
sec-butyl		*s*-Bu



tert-butyl		*t*-Bu

The complete IUPAC rules for naming alkanes are:

1. The name for an alkane with an unbranched chain of carbon atoms consists of a prefix showing the number of carbon atoms in the chain (table 2.8) and the ending–*ane*.
2. For branched-chain alkanes, the longest chain of carbon atoms is the parent chain, and its name becomes the root name.
3. For an alkane with one substituent, number the parent chain so that the carbon atom bearing the substituent is given the lowest possible number. For example, we number the five-carbon chain in the following compound from the right-hand end.

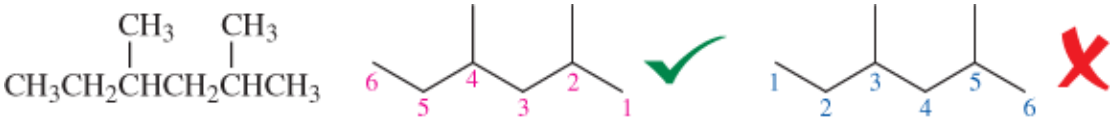


4. Give the substituent on the parent chain a name and a number. The number shows the carbon atom of the parent chain to which the substituent is bonded. Use a hyphen to connect the number to the name. For example, the methyl group in 2-methylpropane is attached to C(2), as shown below.



2-methylpropane

5. If there are two or more identical substituents, number the parent chain from the end that gives the lower number to the substituent closest to the end of the chain. If there are two or more identical substituents, the number of times they occur is indicated by the prefixes *di-*, *tri-*, *tetra-*, *penta-*, *hexa-* and so on. A comma is used to separate position numbers. Of the two possibilities below, we choose the one that numbers the carbon atoms to which the methyl groups are attached as 2 and 4, rather than 3 and 5.



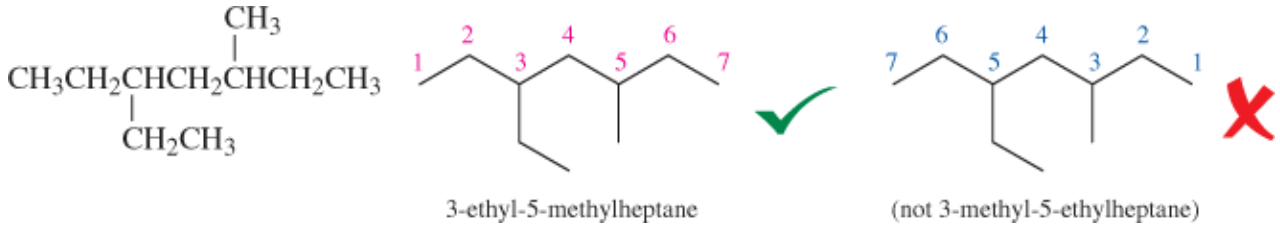
2,4-dimethylhexane (not 3,5-dimethylhexane)

6. If step 5 leads to more than one possibility, number the parent chain such that the first point of difference has the lowest possible number. Of the two possibilities below, we choose the one that numbers the methyl group shown in red 3 rather than 4.



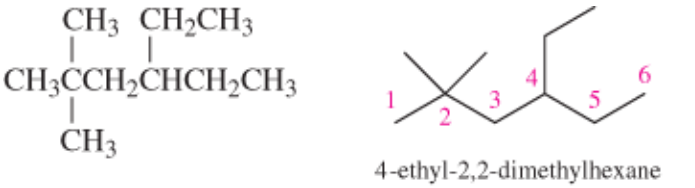
2,3,5-trimethylhexane (not 2,4,5-trimethylhexane)

7. If there are two or more different substituents, list them in alphabetical order, and (as usual) number the chain from the end that gives the lower number to the substituent encountered first or that provides the first point of difference. If there are different substituents in equivalent positions on opposite ends of the parent chain, the substituent of lower alphabetical order is given the lower number. The importance of alphabetically ordering the substituents is shown in the following example.



3-ethyl-5-methylheptane (not 3-methyl-5-ethylheptane)

8. The prefixes *di-*, *tri-*, *tetra-* and so on, and the hyphenated prefixes *sec-* and *tert-* are disregarded for the purposes of placing the substituents in alphabetical order. Note that both isobutyl and isopropyl substituents are treated as beginning with the letter 'i'. Put the names of the substituents in alphabetical order first, and then insert the prefix. In the following example, the substituents are ordered as ethyl and methyl, not dimethyl and ethyl.



4-ethyl-2,2-dimethylhexane
(not 2,2-dimethyl-4-ethylhexane)

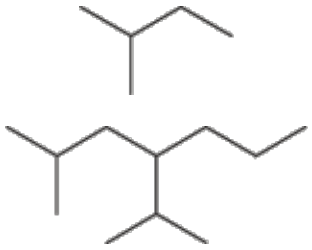
WORKED EXAMPLE 2.13

Writing IUPAC names for alkanes

Write IUPAC names for the following alkanes.

(a)

(b)



Analysis

We need to follow the rules for naming alkanes outlined previously. When naming alkanes, start by identifying the longest carbon chain, and then identify and number the substituents.

Solution

We will consider each alkane in turn. The longest carbon chain in (a) contains four carbon atoms and therefore will be named as a substituted butane. We then number the parent chain to give the methyl substituent the lowest possible number. This is done in either of the two equivalent ways shown below (note that the substituent is at C(2) in both cases).

(a)

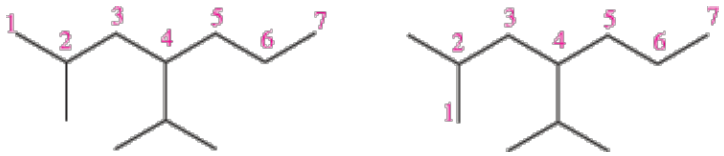


We now name the substituent and specify its position on the parent chain to obtain the full name. This alkane is therefore named 2-methylbutane.

The longest carbon chain in (b) contains seven carbon atoms, and therefore it will be named as a substituted heptane. There are two substituents in this molecule: a methyl group and an isopropyl group, and therefore we must number the chain to give the substituent closest to the end of the chain the lowest

number. This is shown in the following diagram, where we again have two equivalent possibilities.

(b)



To name the alkane, list the substituents in alphabetical order and specify their positions on the parent chain. As isopropyl comes before methyl, this alkane is named 4-isopropyl-2-methylheptane.

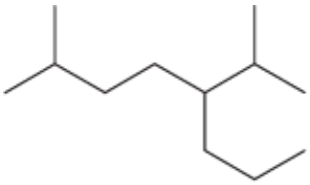
Is our answer reasonable?

The easiest way to check the answers to this type of question is to work backwards from the name we have deduced, and derive the chemical structure. If we do that in this case, we find that our answers are correct.

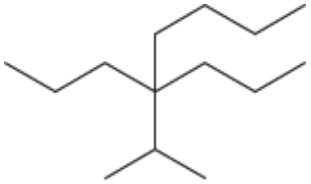
PRACTICE EXERCISE 2.16

Write the IUPAC names for the following alkanes.

(a)

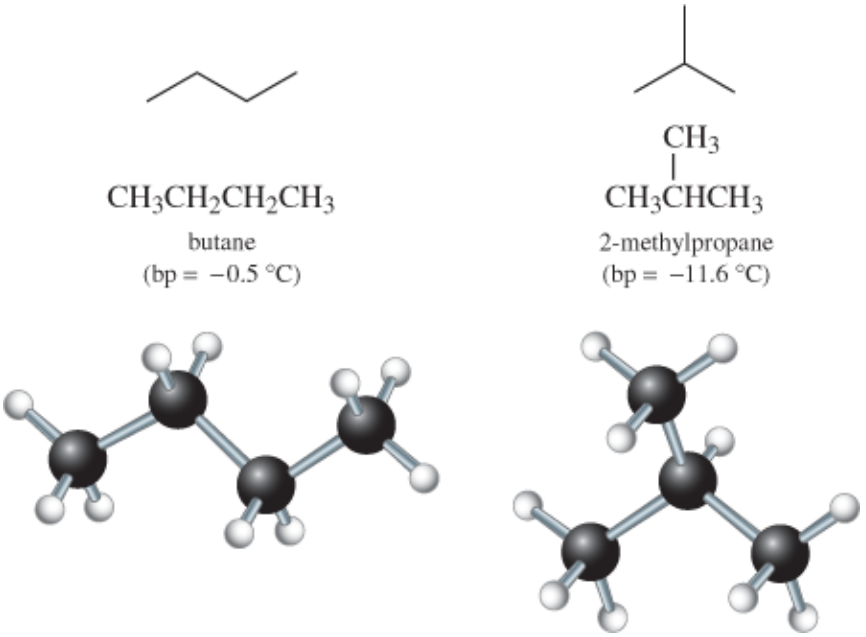


(b)

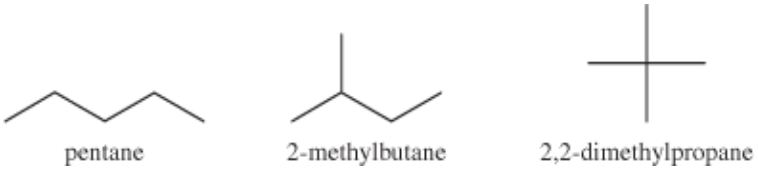


Constitutional Isomerism in Alkanes

The concept of isomerism was mentioned previously with respect to the relative positioning of the two methyl groups in 1,2-dimethylcyclopentane. The alkanes provide an excellent example of the different ways in which a particular number of carbon and hydrogen atoms may be joined. There is only one order of attachment, and hence one way of writing CH_4 (methane), C_2H_6 (ethane) and C_3H_8 (propane). However, when we come to C_4H_{10} two orders of attachment of atoms are possible.



In one of these, butane, the four carbon atoms are bonded in a straight chain; in the other, 2-methyl propane, three carbon atoms are bonded in a straight chain, with the fourth carbon atom as a branch. Butane and 2-methylpropane are constitutional isomers. **Constitutional isomers** are compounds with the same chemical formula but a different order of attachment of the constituent atoms. Constitutional isomers can usually be distinguished by their differing physical properties; butane and 2-methylpropane provide a good example of this; butane boils at -0.5 °C, while 2-methyl propane boils at -11.6 °C. If we consider C_5H_{12}, we can obtain the three constitutional isomers shown below.



The number of possible constitutional isomers becomes very large very quickly. For example, the alkane with the chemical formula $C_{25}H_{52}$ has a staggering 36 797 588 possible constitutional isomers. Constitutional isomers are not unique to alkanes, and can be found throughout organic chemistry; indeed, worked examples 2.10 and 2.11 involved drawing constitutional isomers of alcohols and aldehydes respectively.

WORKED EXAMPLE 2.14

Recognising constitutional isomers

Do the structural formulae in each of the following pairs of molecules represent the same compound or constitutional isomers?

(a) $CH_3CH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2CH_2(CH_2CH_2CH_3)$ (each is C_6H_{14})

(b) $CH_3CH(CH_3)CH_2CH(CH_3)CH_3$ and $CH_3CH_2CH(CH_3)CH(CH_3)CH_3$ (each is C_7H_{16})

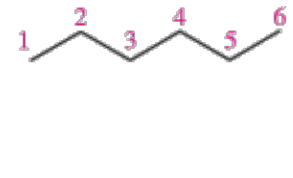
Analysis

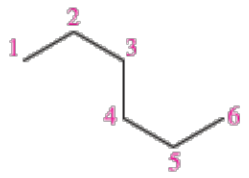
To determine whether these structural formulae represent the same compound or constitutional isomers,

we must first find the longest chain of carbon atoms. Note that it makes no difference whether the chain is drawn straight or bent. We then number the longest chain from the end nearest the first branch and compare the lengths of each chain, and the sizes and locations of any branches. Structural formulae that have the same order of attachment of atoms represent the same compound; those which have different orders of attachment of atoms represent constitutional isomers. Note that similarities or differences between structural formulae are sometimes made clearer if they are drawn as line structures.

Solution

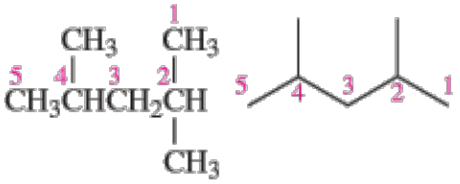
(a) Each structural formula has an unbranched chain of six carbon atoms. The two structures are identical and represent the same compound.





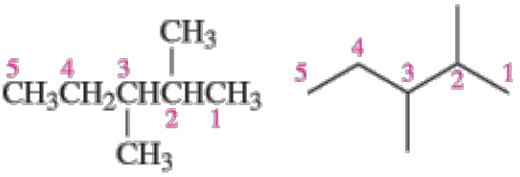
$$\overset{1}{\mathrm{CH_3}}\overset{2}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_2}}\overset{5}{\mathrm{CH_2}}\overset{6}{\mathrm{CH_3}} \quad \text{and} \quad \overset{1}{\mathrm{CH_3}}\overset{2}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\mathrm{CH_2}\overset{4}{\mathrm{CH_2}}\overset{5}{\mathrm{CH_2}}\overset{6}{\mathrm{CH_3}}$$

(b) Each structural formula has a chain of five carbon atoms with two branches. Although the branches are identical, they are at different locations on the chains. Therefore, these structural formulae represent constitutional isomers.



2,4-dimethylpentane
(bp = 80.6 °C)

and

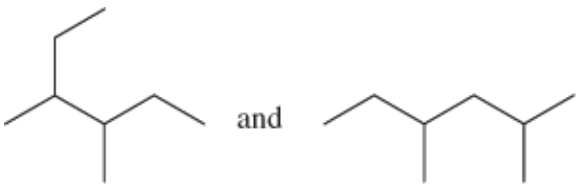


2,3-dimethylpentane
(bp = 89.8 °C)

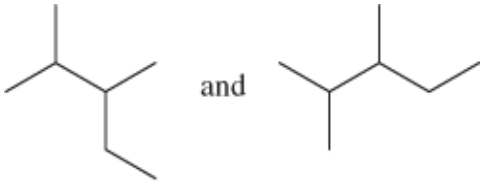
PRACTICE EXERCISE 2.17

Do the structural formulae in each of the following pairs of molecules represent the same compound or constitutional isomers?

(a)



(b)



WORKED EXAMPLE 2.15

Drawing constitutional isomers

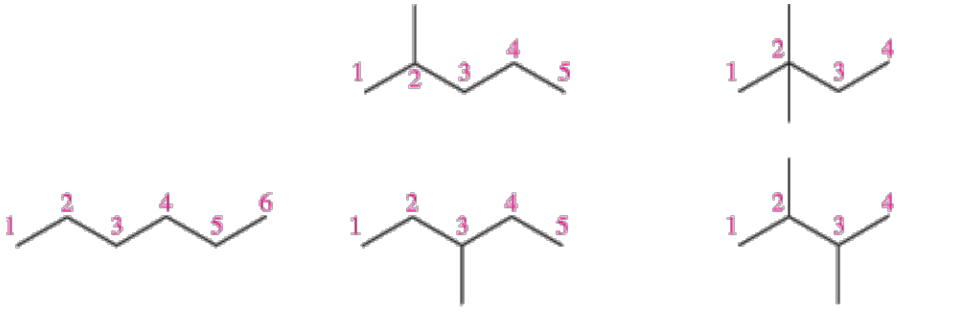
Draw structural formulae for the five constitutional isomers with the molecular formula C_6H_{14}.

Analysis

There are six carbon atoms in the molecule, so we can expect constitutional isomers with longest carbon chain lengths of six, five, four and possibly three. We must draw all possible isomers with these chain lengths.

Solution

The constitutional isomers of C_6H_{14} are as follows.



6 carbon atoms in an unbranched chain

5 carbon atoms in a chain; 1 carbon atom as a branch

4 carbon atoms in a chain; 2 carbon atoms as branches

Note that we find that there is no way of writing C_6H_{14} with only three carbon atoms in the longest chain.

Is our answer reasonable?

There are no other possible arrangements of six carbon atoms and fourteen hydrogen atoms, each singly bonded to each other. Therefore, we can be confident our answers are correct.

PRACTICE EXERCISE 2.18

Draw the nine constitutional isomers with the formula C_7H_{16}.

General Organic Nomenclature

The principles of IUPAC nomenclature as applied to alkanes can be extended to the naming of any organic compound. The name we give to any compound with a chain of carbon atoms consists of three parts: a prefix, an infix and a suffix. Each part provides specific information about the structural formula of the compound.

1. The prefix shows the number of carbon atoms in the parent chain. Prefixes that show the presence of 1 to 10 carbon atoms in a chain were given in table 2.8.
2. The infix shows the nature of the carbon–carbon bonds in the parent chain. The three possibilities are given in table 2.10.

TABLE 2.10 The Three Possible Infixes and Their Meanings

Infix	Nature of carbon–carbon bonds in the parent chain
-an-	all single bonds
-en	one or more double bonds
-yn-	one or more triple bonds

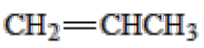
3. The suffix shows the class of compound to which the substance belongs, and therefore the functional group(s) present in the compound. The suffixes for the classes of compound we have already met are as shown in table 2.11.

TABLE 2.11 Some Suffixes and the Class of Compound that they Designate

Suffix	Class of compound
-e	hydrocarbon
-ol	alcohol
-al	aldehyde
-one	ketone
-oic acid	carboxylic acid

We can illustrate the use of prefixes, infixes and suffixes with respect to the following four organic compounds. We will divide each name into a prefix, an infix and a suffix, and specify the information about the structural formula that is contained in each part of the name.

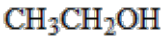
(a)



propene

The prefix *prop-* means three carbon atoms in the parent chain. The infix *-en-* refers to the presence of one or more C═C double bonds in the molecule, while the suffix *-e* means that the compound is a hydrocarbon, composed of only carbon and hydrogen atoms.

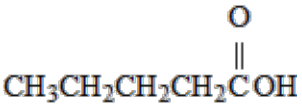
(b)



ethanol

The prefix *eth-* means two carbon atoms in the parent chain. The infix *-an-* means there are no carbon–carbon multiple bonds in the molecule, and the suffix *-ol* means that there is an alcohol functional group in the molecule.

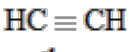
(c)



pentanoic acid

The prefix *pent-* means five carbon atoms in the parent chain. The infix *-an-* means there are no carbon–carbon multiple bonds in the molecule, and the suffix *-oic acid* refers to the presence of a carboxylic acid in the molecule.

(d)



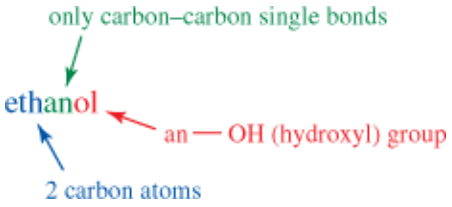
ethyne (d)

The prefix *eth-* means two carbon atoms in the parent chain. The infix *-yn-* means that there are one or more C≡C triple bonds in the molecule. The suffix *-e* means that the compound is a hydrocarbon, composed of only carbon and hydrogen atoms.

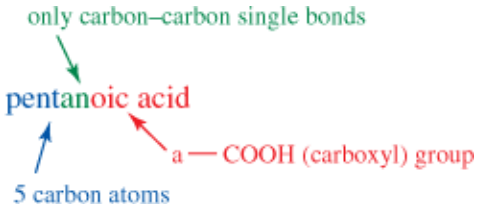
We can summarise this information in the following diagram.

(a)

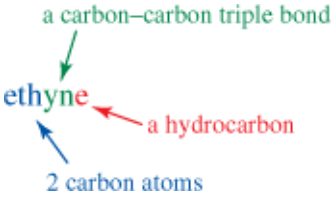
(b)



(c)



(d)

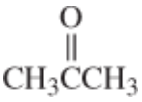


Notice that, in each of these examples, there is no ambiguity about the position of the functional group. We will deal later with examples where the position is not as clear.

PRACTICE EXERCISE 2.19

Combine the proper prefix, infix and suffix, and write the IUPAC name for each of the following compounds.

(a)



(b)



The examples given in this section serve only as an introduction to organic nomenclature; you will find more detailed examples in the appropriate chapters later in the book.

We have seen in this chapter that such apparently disparate topics as units, nomenclature and representations of molecules are all part of the language of chemistry. There is still much of this language for you to learn, but this chapter has introduced many of the fundamentals that you will need in order to understand and appreciate the following chapters. Indeed, it is likely that you will often need to refer back to this chapter when you come across examples of measurement, representations of molecules or nomenclature later in this book.

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SUMMARY

Measurement

All measurements have an associated unit and uncertainty. The units used for measurements are based on the set of seven SI base units, which can be combined to give various derived units. The SI base units are the metre, kilogram, second, kelvin, mole, ampere and candela. Prefixes can be used to denote multiplication of these units by powers of 10. Dimensional analysis, which uses the fact that units undergo the same kinds of mathematical operations as the numbers to which they are attached, can be used as an aid to determining the correct form of an equation. Some non-SI units are in common usage but can be converted to SI units using a conversion factor.

Uncertainties arise in any measurement from the limitations of the apparatus used to make the measurement. Some idea of the uncertainty and therefore precision in a measurement can be obtained from the number of significant figures to which the measurement is quoted.

Expressing a number in scientific notation can make it easier to determine the number of significant figures. There will always be uncertainty in the final figure of any measurement. The accuracy of a measurement shows how close to the true value the measurement is, while the precision of a measurement represents how reproducible it is.

When measurements are manipulated in equations, the following rules apply:

- When measurements are multiplied or divided, the number of significant figures in the answer should not be greater than the number of significant figures in the least precise measurement.
- When measurements are added or subtracted, the answer should have the same number of decimal places as the quantity with the fewest number of decimal places.

Representations of Molecules

The chemical formula of a substance shows the relative number of each type of atom present, but gives no structural information. The rules for writing chemical formulae of binary compounds are as follows:

1. With the exception of hydrogen, the element further to the left in the periodic table appears first.
2. If hydrogen is present, it appears last except when the other element is from group 16 or 17 of the periodic table.
3. If both elements are from the same group of the periodic table, the lower one appears first.

The chemical formulae of ionic compounds are written with the cation followed by the anion, while organic compounds have C and H first, followed by the rest of the elements in alphabetical order.

Structural formulae attempt to show particular aspects of molecular structure in both two and three dimensions. Such depictions are especially important in organic chemistry where catenation leads to an enormous number of possible carbon-based molecules. Structural formulae are drawn using one line to represent single bonds, two lines for double bonds and three lines for triple bonds. Carbon atoms at the end of a carbon chain are called terminal carbon atoms. Structural formulae can help distinguish between isomers. Two types of shorthand structural formulae are widely used; condensed structural formulae do not include explicit depictions of bonds between atoms, while line structures remove atom labels for carbon atoms and all hydrogen atoms that are bonded to carbon atoms. Three-dimensional aspects can be introduced into structural formulae through the use of hashed and solid wedges, which show bonds going away from and coming towards the observer respectively.

Ball-and-stick models and space-filling models are two other methods where three-dimensionality may be shown.

Mechanistic arrows can be used to show the movement of electrons in chemical processes. The tail of the arrow is situated at the electron source and the arrow head shows the destination.

Nomenclature

Chemical species can be named according to sets of rules prescribed by IUPAC. The rules for naming nonmetallic binary compounds are as follows:

1. The element closer to the left of the periodic table appears first. If both elements are from the same group of the periodic table, the lower one appears first.
2. The element that appears first retains its elemental name.
3. The second element begins with a root derived from its elemental name and ends with the suffix *-ide*.
4. When there is more than one atom of a given element in the formula, the name of the element usually contains a prefix that specifies the number of atoms present.

Binary compounds containing hydrogen can be named with hydrogen either first or second, depending on the position of the other element in the periodic table, according to the above rules.

Ionic compounds are named with the cation first, followed by the anion, while oxoanions are named according to an extensive set of rules.

Organic compounds are named primarily according to their functional group; those of importance in this chapter are the —OH group found in alcohols, the —CHO group found in aldehydes, the C═O group found in ketones and the —COOH group found in carboxylic acids. Alkanes belong to the group of compounds called hydrocarbons and are sometimes called saturated hydrocarbons. Those consisting solely of chains of carbon atoms are called acyclic alkanes, while those containing one or more rings of carbon atoms are called cycloalkanes. Their nomenclature is based on the longest carbon chain within the molecule, with a prefix denoting the length of that chain. Substituents on the chain are numbered such that the sum of the numbers for the substituents present is the lowest possible number. Names of organic compounds generally comprise a prefix, infix and suffix. The prefix shows the number of carbon atoms in the parent chain, the infix shows the nature of the carbon–carbon bonds in the parent chain, and the suffix shows the class of compound to which the substance belongs, and therefore the functional group(s) present in the compound.

Constitutional isomers of alkanes have the same chemical formulae but different structural formulae and hence different names. These isomers generally have different physical properties.

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KEY CONCEPTS AND EQUATIONS

SI units *(section 2.1)*

The base SI units: metre, kilogram, second, kelvin, mole, ampere and candela are used either directly or to derive units for any measurement in chemistry.

SI prefixes *(section 2.1)*

SI prefixes are used to create larger and smaller units. The prefixes help us to convert between differently sized units.

Dimensional analysis *(section 2.1)*

Dimensional analysis assists in determining the correct form of an equation through knowledge of the units of all components of the equation.

Rules for significant figures in calculations *(section 2.1)*

The following rules are used to round answers to the correct number of significant figures.

- When measurements are multiplied or divided, the number of significant figures in the answer should not be greater than the number of significant figures in the *least* precise measurement.
- When measurements are added or subtracted, the answer should have the same number of decimal places as the quantity with the *fewest* number of decimal places.

Rules for writing chemical formulae of binary compounds *(section 2.2)*

The following rules are used to write the correct chemical formulae for compounds containing only two elements.

1. With the exception of hydrogen, the element further to the left in the periodic table appears first.
2. If hydrogen is present, it appears last except when the other element is from group 16 or 17 of the periodic table.
3. If both elements are from the same group of the periodic table, the lower one appears first.
4. If the compound is ionic, we write the cation first, followed by the anion.

Rules for drawing line structures *(section 2.2)*

These rules are used for converting structural formulae to line structures, and can also be used to carry out the reverse operation.

1. All bonds except C—H bonds are shown as lines.
2. C—H bonds and H atoms attached to carbon are not shown in the line structure.
3. Single bonds are shown as one line; double bonds are shown as two lines; triple bonds are shown as three lines.
4. Carbon atoms are not labelled. All other atoms are labelled with their elemental symbols.

Hashed and solid wedges *(section 2.2)*

These are used to introduce three-dimensional aspects into structural formulae.

A solid wedge () represents a bond coming out of the page, while a hashed wedge () represents a bond going back into the page. A normal line is used for bonds in the plane of the page.

Mechanistic arrows *(section 2.2)*

These are used to show the movement of electrons in chemical processes. Single-headed arrows show the movement of a single electron, while two-headed arrows show the movement of electron pairs. The direction of electron movement is from the tail of the arrow to the head.

Naming nonmetallic binary compounds *(section 2.3)*

These rules are used to name compounds containing only two nonmetallic elements.

1. The element closer to the left of the periodic table appears first. If both elements are from the same group of the periodic table, the lower one appears first.
2. The element that appears first retains its elemental name.
3. The second element begins with a root derived from its elemental name and ends with the suffix *-ide*.
4. When there is more than one atom of a given element in the formula, the name of the element usually contains a prefix that specifies the number of atoms present.

Naming oxoanions *(section 2.3)*

These rules are used to name anions containing oxygen and at least one other element.

1. The name has a root taken from the name of the central atom.
2. When an element forms two different oxoanions, the one with fewer oxygen atoms ends in-*ite* and the other ends in-*ate*.
3. Chlorine, bromine and iodine each form four different oxoanions that are distinguished by prefixes and suffixes.
4. A polyatomic anion with a charge more negative than 1–may add H^+ to give another anion. These anions are named from the parent anion by adding the word *hydrogen*.

Functional groups *(section 2.3)*

Functional groups are the basis for naming organic compounds.

- Alcohols contain a hydroxyl group.
- Aldehydes contain a terminal carbonyl group.
- Ketones contain a non-terminal carbonyl group.
- Carboxylic acids contain a carboxyl group.

Naming alkanes *(section 2.3)*

There are two parts to the name of an alkane: a prefix, indicating the number of carbon atoms in the chain, and the suffix *-ane*.

Prefixes for carbon chain length *(section 2.3)*

Knowledge of these prefixes is necessary for naming any organic compound: 1, meth-; 2, eth-; 3, prop-; 4, but-; 5, pent-; 6, hex-; 7, hept-; 8, oct-; 9, non-; 10, dec-.

General organic nomenclature *(section 2.3)*

The prefix, infix and suffix of the name of an organic compound reflect the structure of that compound.

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REVIEW QUESTIONS

Measurement

2.1 Why must measurements always be written with a unit?

2.2 What does the abbreviation SI stand for?

2.3 Which SI base unit is defined in terms of a physical object?

2.4 What is the only SI base unit that includes a decimal prefix?

2.5 Newton's second law states that force is equal to mass times acceleration. What is the SI derived unit for force? (The unit is called the newton, abbreviated N.)

2.6 What is the meaning of each of the following prefixes?

(a) centi
(b) milli-
(c) kilo-
(d) micro-
(e) nano-
(f) pico
(g) mega

2.7 What abbreviation is used for each of the prefixes named in question 2.6?

2.8 What units are most useful in the laboratory for measuring the following?

(a) length
(b) volume
(c) mass

2.9 Define the term ‘significant figures’.

2.10 What is the difference between ‘accuracy’ and ‘precision’?

2.11 A concentration of 1.5 μg mL^{-1} of a toxin is found in a sample of a patient's blood. How high might the concentration actually have been? Suppose that the measurement had been written as 1.50 μg mL^{-1} of blood. How high might the concentration have been in this case?

2.12 There are 3600 s in 1 hour. By what conversion factor would you multiply 250 s to convert it to hours? By what conversion factor would you multiply 3.84 h to convert it to seconds?

Representations of Molecules

2.13 List the rules for the conversion of structural formulae to line structures.

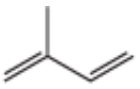
2.14 What must be true about two substances if they are to be called isomers of each other?

2.15 Write the chemical formula for each of the following substances.

(a) stearic acid, which contains 36 hydrogen atoms, 18 carbon atoms and 2 oxygen atoms
(b) silicon tetrachloride, which contains 1 silicon atom and 4 chlorine atoms
(c) Freon-113, which contains 3 atoms each of fluorine and chlorine and 2 atoms of carbon

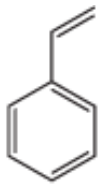
2.16 The line structures that follow represent starting materials for making plastics. For each of them, draw the structural formula and give the chemical formula.

(a)



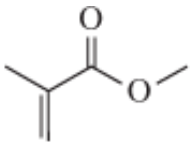
isoprene
(sourced from nature to produce rubber)

(b)



styrene
(used to make styrofoam)

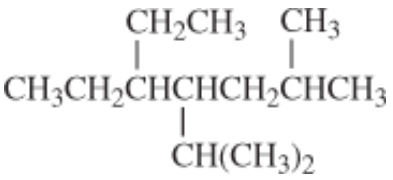
(c)



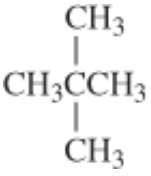
methyl methacrylate
(used to make perspex)

2.17 Write line structures for compounds (a) to (f).

(a)

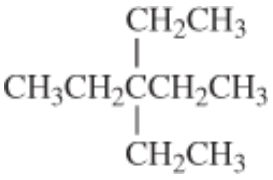


(b)



(c) $(CH_3)_2CHCH(CH_3)_2$

(d)

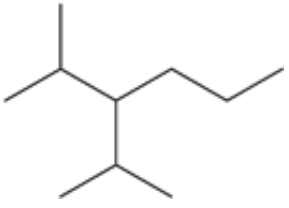


(e) $(CH_3)_3CH$

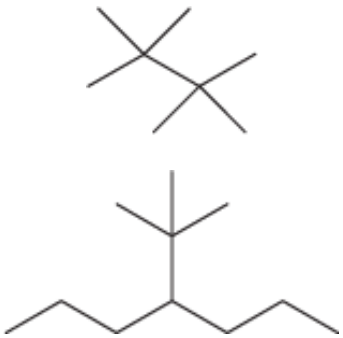
(f) $CH_3(CH_2)_3CH(CH_3)_2$

2.18 Write the chemical formula and the condensed structural formula for each of the following alkanes.

(a)



(b)

(c) 

2.19 Provide an even more abbreviated formula for each of the following condensed structural formulae, using parentheses and subscripts.

(a) $CH_3CH_2CH_2CH_2CH_2CH(CH_3)$

(b) $CH_3C(CH_2CH_2CH_3)(CH_2CH_2CH_3)CH_2CH_2CH_2CH_2CH_3$

(c) $HC(CH_2CH_2CH_3)(CH_2CH_2CH_3)CH_2CH_2CH_3$

Nomenclature

2.20 Write chemical formulae for the following compounds.

(a) chlorine monofluoride
(b) selenium trioxide
(c) hydrogen bromide
(d) silicon tetrachloride
(e) sulfur dioxide
(f) hydrogen peroxide

2.21 Name the following compounds.

(a) ClF_3
(b) H_2Se
(c) ClO_2
(d) $SbCl_3$
(e) PCl_5
(f) N_2O_5
(g) N_2Cl_4
(h) NH_3

2.22 Draw the structural formulae of the following molecules.

(a) butane
(b) 3-methylpentane
(c) 2,3-dimethylhexane

2.23 Why do we not have to label aldehydes as primary or secondary, or carboxylic acids as being primary, secondary or tertiary?

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REVIEW PROBLEMS

2.24 What number should replace the question mark in each of the following?

(a) 1 cm = ? m

(b) 1 km = ? m

(c) 1 m = ? pm

(d) 1 dm = ? m

(e) 1 g = ? kg

(f) 1 cg = ? g

(g) 1 nm = ? m

(h) 1 μg = ? g

(i) 1 kg = ? g

(j) 1 Mg = ? g

(k) 1 mg = ? g

(l) 1 dg = ? g

2.25 Convert each of the following measurements to the given units.

(a) 60 °C to K

(b) -30 °C to K

(c) 273 K to °C

(d) 299 K to °C

(e) 40 °C to K

2.26 Natural gas is mostly methane, a substance that boils at a temperature of 111 K. What is its boiling point in °C?

2.27 Helium has the lowest boiling point of any liquid. It boils at 4 K. What is its boiling point in °C?

2.28 How many significant figures do the following measured quantities have?

(a) 37.53 cm

(b) 37.240 cm

(c) 202.0 g

(d) 0.000 24 kg

(e) 0.070 80 m

(f) 2400 mL

2.29 How many significant figures do the following measured quantities have?

(a) 0.0230 g

(b) 105.303 m

(c) 0.007 kg

(d) 614.00 mg

(e) 10 L

(f) 3.8105 mm

2.30 How many significant figures do the following measured quantities have?

(a) 1.0230 kg

(b) 3.0200 m

(c) 0.0030 L

(d) 27.300 g

(e) 0.043 20 mm

2.31 How many significant figures do the following measured quantities have?

(a) 2.303 ng

(b) 0.040 30 kg

(c) 20 030 mL

(d) 9200 g

(e) 0.0101 dL

2.32 Perform the following arithmetic and round the answers to the correct number of significant figures.

(a) 0.0023 m × 315 m

(b) 84.25 kg - 0.010 75 kg

(c) (84.45 g - 94.45 g)/(31.4 mL - 9.9 mL)

(d) (23.4 g + 102.4 g + 0.003 g)/(6.478 mL)

(e) (313.44 cm - 209.1 cm) × 8.2234 cm

2.33 Perform the following arithmetic and round the answers to the correct number of significant figures.

(a) 3.58 g/1.739 mL

(b) 4.02 mL + 0.001 mL

(c) (22.4 g - 8.3 g)/(1.142 mL - 0.002 mL)

(d) (1.345 g + 0.022 g)/(13.36 mL - 8.4115 mL)

(e) (74.335 m - 74.332 m)/(4.75 s × 1.114 s)

2.34 Express the following numbers in scientific notation to three significant figures.

(a) 4340

(b) 32 000 000

(c) 0.003 287

(d) 42 000

(e) 0.000 008 00

(f) 324 300

2.35 Express the following numbers in scientific notation. Assume, in this problem, that only the non-zero digits are significant figures.

(a) 489

(b) 0.003 75

(c) 82 300

(d) 0.012 25

(e) 2.43

(f) 27 320

2.36 Write the following numbers in standard (non-scientific) form.

(a) 3.1×10^{5}

(b) 4.35×10^{-6}

(c) 3.9×10^{3}

(d) 4.4×10^{-12}

(e) 35.6×10^{-7}

(f) 8.8×10^{8}

2.37 Write the following numbers in standard (non-scientific) form.

(a) 5.27×10^{-8}

(b) 7.12×10^{5}

(c) 43.5×10^{-9}

(d) 2.35×10^{-2}

(e) 4.0000×10^{7}

(f) 37.2×10^{2}

2.38 Perform the following arithmetic and express the answers in scientific notation.

(a) $(4.0 \times 10^{7}) - (2.1 \times 10^{5})$

(b) $(3.0 \times 10^{-2}) + (3.21 \times 10^{-5})$

(c) $(2.1 \times 10^{7}) \times (2.1 \times 10^{5})$

(d) $(3.0 \times 10^{4}) \times (8.2 \times 10^{-5})$

(e) $(9.10 \times 10^{12})/(2.0 \times 10^{-3})^{2}$

2.39 Perform the following arithmetic and express the answers in scientific notation.

(a) $(3.0 \times 10^{4}) \times (2.1 \times 10^{5})$

(b) $(8.0 \times 10^{12})/(2.0 \times 10^{-3})^{2}$

(c) $(6.7 \times 10^{-5}) \times (8.2 \times 10^{-5})$

(d) $(1.4 \times 10^{5}) - (3.0 \times 10^{4})$

(e) $(3.3 \times 10^{-4}) + (2.52 \times 10^{-2})$

2.40 Convert each of the following measurements to the given units.

(a) 32.0 dm to km

(b) 8.2 mg to μg

(c) 75.3 mg to kg

(d) 137.5 mL to L

(e) 0.025 L to mL

(f) 342 pm to dm

2.41 Convert each of the following measurements to the given units.

(a) 92 dL to mL

(b) 22 ng to μg

(c) 83 pL to nL

(d) 230 km to m

(e) 87.3 cm to km

(f) 238 mm to nm

2.42 Convert each of the following measurements to the given units and express your answers in scientific notation.

(a) 230 km to cm

(b) 423 kg to mg

(c) 423 kg to Mg

(d) 430 μL to mL

(e) 27 ng to kg

(f) 730 nL to kL

2.43 Convert each of the following measurements to the given units and express your answers in scientific notation.

(a) 183 nm to cm

(b) 3.55 g to dg

(c) 6.22 km to nm

(d) 33 dm to mm

(e) 0.55 dm to km

(f) 53.8 ng to pg

2.44 Which functional group does each of the following compounds contain?

(a) $CH_3CH{=}CH_2$

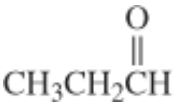
(b) CH_3CH_2OH

(c) $CH_3CH_2CH_2COOH$

(d) $HOCH_2CH_2CH_3$

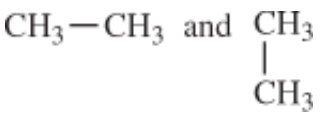
2.45 Which functional group does each of the following compounds contain?

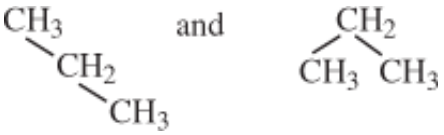
(a) $CH_3C{\equiv}CH$

(b) 

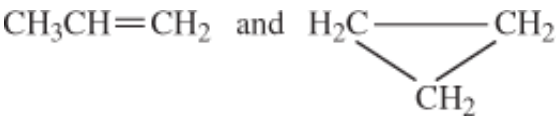
(c) 

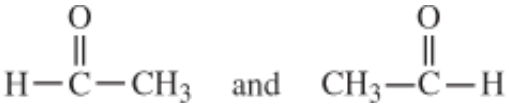
2.46 Decide whether the members of each pair are identical, isomers or unrelated.

(a) 

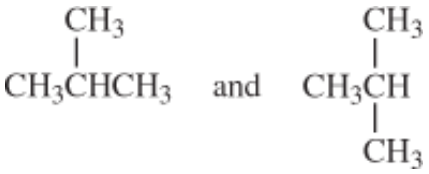
(b) 

(c) CH_3CH_2OH and $CH_3CH_2CH_2OH$

(d) 

(e) 

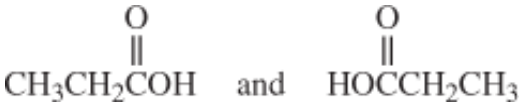
(f)



(g) $CH_3CH_2CH_2NH_2$ and $CH_3CH_2—NH—CH_3$

2.47 Examine each pair and decide if they are identical, isomers or unrelated.

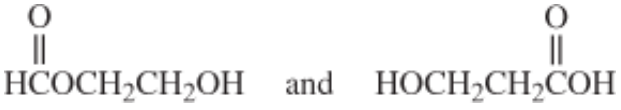
(a)



(b)



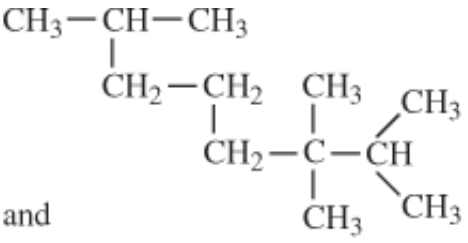
(c)



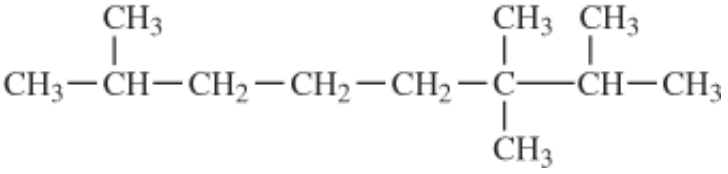
(d)



(e)



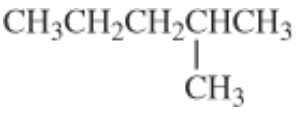
and



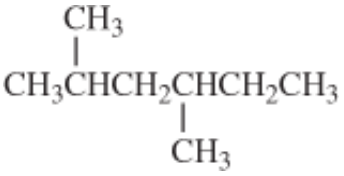
2.48 Write the IUPAC names of the following hydrocarbons.

(a) $CH_3CH_2CH_2CH_2CH_3$

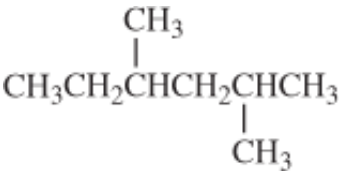
(b)



(c)



(d)

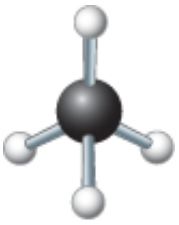


2.49 Write structural formulae for all of the saturated alcohols with three or fewer carbon atoms per molecule.

2.50 Write structural formulae for all of the possible alcohols with the general formula $C_4H_{10}O$.

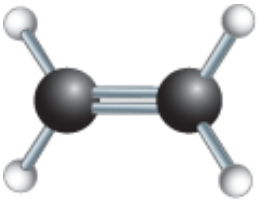
2.51 Write chemical formulae for the molecules whose ball-and-stick models follow.

(a)



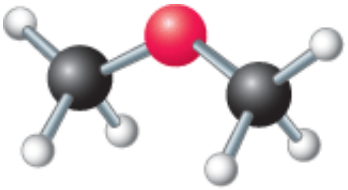
methane

(b)



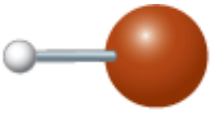
ethene

(c)



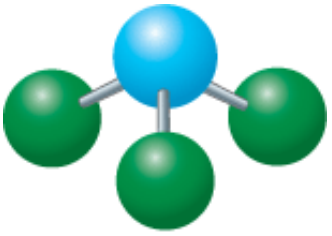
dimethyl ether

(d)



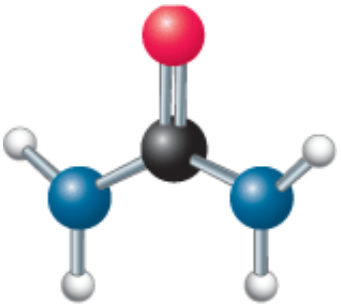
hydrogen bromide

(e)



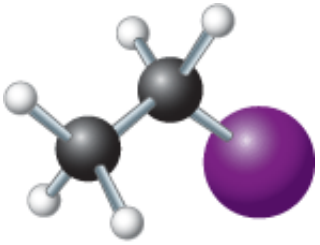
phosphorus trichloride

(f)



urea

(g)



iodoethane

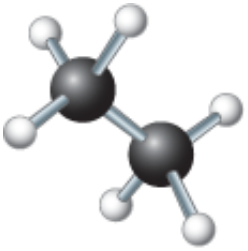
2.52 Write chemical formulae for the molecules whose ball-and-stick models follow.

(a)



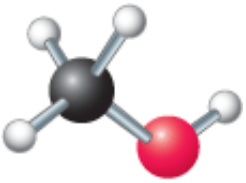
ammonia

(b)



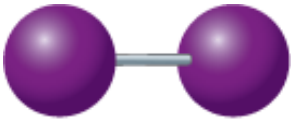
ethane

(c)



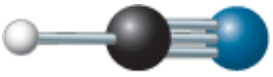
methanol

(d)



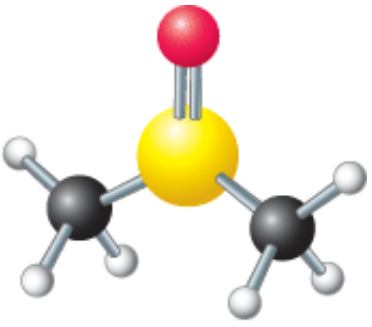
iodine

(e)



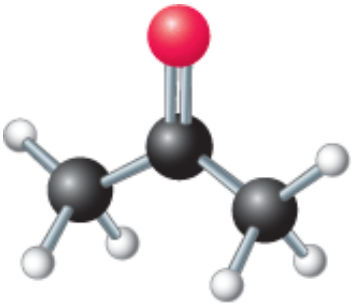
hydrogen cyanide

(f)



dimethylsulfoxide

(g)

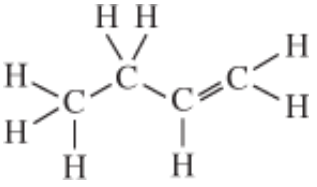


acetone

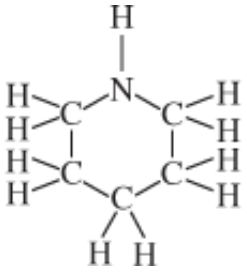
2.53 Write structural formulae for the molecules in questions 2.51 and 2.52.

2.54 Convert the following structural formulae into line structures.

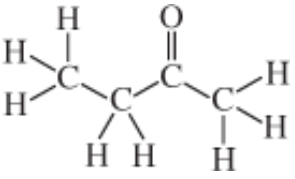
(a)



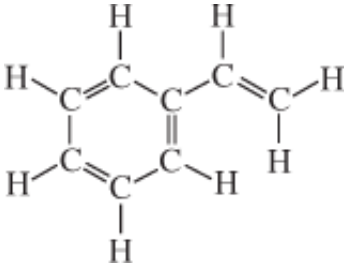
(b)



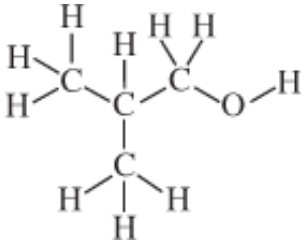
(c)



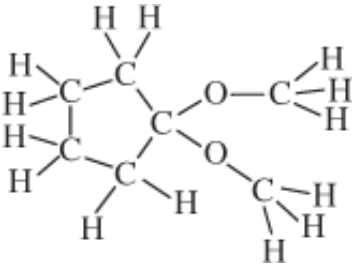
(d)



(e)

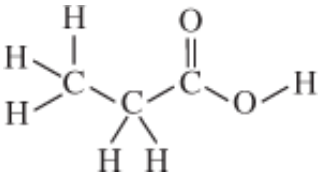


(f)

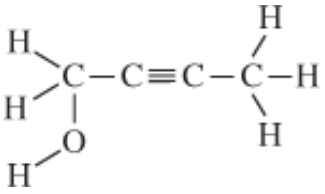


2.55 Convert the following structural formulae into line structures.

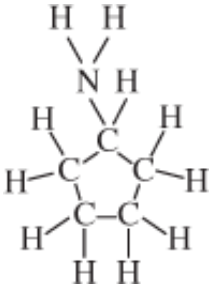
(a)



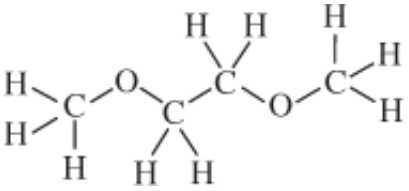
(b)



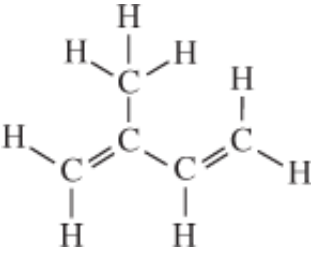
(c)



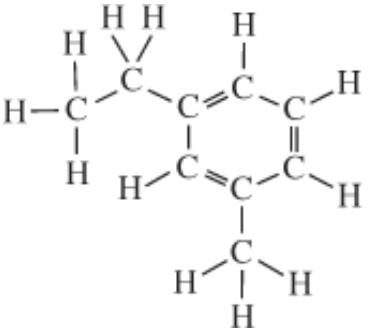
(d)



(e)

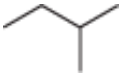


(f)



2.56 Convert the following line structures into structural formulae.

(a)



(b)

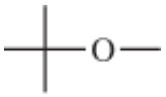


(c)



(d)

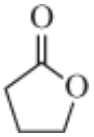
(e)



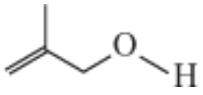
(f)



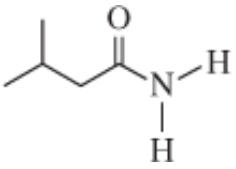
(g)



(h)



(i)

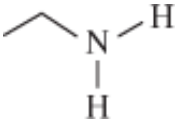


2.57 Convert the following line structures into structural formulae.

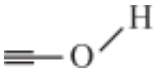
(a)



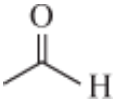
(b)



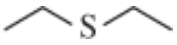
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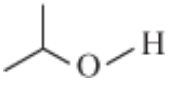
(d)



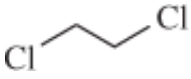
(e)



(f)



(g)



2.58 Which of the following statements are true about constitutional isomers?

(a) They have the same chemical formula.

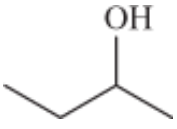
(b) They have the same atomic mass.

(c) They have the same order of attachment of atoms.

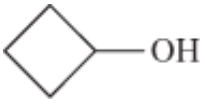
(d) They have the same physical properties.

2.59 Each member of the following set of compounds is an alcohol.

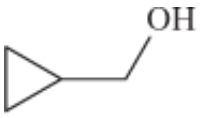
i.



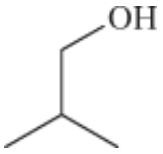
ii.



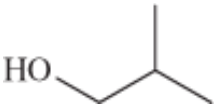
iii.



iv.



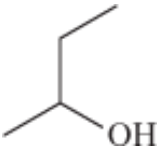
v.



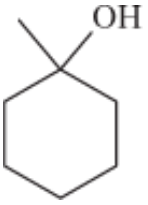
vi.



vii.



viii.



Which structural formulae represent:

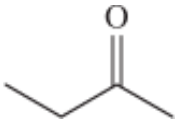
(a) the same compound?

(b) different compounds that are constitutional isomers?

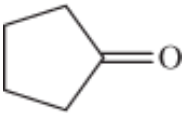
(c) different compounds that are not constitutional isomers?

2.60 Each member of the following set of compounds is either an aldehyde or a ketone.

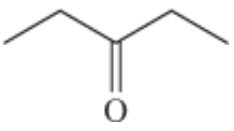
i.



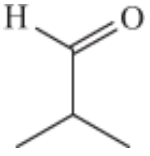
ii.



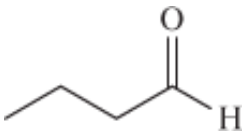
iii.

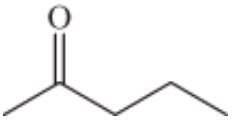


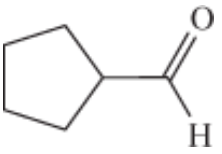
iv.



v.

vi. 

vii. 

viii. 

Which structural formulae represent:

(a) the same compound?

(b) different compounds that are constitutional isomers?

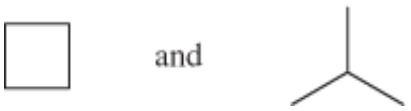
(c) different compounds that are not constitutional isomers?

2.61 For each of the following pairs of compounds, determine whether the structural formulae shown represent:

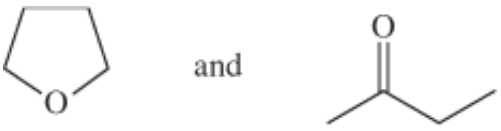
i. the same compound

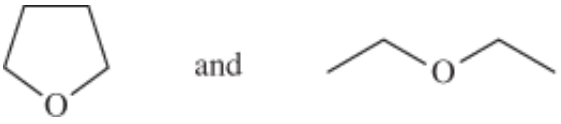
ii. different compounds that are constitutional isomers

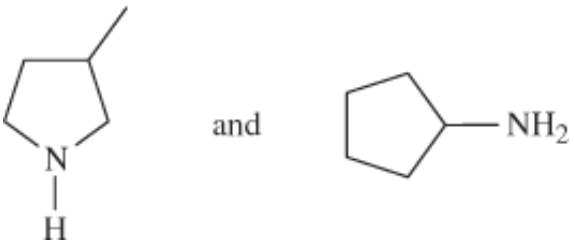
iii. different compounds that are not constitutional isomers.

(a) 

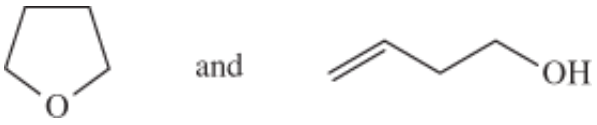
(b) 

(c) 

(d) 

(e) 

(f)



2.62 Which sets of compounds are constitutional isomers?

(a) CH_3CH_2OH and CH_3OCH_3

(b) $CH_3\overset{\overset{O}{\|}}{C}CH_3$ and $CH_3CH_2\overset{\overset{O}{\|}}{C}H$

(c) $CH_3\overset{\overset{O}{\|}}{C}OCH_3$ and $CH_3CH_2\overset{\overset{O}{\|}}{C}OH$

(d) $CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_3$ and $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$

(e)  and $CH_3CH_2CH_2CH_2CH_3$

(f)  and $CH_2{=}CHCH_2CH_2CH_3$

2.63 Draw line structures for:

(a) four alcohols with chemical formula $C_4H_{10}O$

(b) two aldehydes with chemical formula C_4H_8O

(c) one ketone with chemical formula C_4H_8O

(d) three ketones with chemical formula $C_5H_{10}O$

(e) four carboxylic acids with chemical formula $C_5H_{10}O_2$.

2.64 Write chemical formulae for these compounds.

(a) methane

(b) hydrogen iodide

(c) calcium hydride

(d) phosphorus trichloride

(e) dinitrogen pentaoxide

(f) sulfur hexafluoride

(g) boron trifluoride

2.65 Write chemical formulae for these compounds.

(a) ammonia

(b) hydrogen sulfide

(c) 2-chloropropane

(d) silicon dioxide

(e) molecular nitrogen

(f) sulfur tetrafluoride

(g) bromine pentafluoride

2.66 Name the following compounds.

(a) S_2Cl_2

(b) IF_7

(c) HBr

(d) N_2O_3

(e) SiC

(f) (f) CH_3OH

2.67 Name the following compounds.

(a) $GeCl_4$

(b) N_2F_4

(c) LiH

(d) SeO_2

(e) CH_3CH_2OH

2.68 Write the chemical formula of each compound.

(a) hydrogen fluoride

(b) calcium fluoride

(c) aluminium sulfate

(d) ammonium sulfide

2.69 Write the chemical formula of each compound.

(a) sodium hypochlorite

(b) lithium periodate

(c) magnesium bromide

2.70 Name each of the following compounds.

(a) CaO

(b) K_2CO_3

(c) HBr

(d) Na_2HPO_4

2.71 Name each of the following compounds.

(a) $(NH_4)_2SO_4$

(b) KBr

(c) H_2S

(d) Na_2S

2.72 Write chemical formulae for these compounds.

(a) sodium sulfate

(b) potassium sulfide

(c) potassium dihydrogenphosphate

(d) sodium hydrogencarbonate

(e) lithium perbromate

2.73 Write chemical formulae for these compounds.

(a) potassium chlorate

(b) ammonium hydrogencarbonate

(c) aluminium chloride

(d) potassium oxide

2.74 Name the following compounds.

(a) K_2CO_3

(b) NaClO

(c) $CuSO_4$

(d) KH_2PO_4

(e) $NaNO_3$

(f) $CaSO_3$

(g) $KMnO_4$

2.75 Name each of the following compounds.

(a) $NaNO_2$

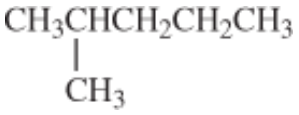
(b) $Mg_3(PO_4)_2$

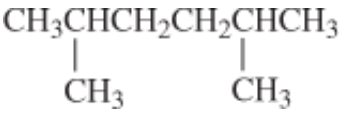
(c) $KHSO_4$

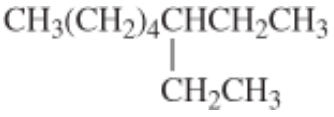
(d) CsBr

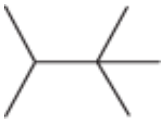
(e) $Al(ClO_4)_3$

2.76 Write IUPAC names for these alkanes.

(a) 

(b) 

(c) 

(d) 

2.77 Draw line structures for these alkanes.

(a) 2,2,4-trimethylhexane

(b) 2,2-dimethylpropane

(c) 3-ethyl-2,4,5-trimethyloctane

(d) 5-butyl-2,2-dimethylnonane

(e) 4-isopropyloctane

(f) 3,3-dimethylpentane

2.78 Explain why each of the following names is an incorrect IUPAC name, and write the correct IUPAC name for the intended compound.

(a) 1,3-dimethylbutane

(b) 4-methylpentane

(c) 2,2-diethylbutane

(d) 2-ethyl-3-methylpentane

(e) 2-propylpentane

(f) 2,2-diethylheptane

(g) 2,2-dimethylcyclopropane

(h) 1-ethyl-5-methylcyclohexane

2.79 Draw a structural formula for each of the following compounds.

(a) ethanol

(b) ethanal

(c) ethanoic acid

(d) butanone

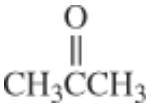
(e) butanal

(f) butanoic acid

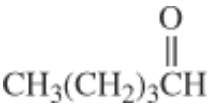
(g) propanal

2.80 Write the IUPAC name for each compound.

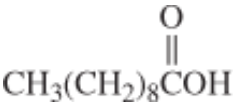
(a)



(b)



(c)

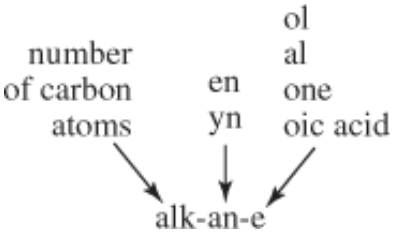


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ADDITIONAL EXERCISES

2.81 When an object is heated to a high temperature, it glows and gives off light. The colour balance of this light depends on the temperature of the glowing object. Photographic lighting is described, in terms of its colour balance, as a temperature in kelvin. For example, a certain electronic flash gives a colour balance (called colour temperature) rated at 5800 K. What is this temperature expressed in °C?

2.82 The IUPAC system divides the name of a compound into a prefix (showing the number of carbon atoms), an infix (showing the presence of carbon–carbon single, double or triple bonds), and a suffix (showing the presence of an alcohol, an aldehyde, a ketone or a carboxylic acid). Assume for the purposes of this problem that, to be an alcohol (-ol), the hydroxyl or amino group must be bonded to a carbon atom which has only single bonds to other attached atoms.



Given this information, write the structural formula of a compound with an unbranched chain of four carbon atoms that is an:

(a) alkane
(b) alkene
(c) alkyne
(d) alkanol
(e) alkenol
(f) alkynol
(g) alkanal
(h) alkenal
(i) alkynal
(j) alkanone
(k) alkenone
(l) alkynone
(m) alkanoic acid
(n) alkenoic acid
(o) alkynoic acid.

(*Note:* There is only one structural formula possible for some parts of this problem. For other parts, two or more structural formulae are possible. Where two or more are possible, we will deal with how the IUPAC system distinguishes between them when we come to the chapters on those particular functional groups.)

2.83 In everyday life, we encounter chemicals with unsystematic names. What is the name a chemist would use for each of the following substances?

(a) dry ice, CO_2
(b) saltpetre, KNO_3
(c) salt, NaCl
(d) baking soda, $NaHCO_3$

(e) soda ash, Na_2CO_3

(f) lye, NaOH

(g) lime, CaO

(h) milk of magnesia, $Mg(OH)_2$

2.84 A mineral is a chemical compound found in the Earth's crust. What are the chemical names of the following minerals?

(a) TiO_2 (rutile)

(b) PbS (galena)

(c) Al_2O_3 (bauxite)

(d) $CaCO_3$ (limestone)

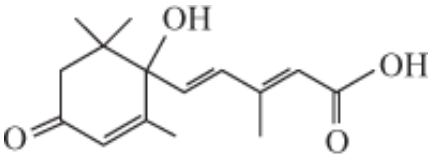
(e) $BaSO_4$ (barite)

(f) HgS (cinnabar)

(g) Sb_2S_3 (stibnite)

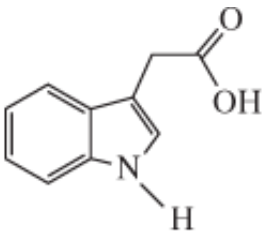
2.85 The line structures of three different plant growth hormones are given below. Write the chemical formula for each compound.

(a)



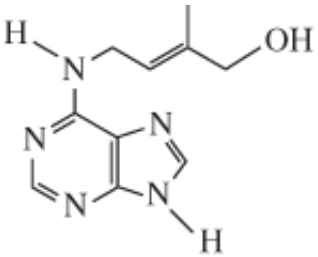
abscisic acid
(inhibits germination)

(b)



indole acetic acid
(promotes growing shoots)

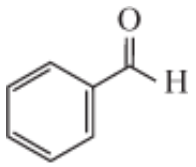
(c)



zeatin
(promotes root growth)

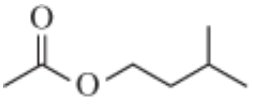
2.86 The following molecules are known for their characteristic fragrances. Convert each line structure into a complete structural formula.

(a)



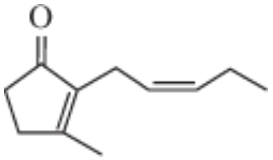
benzaldehyde
(almond)

(b)



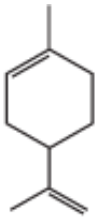
methylbutyl acetate
(banana)

(c)



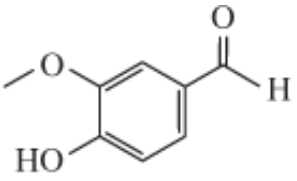
jasmone
(jasmine)

(d)



limonene
(lemon)

(e)



vanillin
(vanilla)

2.87 The compounds in the following pairs of substances are quite different from each other despite having similar names. Write correct formulae for each pair.

(a) sodium nitrite and sodium nitrate

(b) potassium carbonate and potassium hydrogencarbonate

(c) iodine and iodide ion

(d) sodium chloride and sodium hypochlorite

(e) nitrogen oxide and nitrogen dioxide

(f) potassium chlorate and potassium perchlorate

(g) ammonia and ammonium ion

2.88 Provide IUPAC-approved names for each of the following compounds.

(a) NH_4Cl

(b) BrF_5

(c) SO_2

2.89 Provide IUPAC-approved names for each of the following compounds.

(a) $KClO_3$

(b) $KClO_2$

(c) KClO

(d) KCl

(e) Na_2HPO_4

2.90 Express the results of the following logarithmic calculations to the correct number of significant figures.

(a) $\log(2.75 \times 10^{-5})$

(b) antilog(-2.53)

(c) ln(2.0)

(d) log(1.56 + 0.254)

(e) $e^{7.21}$

(f) $\ln\left[\dfrac{6.91 \times 10^{-2} \times 4.667 \times 10^{-4}}{2.0 \times 10^{-3}}\right]$

2.91 Surface tension (γ), the phenomenon that allows small insects to 'walk on water', can be defined by the following equation.

$$\gamma = \frac{\Delta E}{\Delta A}$$

Given that *E* (energy) is measured in J, and *A* (area) is measured in m^2, determine the units of surface tension.

2.92 Remembering that J is a derived unit (see table 2.2), express your answer to question 2.91 using only SI units.

2.93 The rate law for the gas-phase reaction

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

is

$$\text{rate of reaction} = k[NO]^2[H_2]$$

Determine the units of the rate constant *k*, given that the rate of reaction has units of mol L^{-1} s^{-1} and the concentrations of NO and H_2 are measured in mol L^{-1}.

2.94 From knowledge of their given units, determine an equation relating each of the following groups of variables and constants.

(a) volume (*V*, L), concentration (*c*, mol L^{-1}) and amount (*n*, mol). Make amount the subject.

(b) speed of light (*c*, m s^{-1}), energy (*E*, J), Planck's constant (*h*, J s) and wavelength (λ, m). Make energy the subject.

(c) specific heat (*c*, J g^{-1} K^{-1}), temperature change (Δ*T*, K), mass (*m*, g) and heat (*q*, J). Make mass the subject.

(d) gas density (*p*, kg m^{-3}), pressure (*p*, Pa), molar mass (*M*, kg mol^{-1}), the gas constant (*R*, J mol^{-1} K^{-1}) and temperature (*T*, K). Make pressure the subject. (*Hint:* Recall that Pa is a derived unit.)

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KEY TERMS

absolute uncertainty
accuracy
acyclic alkanes
alkane
alkyl group
ampere (A)
anhydrous
ball-and-stick model
binary compound
candela
catenation
chemical formula
condensed structural formula
constitutional isomers
cycloalkane
dimensional analysis
functional group
hashed wedge
heterolytic
homolytic
hydrate
hydrocarbon
isomers
kelvin
kilogram
line structure
mechanistic arrows
metre
mole
molecular formula
nomenclature
oxoanion
parent chain
percentage uncertainty
precision
primary carbon atom
saturated hydrocarbon
scientific notation
second
secondary carbon atom
SI (Système International) units
significant figures
solid wedge
space-filling model
structural formula
substituent
terminal carbon
tertiary carbon atom
unit

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CHAPTER

3 Chemical Reactions and Stoichiometry

Chemical plants produce large quantities of basic chemicals used in everyday consumer goods, industrial processes and research laboratories. However, if you manage a plant like the Queensland Alumina Refinery (pictured) and want to run it efficiently, you must know how much starting material is needed to synthesise a product with the best possible yield. Some of the information comes from chemical equations. Chemical equations conveniently and succinctly summarise information about chemical reactions. They show the substances you start with and the substances you end up with. They also show the relative amounts of each substance. In this chapter, you will learn how to use balanced chemical equations and the rules of stoichiometry to work out the mass of the substances required to form a desired mass of a product. A good understanding of stoic involved hiometry is essential for industrial-scale production, pharmaceutical manufacture and controlling reactions in research laboratories. It is also essential for students wanting to understand basic chemistry.



KEY TOPICS

3.1 Chemical equations
3.2 Balancing chemical equations
3.3 The mole

3.4 Empirical formulae
3.5 Stoichiometry, limiting reagents and percentage yield
3.6 Solution stoichiometry

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3.1 Chemical Equations

The production of new substances from one or more chemical species is called a **chemical reaction**. A **chemical equation**, a concept we briefly introduced in chapter 1, may be used to describe what happens when a chemical reaction occurs. It uses chemical formulae to provide a before-and-after picture of the chemical substances involved. Consider, for example, the reaction between hydrogen and oxygen (a combustion reaction) to give water. The chemical equation that describes this reaction is:

$$2H_2 + O_2 \rightarrow 2H_2O$$

The two formulae that appear to the left of the arrow are those of the **reactants**, hydrogen and oxygen, i.e. the substances that react to form the product. The formula of the product, water, is written to the right of the arrow. **Products** are the substances that are formed in the reaction. The arrow means 'react to produce'. Thus, this equation tells us that *hydrogen and oxygen react to produce water*. The reverse process, the reaction of water to form hydrogen and oxygen, can also occur, but only to a very small extent. Reactions in which both the forward and reverse reactions occur are called **reversible reactions**. The majority of chemical reactions are reversible to some extent, but, for now, we will be concerned only with the forward reaction. We will learn more about reversible reactions in chapter 9.

In this example, only one substance is formed in the reaction, so there is only one product. As we will see, however, in most chemical reactions there is more than one product. If we are concerned only with determining the identity of the products, we are engaged in **qualitative analysis**; we simply determine which substances are present in a sample without measuring their amounts. By contrast, in **quantitative analysis**, our goal is to measure the amounts of the various substances in a sample.

Stoichiometry (from the Greek *stoicheion* meaning 'element' and *metrein* meaning 'measuring') is concerned with the relative amounts of reactants and products in a chemical reaction. In the equation for the reaction of hydrogen and oxygen, the number 2 precedes the formulae of hydrogen and water. The numbers in front of the formulae are called **stoichiometric coefficients**, and they indicate the number of molecules of each kind among the reactants and products. Thus, $2H_2$ means 2 molecules of H_2, and $2H_2O$ means 2 molecules of H_2O. When no number is written, the stoichiometric coefficient is 1 (so the coefficient of O_2 equals 1). Stoichiometric coefficients can also refer to ions or atoms.

Stoichiometric coefficients are required to ensure the equation conforms to the law of conservation of mass (section 1.2). Because atoms cannot be created or destroyed in a chemical reaction, we must have the same number of atoms of each kind present before and after the reaction (i.e. on both sides of the arrow), as shown in figure 3.1. This is an example of a **balanced chemical equation**. Another example is shown in figure 3.2: the equation for the reaction of butane, C_4H_{10}, with oxygen, O_2. Butane can be used as the fuel in camping stoves.

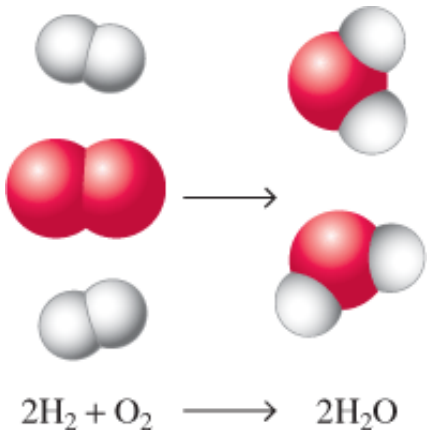


FIGURE 3.1 The reaction between 2 molecules of hydrogen and 1 molecule of oxygen gives 2 molecules of water as depicted by the space-filling models and chemical equation shown here.

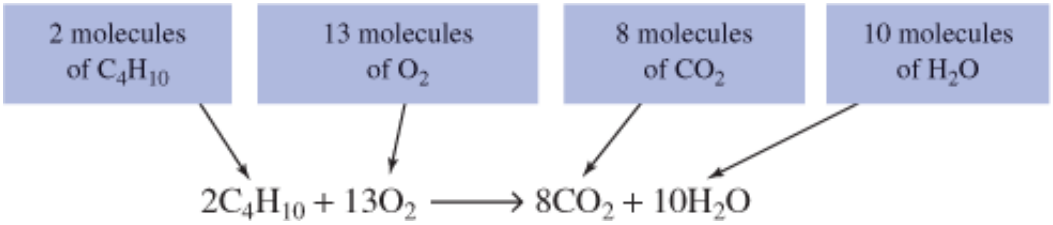


FIGURE 3.2 The chemical equation for the combustion of butane, C_4H_{10}. The products are carbon dioxide and water vapour.

The 2 before C_4H_{10} tells us that 2 molecules of butane are involved in the reaction. This involves a total of 8 carbon atoms and 20 hydrogen atoms (see figure 3.3). Notice that we have multiplied the numbers of atoms of C and H in 1 molecule of C_4H_{10} by the coefficient 2. The 13 in front of O_2 means that 13 molecules of O_2 are required for complete reaction of 2 molecules of C_4H_{10}. On the right, we find 8 molecules of CO_2, which contain a total of 8 carbon atoms. Similarly, 10 water molecules contain 20 hydrogen atoms. Finally, we can count 26 oxygen atoms on both sides of the equation.

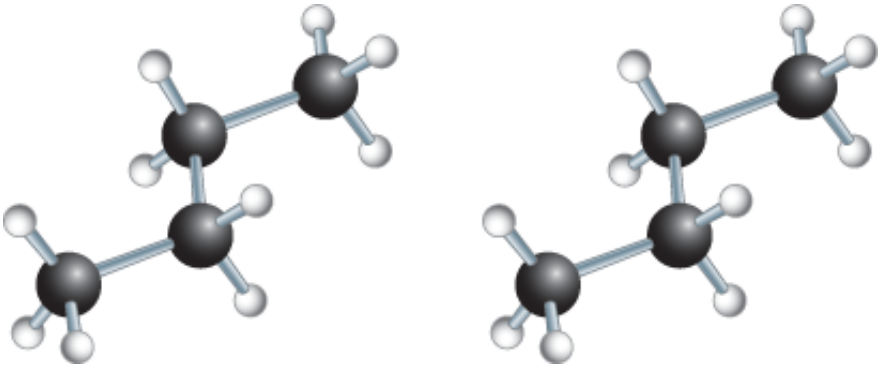


FIGURE 3.3 Understanding coefficients in an equation. The expression $2C_4H_{10}$ describes 2 molecules of butane (depicted here as ball-and-stick models), each of which contains 4 carbon and 10 hydrogen atoms. This gives a total of 8 carbon and 20 hydrogen atoms.

Specifying States of Matter

In a chemical equation, it is useful to specify the physical states of the reactants and products, i.e. whether they are solids, liquids or gases. This is done by writing (s) for solid, (l) for liquid or (g) for gas after the chemical formula. For example, the equation for the combustion of carbon in a charcoal briquette can be written as:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

At times, we will also find it useful to indicate that a particular substance is dissolved in water. We do this by writing (aq), meaning ‘aqueous solution’, after the formula. For instance, the re action between stomach acid (an aqueous solution of HCl) and $CaCO_3$, the active ingredient in some antacids, is:

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

This type of chemical equation is called a molecular equation. It shows all reactants and products, with molecular substances written as discrete molecules and ionic compounds written in terms of their empirical formulae (see section 3.4). If ionic compounds are involved we can also write net ionic equations that only show the ions involved in the actual reaction (see p. 97).

PRACTICE EXERCISE 3.1

How many atoms of each element appear on each side of the arrow in the following equation?

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

PRACTICE EXERCISE 3.2

Rewrite the equation in practice exercise 3.1 to show that $Mg(OH)_2$ is a solid, HCl and $MgCl_2$ are dissolved in water, and H_2O is a liquid.

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3.2 Balancing Chemical Equations

We have learned that a chemical equation is a shorthand, quantitative description of a chemical reaction. An equation is *balanced* when the atoms present among the reactants are also present in the same number among the products. As we learned, stoichiometric coefficients (the numbers in front of formulae) are multiplier numbers for their respective formulae, and the values of the coefficients determine whether an equation is balanced.

Always approach the balancing of an equation as a two-step process.

Step 1: *Write the unbalanced 'equation'*. Organise the formulae in the pattern of an equation with plus signs and an arrow.

Step 2: *Adjust the coefficients so that there are equal numbers of each kind of atom on each side of the arrow.* Apply the following guidelines in sequence:

a. Balance elements other than H and O.
b. Balance as a group those polyatomic ions (ions consisting of two or more covalently bonded atoms; see chapter 2) that appear unchanged on both sides of the arrow.
c. Balance ions so that the overall charge is the same on both sides of the arrow.
d. Balance those species that appear on their own (as elements or ions).
e. Balance the number of H and O atoms on both sides (e.g. by using H_2O or OH^-).

The guidelines are derived from experience, but are not hard and fast rules. The sequence of rules is chosen so that the species that are most difficult to balance are handled first and the easiest ones last (H and O are easily balanced in aqueous solutions).

When you carry out step 2, make no changes in the formulae, either in the atomic symbols or their subscripts. If you do, the equation will involve different substances from those intended. It may still balance, but the equation will not be for the reaction you want.

We will begin with simple equations that can be balanced by inspection. An example is the reaction of aluminium metal with hydrochloric acid (see figure 3.4). First, we need the correct formulae and the correct physical states. In this example, we use the molecular equation (see above) even though both HCl and $AlCl_3$ exist as ions in aqueous solution. The reactants are aluminium, Al(s), and hydrochloric acid, HCl(aq). We also need formulae for the products. The reaction results in the formation of aqueous aluminium chloride, which we write as $AlCl_3$(aq), and hydrogen gas, H_2(g). Recall from the chemical equation on p. 4 that hydrogen normally exists as diatomic molecules and not as individual atoms.

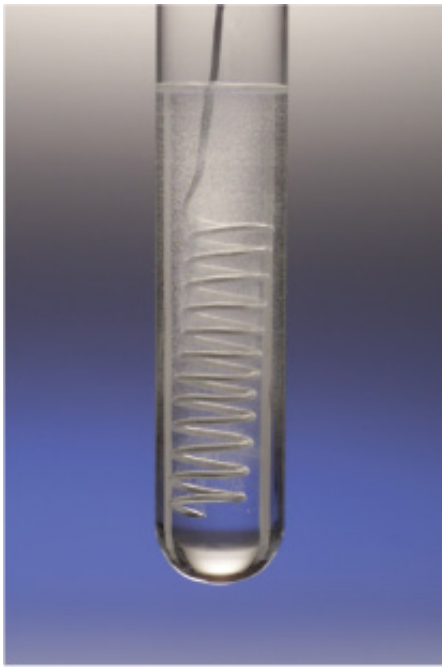


FIGURE 3.4 Aluminium and hydrochloric acid react to form aluminium chloride and hydrogen gas.

Step 1: Write an unbalanced equation.

$$Al(s) + HCl(aq) \rightarrow AlCl_3(aq) + H_2(g) \quad \text{(unbalanced)}$$

Step 2: Adjust the coefficients to get equal numbers of each kind of atom on both sides of the arrow by applying the guidelines in the order given above. Using the guidelines, we will look at Cl first in our example. Because there are 3 Cl atoms to the right of the arrow but only 1 to the left, we put a 3 in front of the HCl on the left side. The result is:

$$Al(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + H_2(g)$$

Since there are no polyatomic ions in this example, we look next at species that appear on their own (Al and H_2, in this example). You can see that Al looks balanced, but there are 3 H atoms on the left and only 2 on the right. We can balance these by putting a coefficient of 3 in front of H_2 and then doubling the coefficient for HCl.

$$Al(s) + 6HCl(aq) \rightarrow AlCl_3(aq) + 3H_2(g)$$

However, Cl is now not balanced; there are 6 Cl atoms on the left and only 3 on the right. Therefore, we need a coefficient of 2 in front of $AlCl_3$.

$$Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

Everything is now balanced except for Al; there is 1 Al atom on the left but 2 on the right. We put a coefficient of 2 in front of Al to give:

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

Now there are 2 Al, 6 H and 6 Cl atoms on each side of the equation and everything is balanced. Note that the equation $4Al(s) + 12HCl(aq) \rightarrow 4AlCl_3(aq) + 6H_2(g)$ is also balanced, but it is usual to write balanced equations using the *smallest* whole-number coefficients.

WORKED EXAMPLE 3.1

Writing a Balanced Equation

Aqueous solutions of calcium hydroxide, $Ca(OH)_2$, and phosphoric acid, H_3PO_4, react to give calcium phosphate, $Ca_3(PO_4)_2$, and water. The calcium phosphate precipitates from solution. Write the balanced equation for this reaction.

Analysis

First, write an unbalanced equation that includes the reactant formulae on the left-hand side and the product formulae on the right. Include the designation (aq) for all substances dissolved in water and (l) for H_2O itself when it is in its liquid state. Then adjust stoichiometric coefficients (*never subscripts!*) until there is the same number of each type of atom on the left and right sides of the equation.

Solution

$$Ca(OH)_2(aq) + H_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(s) + H_2O(l) \quad \text{(unbalanced)}$$

There are several things not in balance, but our guidelines suggest that we work with Ca first, rather than with O and H atoms, or the PO_4^{3-} polyatomic ions, which remain unchanged on both sides of the equation. There are 3 Ca atoms on the right side, so we put a 3 in front of $Ca(OH)_2$ on the left, as a trial.

$$3Ca(OH)_2(aq) + H_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(S) + H_2O(l) \quad \text{(unbalanced)}$$

Now the Ca atoms are in balance. The PO_4^{3-} anions are not balanced; there are 2 on the right side and only 1 on the left side. We put a 2 in front of H_3PO_4 as the next step.

$$3Ca(OH)_2(aq) + 2H_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(s) + H_2O(l) \quad \text{(unbalanced)}$$

Not counting the PO_4^{3-} anions, we have on the left 6 O and 6 H atoms in $3Ca(OH)_2$ plus 6 H atoms in H_3PO_4, for a net total of 6 O and 12 H atoms on the left. On the right, in H_2O, we have 1 O and 2 H atoms. The ratio of 6 O to 12 H atoms on the left is equivalent to the ratio of 1 O to 2 H atoms on the right, so we write the multiplier (coefficient) 6 in front of H_2O.

$$3Ca(OH)_2(aq) + 2H_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(s) + 6H_2O(l) \quad \text{(balanced)}$$

We now have a balanced equation.

Is our answer reasonable?

A count of the total number of atoms on each side of the equation shows that they are the same. On each side we have 3 Ca, 12 H, 2 P and 14 O atoms. The coefficients used cannot be reduced to smaller whole numbers and so we have an equation balanced with the smallest whole-number coefficients.

PRACTICE EXERCISE 3.3

When aqueous solutions of barium chloride, $BaCl_2$, and aluminium sulfate, $Al_2(SO_4)_3$, are

mixed, a reaction occurs in which solid barium sulfate, $BaSO_4$, precipitates from the solution. The other product is $AlCl_3(aq)$. Write the balanced equation for this reaction.

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3.3 The Mole

In the preceding sections, you have seen that chemical formulae tell us about the relative numeri cal proportions of atoms in molecules or ionic compounds, and that chemical equations are a convenient way to summarise what happens in chemical reactions. In this and the following sections, you will investigate the quantitative relationships further and find that these are governed by the rules of stoichiometry.

In a chemical reaction, the relative ratios of reactants resulting in a given ratio of products are given by the chemical equations that we looked at in earlier sections of this chapter. That, however, is on an atomic or molecular level. For example:

$$A + 2B \rightarrow AB_2$$

tells you that 1 molecule of *A* reacts with 2 molecules of *B* to form 1 molecule of AB_2. Suppose that we wanted to carry out this reaction in the laboratory. Given that we cannot see or count individual atoms, ions or molecules, we need to weigh out and work with larger quantities, but how do we know what masses of *A* and *B* to use? It turns out that some of the information we need to answer this question is given in the balanced chemical equation.

Think about it this way. If you need 50 000 sheets of white photocopy paper and you order them from a paper mill, the mill will weigh them out rather than counting the individual sheets. This procedure is much simpler and quicker and relies on the fact that we know the mass of one sheet of paper, and that every sheet of paper weighs the same (at least to a very good approximation). It is, therefore, easy to calculate the weight that corresponds to 50 000 sheets of paper. The same principle applies to counting large numbers of coins if you want to deposit them at a bank.

We can take a similar approach to ‘counting’ ions, atoms and molecules. Every atom has a certain mass. As we saw in chapter 1, the masses of individual atoms can be measured in atomic mass units (u), where 1 u = 1.660 54 × 10^{-24} g, exactly $\frac{1}{12}$ of the mass of a ^{12}C atom. If we reverse this definition, we see that 6.022 14 × 10^{23} u = 1 g, so 12 g of ^{12}C contains exactly 6.022 14 × 10^{23} atoms. It is clear that even a small mass of a substance contains a very large number of atoms. Therefore, we use a quantity called the **mole**. The mole (unit symbol: mol) is the SI unit of **amount of substance**. One mole is the amount of substance that contains the same number of specified entities as there are atoms in exactly 12 g of ^{12}C. This number is called the **Avogadro constant (N_A)**, and it underpins all of chemistry.

$$N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$$

We will generally quote the Avogadro constant to four significant figures. When we talk about an amount, we mean an amount of substance in moles. The numerical value of the Avogadro constant is almost beyond comprehension. For example, 6.022 × 10^{23} grains of sand would cover Australia and New Zealand to a depth of about 1.3 metres. However, because atoms are so incredibly small, a mole of atoms, molecules or ions takes up comparatively little space (see figures 3.5 and 3.6). One mole of anything contains 6.022 × 10^{23} entities. In chemistry terms, these entities are usually atoms, ions or molecules, but the definition of a mole does not restrict the nature of these entities. For example, one mole of eggs would contain 6.022 × 10^{23} eggs. We can in fact think of the mole as being the ‘chemist's dozen’ — just as 12 eggs constitute a dozen, 6.022 × 10^{23} eggs constitute a mole. Most importantly, the mole conveniently links atomic mass and macroscopic amounts; whatever anything weighs in atomic mass units, a mole of it will weigh in grams.



FIGURE 3.5 One mole of different elements (clockwise from top left: sulfur, aluminium, mercury and copper). Each sample of these elements contains 6.022×10^{23} atoms.



FIGURE 3.6 One mole of different compounds (clockwise from top left): copper sulfate pentahydrate, water, sodium chromate and sodium chloride.

It is important that we specify exactly which particular species we are discussing when we use the mole. For example, the phrase '1 mole of oxygen' is ambiguous, because we have not specified whether we are talking about 1 mole of oxygen atoms, O, or oxygen molecules, O_2, so it is usual to include a chemical formula whenever the mole is used.

Of particular interest to us in chemistry is the mass of 1 mole. We saw in the definition of the mole above that 1 mol of ^{12}C weighs 12 g, but it stands to reason that 1 mol of eggs is going to weigh rather more than this. Therefore, while the number of specified entities in a mole is constant, the mass of 1 mole of those entities depends on the mass of the individual entities. We call the mass of 1 mol of any specified entity the **molar mass (*M*)**. This serves as the link between mass (*m*) and amount of substance (*n*) through the equation:

$$M = \frac{m}{n}$$

The SI unit of molar mass is actually kg mol^{-1}, but this is rarely used in practice. Molar mass values are almost always quoted in units of g mol^{-1}; that is, the number of grams per mole of substance.

In chapter 1, we introduced the concept of atomic mass, the mass of a single atom of an element, which we measured in atomic mass units. The molar mass, which as the mass of 1 mole of atoms of an element, is numerically equal to the atomic mass, but the units differ. Values of molar mass for the elements are tabulated inside the front cover of this book, and it is informative to look at some of these. Note that these values refer to a mole of atoms of the elements, regardless of whether the elements themselves exist in atomic form. For example, the tabulated molar mass of H is 1.007 94 g mol^{-1} even though elemental hydrogen exists as H_2 molecules, not H atoms. The molar mass of C is 12.0107 g mol^{-1}, a value that might surprise you, given that we stated previously that 1 mole of ^{12}C weighs exactly 12 g. We need to appreciate that the molar mass of an element is determined by the isotopic make-up of that element. Carbon, for example, has two major naturally occurring isotopes, namely ^{12}C and ^{13}C, and any sample of carbon will contain these isotopes in 98.89% and 1.11% abundance, respectively. This means that the molar mass of *naturally occurring* carbon is not exactly 12 g mol^{-1}, but just a little greater, reflecting the small amount of the heavier ^{13}C isotope present. The molar masses of all elements with more than one naturally occurring isotope reflect the relative mass and abundance of each isotope.

Because no element has a molar mass exactly equal to an integer (even those with a single isotope, as we saw on p. 10), for simplicity of calculations in this book we will usually use molar masses to four significant figures. There is no need to learn the values of molar mass (they will always be available), but it is important to learn how to use them. The equation:

$$M = \frac{m}{n}$$

which defines molar mass, is one of the most important in all of chemistry, and we will use it often. With it, and just one other equation (which we will encounter later in this chapter), we have everything we need to solve *any* stoichiometry problem. The approach to doing stoichiometry problems is deciding how to apply these two equations.

WORKED EXAMPLE 3.2

Calculating an Amount from a Mass

The *Golden Jubilee* diamond is the largest faceted diamond in the world. It has a mass of 109.13 g. If the stone consists of pure carbon, what amount of C does the stone contain, given that the molar mass of C is 12.01 g mol^{-1}?

Analysis

A good method to follow when beginning any stoichiometry problem is to ask two questions: 'What value does the question want me to determine?', and 'What data have I been given?'. Write down the answers to these questions and then look for an equation that contains as many as possible of these. In this case, we are asked to determine an amount (n), and we have been given a molar mass (M) and a mass (m). The equation that contains all of these is $M = \frac{m}{n}$.

Solution

We rearrange $M = \frac{m}{n}$ to solve for n: $n = \frac{m}{M}$ Hence:

$$n = \frac{109.13\ \text{g}}{12.01\ \text{g mol}^{-1}} = 9.087\ \text{mol}$$

Therefore, this diamond contains 9.087 moles of carbon.

Is our answer reasonable?

We have 109.13 g of carbon in the diamond. Given that 1 mole of C has a mass of 12.01 g, 10 moles would have a mass of 120.1 g. We should therefore expect an answer of slightly fewer than 10 moles, which we have. Our answer therefore seems reasonable.

PRACTICE EXERCISE 3.4

What amount of sulfur molecules, S_8, is present in 35.6 g of sulfur? The molar mass of atomic sulfur, S, is 32.06 g mol $^{-1}$.

When solving this type of problem, always check the units of the answer. This is especially important if it is necessary to rearrange the equation to solve the problem. The units will *always* be correct if you have rearranged the equation correctly. In worked example 3.2, we are dividing mass by molar mass. Grams in the numerator (the top line) will cancel grams in the denominator (the bottom line), leaving $\frac{1}{\text{mol}^{-1}}$ as our final unit. This is the same as $\frac{1}{\frac{1}{\text{mol}}}$, which is mol, meaning that our units are correct. As we saw on p. 28, units are also very powerful in helping you to remember equations. The equation $M = \frac{m}{n}$ is easy to remember if you know that the units of molar mass are g mol^{-1}: in other words, grams (the unit of mass) divided by moles (the unit of amount). This then gives the correct form of the equation.

WORKED EXAMPLE 3.3

Calculating a Mass from an Amount

Calcium phosphate, $Ca_3(PO_4)_2$, is often used to coat some of the surfaces of bone or dental implants to permit bone to bond with the implant surface. A schematic is shown in figure 3.7.

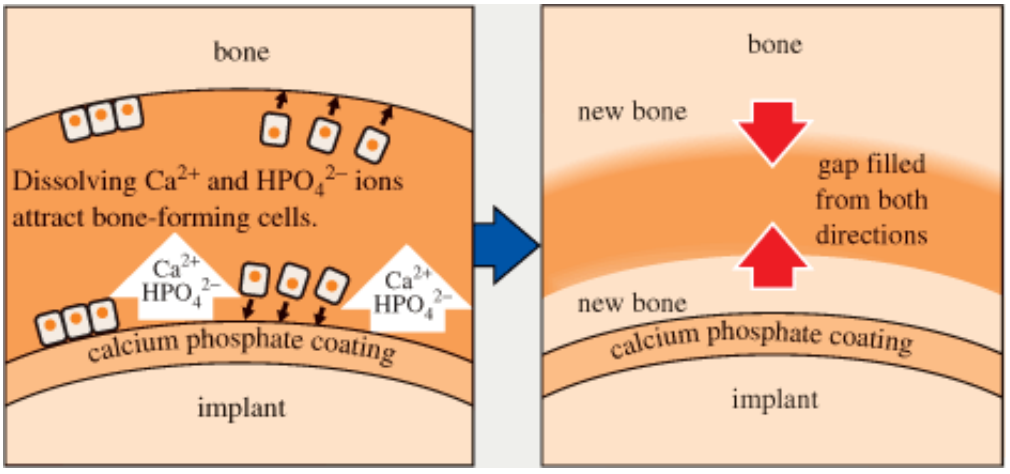


FIGURE 3.7 Some surfaces on bone implants are coated with calcium phosphate to permit bone to bond to the surface.

If a coating procedure can deposit 0.115 mol of pure $Ca_3(PO_4)_2$ on an implant, what is the mass of the coating? The molar mass of Ca is 40.08 g mol^{-1}, of P is 30.97 g mol^{-1} and of O is 16.00 g mol^{-1}.

Analysis

We are asked to calculate a mass (m) and we are given an amount (n) and the molar masses (M) of Ca, P and O. We will therefore use $M = \frac{m}{n}$ again, but we will have to calculate the molar mass of $Ca_3(PO_4)_2$ from the individual molar masses of the elements before we can substitute the data into the equation.

Solution

$$\begin{aligned} M_{Ca_3(PO_4)_2} &= \left(3 \times 40.08\ \text{g mol}^{-1}\right) + \left(2 \times 30.97\ \text{g mol}^{-1}\right) + \left(8 \times 16.00\ \text{g mol}^{-1}\right) \\ &= 310.2\ \text{g mol}^{-1} \end{aligned}$$

We now rearrange $M = \frac{m}{n}$ to make m the subject:

$$m = Mn$$

Substitution of the data gives:

$$\begin{aligned} m &= 310.2\ \text{g mol}^{-1} \times 0.115\ \text{mol} \\ &= 35.7\ \text{g} \end{aligned}$$

Therefore, the coating of $Ca_3(PO_4)_2$ weighs 35.7 g.

Is our answer reasonable?

The coating contains a little over 0.1 of a mole of $Ca_3(PO_4)_2$. Since 0.1 of 310 g is 31 g, and our answer of 35.7 g is slightly more than 31 g, it makes sense.

PRACTICE EXERCISE 3.5

What mass of sodium carbonate, Na_2CO_3, corresponds to 0.125 mol of Na_2CO_3?

PRACTICE EXERCISE 3.6

Determine the amount of H_2SO_4 in a 45.8 g sample of H_2SO_4.

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3.4 Empirical Formulae

Whenever a new compound is prepared, it is usually analysed to determine the mass percentages of the elements it contains. From these mass percentages, it is possible to obtain an empirical formula of the compound. The **empirical formula** is the simplest whole-number ratio of atoms within that compound. For example, the empirical formula of butane (chemical formula C_4H_{10}) is C_2H_5. If we know the ratio by mass of each element within a compound, we can determine its empirical formula using the relationship $M = \frac{m}{n}$.

Chemical Connections

Campbell Microanalytical Laboratory

Arguably the most important aspect of chemistry is the synthesis of new compounds. Chemists around the world prepare at least one million never-before-made compounds every year, and every one of these must be characterised in some way. One of the fundamental techniques used is elemental analysis, in which the mass percentages of elements in the new compound are determined. As we will see in this chapter, mass percentage data allow us to obtain an empirical formula for the compound; we can use this, in combination with a variety of other methods, which we will meet in later chapters, to determine its structure.

The Campbell Microanalytical Laboratory in the Department of Chemistry at the University of Otago is one of the very few microanalytical services available in Australasia. It has over 50 years of expertise in elemental analysis and carries out analyses for many universities in New Zealand and Australia.

Routine elemental analyses involve determination of the mass percentages of C, H, N and S in a compound, and are often carried out using an automated elemental analyser such as the one shown in the schematic diagram in figure 3.8. The samples are combusted with oxygen at high temperature (oxidation) in the presence of a catalyst. The resulting gases are then passed over a catalyst layer and through copper to remove excess O_2 and to reduce nitrogen oxides to nitrogen (reduction). The gases, CO_2, H_2O, SO_2 and N_2, are then separated by injection onto a chromatography column, and the amount of each is measured using a very sensitive thermal conductivity detector. These data are then converted to mass percentages of C, H, N and S, respectively.

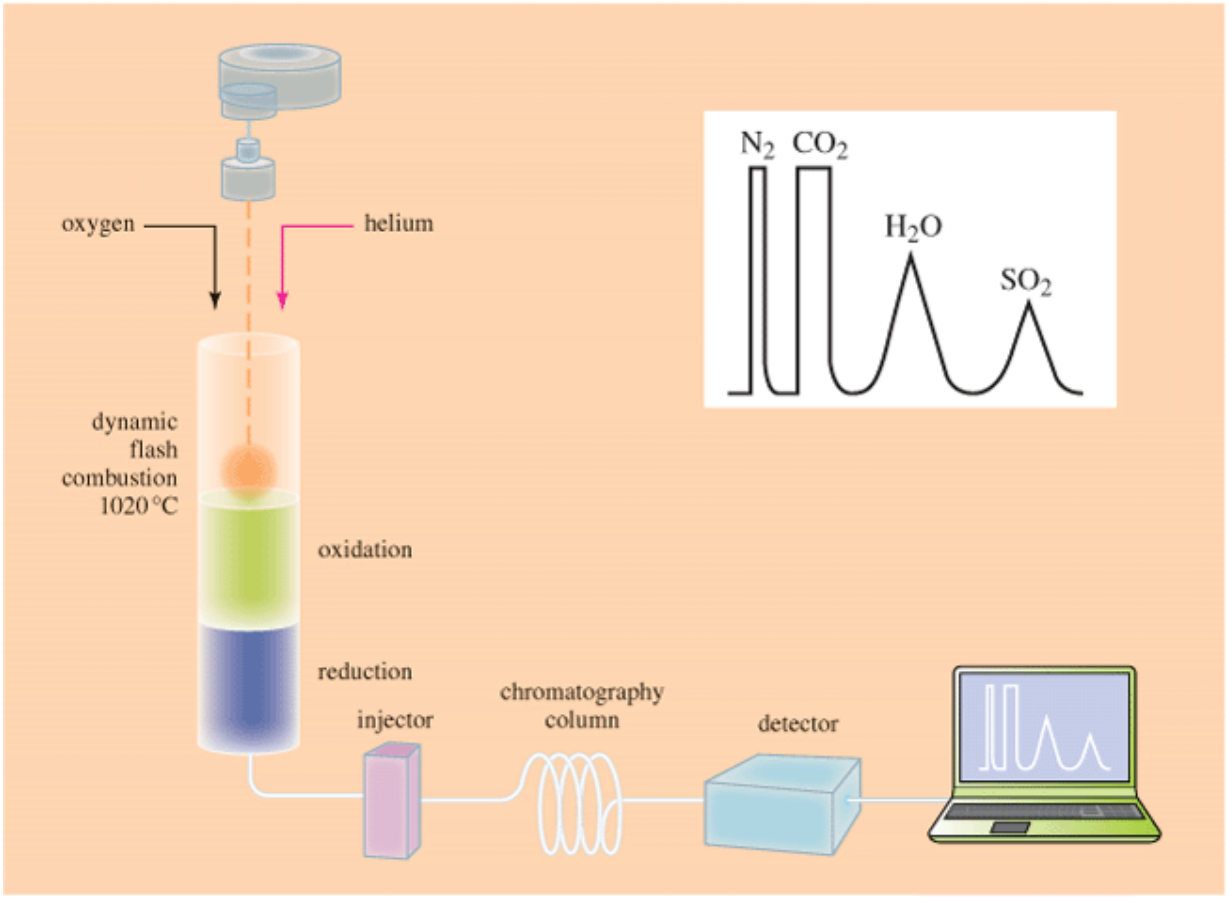


FIGURE 3.8 Diagram of an automated elemental analysis system for carbon, hydrogen, nitrogen and sulfur. The diagram illustrates the combustion chamber, the chromatography column, a thermal conductivity detector, and a sample of a chromatogram with peaks for N_2, CO_2, H_2O and SO_2.

Elements other than C, H, N or S in a sample must be analysed manually, and standard methods are available for these. Note that O is not usually analysed directly, and its mass percentage in an organic compound is generally obtained by subtracting the total mass percentages of all the other elements from 100.

Mole Ratios from Chemical Formulae

Consider the chemical formula for water, H_2O:

- 1 molecule of water contains 2 H atoms and 1 O atom.
- 2 molecules of water contain 4 H atoms and 2 O atoms.
- 1 dozen molecules of water contain 2 dozen H atoms and 1 dozen O atoms.
- 1 mole of molecules of water contains 2 moles of H atoms and 1 mole of O atoms.

Whether we are dealing with atoms, dozens of atoms or moles of atoms, the chemical formula tells us that the ratio of H atoms to O atoms in H_2O is always 2 to 1. *For chemical compounds, mole ratios are the same as the ratios of the individual atoms.*

This fact lets us prepare mole-to-mole conversion factors involving elements in compounds as we need them. For example, in the formula P_4O_{10}, the subscripts mean that there are 4 moles of P for every 10 moles of O in this compound. We also know that 1 mole of P_4O_{10} contains 4 moles of P and 10 moles of O.

In the laboratory, stoichiometry is commonly used to relate the masses of two starting materials that are needed to synthesise a compound and to determine reaction yields, as we will see later in this chapter.

WORKED EXAMPLE 3.4

Calculating Amounts of Elements Within a Compound

Leaves have a characteristic green colour (figure 3.9) due to the presence of the green pigment chlorophyll, which has the formula $C_{55}H_{72}MgN_4O_5$. A particular sample of chlorophyll was found to contain 0.0011 g

of Mg. What mass of carbon was present in the sample? (M_C = 12.01 g mol^{-1}; M_{Mg} = 24.31 g mol^{-1})



FIGURE 3.9 The characteristic green colour of leaves is imparted by the presence of the pigment chlorophyll.

Analysis

We are asked to calculate a mass of carbon (m_C) and are given a mass of magnesium (m_{Mg}) and molar masses of both carbon and magnesium. The data given allow us to calculate the amount of magnesium (n) in the sample using $M = \frac{m}{n}$; we then use the mole ratio between Mg and C, which is implicit in the formula of chlorophyll, to determine the amount of C present.

Once we have this amount, we then use $M = \frac{m}{n}$ again to convert it to mass.

Solution First, we calculate the amount of Mg corresponding to 0.0011 g of Mg:

$$\begin{aligned} M &= \frac{m}{n} \\ n &= \frac{m}{M} \\ &= \frac{0.0011\,\text{g}}{24.31\,\text{g mol}^{-1}} \\ &= 4.5 \times 10^{-5}\,\text{g mol} \end{aligned}$$

We now look at the formula of chlorophyll, $C_{55}H_{72}MgN_4O_5$, to obtain the mole ratio between Mg and C. In 1 molecule of chlorophyll, we have 1 atom of Mg and 55 atoms of C. Therefore, in 1 mole of chlorophyll, we have 1 mole of Mg and 55 moles of C. The mole ratio between Mg and C is therefore 1 : 55, meaning that there is 55 times the amount of C as there is Mg in chlorophyll. In this problem, we have 4.5 × 10^{-5} mol Mg, so we obtain the amount of C from:

$$\begin{aligned} n_C &= n_{Mg} \times 55 \\ &= 4.5 \times 10^{-5}\,\text{mol} \times 55 \\ &= 2.5 \times 10^{-3}\,\text{mol} \end{aligned}$$

Now we know the amount of carbon, we can convert this to mass:

$$\begin{aligned} m &= Mn \\ &= 12.01\,\text{g mol}^{-1} \times \left(2.5 \times 10^{-3}\,\text{mol}\right) \\ &= 3.0 \times 10^{-2}\,\text{g} \end{aligned}$$

Therefore, 0.030 g C was present in the sample.

Is our answer reasonable?

The molar mass of magnesium is about twice that of C. Since we need 55 mol C for every 1 mol Mg, the mass of C we require should be about 30 times that of Mg. Our answer was 0.030 g C for 0.0011 g Mg, so the mass of C we got is about 30 times the mass of the magnesium we started with. This seems reasonable.

PRACTICE EXERCISE 3.7

What mass of iron is in a 15.0 g sample of Fe_2O_3?

PRACTICE EXERCISE 3.8

What mass of iron is required to react with 25.6 g of O to form Fe_2O_3? Assume that the reaction proceeds to completion.

The Determination of Chemical Formulae

In research laboratories, chemists often synthesise entirely new compounds or isolate previously unknown compounds from plant and animal tissues. They must then determine the formula and structure of the compound. This usually involves mass spectrometry (see chapter 20), which gives an experimental value for the molar mass. The compound can also be decomposed chemically to find the masses of elements within a given amount of compound, a process called **elemental analysis** (see Chemical Connections on p. 78). Let us see how experimental mass measurements can be used to determine the compound's formula.

The usual form for describing the relative masses of the elements in a compound is a list of percentages by mass called the compound's **mass percentage composition**. In general, a **percentage by mass** is found by using the following equation:

$$\%\text{by mass of element} = \frac{\text{mass of element present in the sample}}{\text{mass of whole sample}} \times 100\%$$

WORKED EXAMPLE 3.5

Calculating a Percentage Composition from Chemical Analysis

A sample of a liquid with a mass of 8.657 g was found to contain 5.217 g of carbon, 0.9620 g of hydrogen and 2.478 g of oxygen. What is the percentage composition of this compound?

Analysis

We must apply the percentage composition equation for each element. The ‘mass of whole sample’ here is 8.657 g, so we take each element in turn and do the calculations.

Solution

$$\text{mass\%(C)} = \frac{5.217\,\text{g}}{8.657\,\text{g}} \times 100\% = 60.26\%$$

$$\text{mass\%(H)} = \frac{0.9620\,\text{g}}{8.657\,\text{g}} \times 100\% = 11.11\%$$

$$\text{mass\%(O)} = \frac{2.478\,\text{g}}{8.657\,\text{g}} \times 100\% = 28.62\%$$

$$\text{Sum of percentages} = 99.99\%$$

One of the useful things about a percentage composition is that it allows us to work out the mass of each of the elements in 100 g of the substance without further calculation. For example, the results in this problem tell us that in 100.00 g of the liquid there is 60.26 g of carbon, 11.11 g of hydrogen and 28.62 g of oxygen.

Is our answer reasonable?

The 'check' is that the percentages must add up to 100% if the individual masses add up to the total mass, allowing for small differences caused by rounding and experimental error.

PRACTICE EXERCISE 3.9

From 0.5462 g of a compound, 0.1417 g of nitrogen and 0.4045 g of oxygen was isolated. What is the percentage composition of this compound? Are any other elements present?

Elements can combine in many different ways. Nitrogen and oxygen, for example, form all of the following compounds: N_2O, NO, NO_2, N_2O_3, N_2O_4 and N_2O_5. To identify an unknown sample of a compound of nitrogen and oxygen, we compare the percentage composition found by experiment with the calculated percentages for each possible formula.

WORKED EXAMPLE 3.6

Calculating a Theoretical Percentage Composition from a Chemical Formula

Are the mass percentages of 25.92% N and 74.09% O consistent with the formula N_2O_5? (M_N = 14.01 g mol $^{-1}$; M_O = 16.00 g mol $^{-1}$)

Analysis

Essentially, we are asked to calculate the mass percentages of N and O in the compound N_2O_5. The data we are given are the molar masses (M) of N and O. The only equation we know that contains molar mass is $M = \frac{m}{n}$ so we will have to use this at some stage. To calculate the theor etical percentages by mass of N and O in N_2O_5, we need the masses of N and O in a specific sample of N_2O_5. If we choose 1 mole of the given compound as the sample, calculating the rest of the data will be easier.

Solution

We know that 1 mole of N_2O_5 contains 2 moles of N and 5 moles of O. The corresponding masses of N and O are found using $M = \frac{m}{n}$ as follows:

$$m_N = M_n = 14.01\ \text{g mol}^{-1} \times 2\ \text{mol} = 28.02\ \text{g}$$
$$m_O = M_n = 16.00\ \text{g mol}^{-1} \times 5\ \text{mol} = 80.00\ \text{g}$$

The mass of 1 mole of N_2O_5 will, therefore, be the sum of the mass of N and the mass of O in 1 mole of the molecule; that is, 28.02 g + 80.00 g = 108.02 g.

We can now calculate the percentages by mass as we did in worked example 3.5:

$$\text{mass \% (N)} = \frac{28.02\,\text{g}}{108.02\,\text{g}} \times 100 = 25.94\%$$
$$\text{mass \% (O)} = \frac{80.00\,\text{g}}{108.02\,\text{g}} \times 100 = 74.06\%$$

Therefore the experimental data are consistent with the formula N_2O_5.

Is our answer reasonable?

We get a good match between the calculated and experimental values, which is always encouraging! In problems like this, you should double-check your calculations and make sure that the percentages of all the elements present add up to 100% if the individual masses add up to the total mass, within rounding and experimental error.

PRACTICE EXERCISE 3.10

Calculate the percentage composition of N_2O_4.

Determination of Empirical Formulae

The compound that forms when phosphorus burns in oxygen consists of molecules with the formula P_4O_{10}. When a formula gives the composition of one *molecule*, it is called the **molecular formula**. Notice, however, that both the subscripts 4 and 10 are divisible by 2, so the *smallest* numbers that tell us the *ratio* of P to O is 2 to 5. A simpler (but less informative) formula that expresses this ratio is P_2O_5. This is sometimes called the *simplest formula* for the compound. It is also called the empirical formula because it can be obtained from an experimental analysis of the compound.

To obtain an empirical formula experimentally, we need to determine the mass of each element in a sample of the compound. From mass, we then calculate amount, from which we obtain the mole ratios of the elements. Because the ratio by moles is the same as the ratio by atoms, we can construct the empirical formula.

Only rarely is it possible to obtain the masses of every element in a compound by the use of just one weighed sample; two or more analyses on different samples may be required. For example, suppose an analyst is given a compound known to consist exclusively of calcium, chlorine and oxygen. The mass of calcium in one weighed sample and the mass of chlorine in another sample would be determined in separate experiments. Then the mass data for calcium and chlorine would be converted to percentages by mass (equivalent to the mass of each of these elements in a sample of 100 g). This allows the data from different samples to be compared directly. The mass percentage of oxygen would then be calculated by difference because %Ca + %Cl + %O = 100%. Each mass percentage can be related to the corresponding amount of the element. The mole proportions are converted to whole numbers as we have just studied, giving us the subscripts for the empirical formula.

Therefore, the three steps necessary to determine an empirical formula are:

1. Assume we are studying 100 g of the compound. Therefore, the individual mass percentages correspond to the actual masses of the elements in 100 g of the compound.

2. Convert the ratio of elements by mass to a ratio by amount, by dividing the mass of each element by its molar mass.
3. Divide the resulting numbers by the smallest one, which will give the smallest ratio of the elements in the compound. If this gives any numbers that are not integers, multiply all numbers in the ratio by the smallest factor that will result in all numbers being integers.

WORKED EXAMPLE 3.7

Calculating An Empirical Formula from Percentage Composition

A white powder used in paints, enamels and ceramics has the following mass percentage composition: Ba, 69.6%; C, 6.09%; and O, 24.3%. What is its empirical formula? (M_{Ba} = 137.3 g mol $^{-1}$; M_C = 12.01 g mol $^{-1}$; M_O = 16.00 g mol $^{-1}$)

Analysis

We are asked to calculate an empirical formula, and we are given mass percentage compositions and molar mass (M) values. We can convert mass percentage to mass (m) simply by choosing 100 g of compound to study. We can then calculate amounts of Ba, C and O by using $M = \frac{m}{n}$, and use these to obtain the necessary mole ratios for the empirical formula.

Solution

A 100 g sample of the compound will contain 69.6 g Ba, 6.09 g C and 24.3 g O. We first relate these masses to amounts:

$$n_{Ba} = \frac{m}{M} = \frac{69.6\,g}{137.3\,g\,mol^{-1}} = 0.507\,mol$$

$$n_{C} = \frac{m}{M} = \frac{6.09\,g}{12.01\,g\,mol^{-1}} = 0.507\,mol$$

$$n_{O} = \frac{m}{M} = \frac{24.3\,g}{16.00\,g\,mol^{-1}} = 1.52\,mol$$

Our ratio of Ba : C : O is therefore 0.507 : 0.507 : 1.52. However, chemical formulae contain whole numbers, so we divide each amount by the smallest amount. The ratio then becomes:

$$\frac{0.507\,mol}{0.507\,mol} : \frac{0.507\,mol}{0.507\,mol} : \frac{1.52\,mol}{0.507\,mol} = 1:1:3$$

Therefore, our mole ratio is 1 Ba : 1 C : 3 O, and the empirical formula is $BaCO_3$.

Is our answer reasonable?

If the formula is correct, there are 3 moles of oxygen for every 1 mole of carbon in the compound. So, for every 1 mole (12 g) of carbon in the compound, there should be 3 moles (48 g) of oxygen. The carbon-to-oxygen mass ratio is 12 : 48, or 1 : 4. This is consistent with the ratio of carbon and oxygen percentages (6.09 : 24.3 ≈ 1 : 4).

PRACTICE EXERCISE 3.11

A white solid used to whiten paper has the following mass percentage composition: Na, 32.4%; S, 22.6%. The rest of the mass is oxygen. What is the empirical formula of the compound?

In practice, a compound is seldom broken down completely to its elements in a quantitative analysis. Instead, the compound is changed into other compounds. The reactions separate the elements by capturing each one entirely (quantitatively) in a separate compound with a known formula.

In the following example, we illustrate an indirect analysis of a compound made entirely of carbon, hydrogen and oxygen. Such compounds burn completely in pure oxygen — the reaction is called **combustion** — and the sole products are carbon dioxide and water vapour. The complete combustion of ethanol, CH_3CH_2OH, for example, occurs according to the following equation.

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

The carbon dioxide and water can be separated and then their masses determined. Notice that all of the carbon atoms in the original compound end up among the CO_2 molecules and all of the hydrogen atoms are in H_2O molecules. In this way at least two of the original elements, C and H, are entirely separated.

Modern microanalytical techniques allow the simultaneous determination of C, H, N and S, as described in Chemical Connections on p. 78. Initial combustion of the sample and subsequent passage of the resulting gas mixture over a catalyst results in the conversion of all C in the sample to CO_2, all the H to H_2O, all the N to N_2 and all the S to S_2. The mass of each gas, and hence the mass of each element (C, H, N and S), is then determined. We convert the masses of the elements into percentages of the element by mass in the compound. We then add up the percentages and subtract from 100 to get the percentage of O. We then calculate the empirical formula from the percentage composition as described earlier.

The empirical formula is all that we need for ionic compounds. For molecular compounds, however, chemists prefer *molecular* formulae because they give the number of atoms of each type in a molecule, rather than just the ratio of the elements in a compound, as the empirical formula does.

Sometimes an empirical formula and a molecular formula are the same. Two examples are H_2O and NH_3. More often, however, the subscripts of a molecular formula are whole-number multiples of those in the empirical formula. The subscripts of the molecular formula P_4O_{10}, for example, are each two times those in the empirical formula, P_2O_5, as we saw earlier. The molar mass of P_4O_{10} is likewise two times the molar mass of P_2O_5. This observation helps us find the molecular formula for a compound, provided we have a way of experimentally determining the molar mass of the compound. If the experimental molar mass *equals* the calculated mass of an empirical formula, the empirical formula itself is also a molecular formula. Otherwise, the experimental molar mass will be some whole-number multiple of the value calculated from the empirical formula. Whatever the whole number is, it is a common multiplier for the subscripts of the empirical formula.

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3.5 Stoichiometry, Limiting Reagents and Percentage Yield

So far we have focused on relationships between elements within a single compound. We have seen that the critical link between amounts of elements within a compound is the mole-to-mole ratio obtained from the formula of the compound. In this section, we will see that the same techniques can be used to relate amounts of substances involved in a chemical reaction. The critical link between amounts of substances involved in a reaction is a mole-to-mole ratio obtained from the chemical equation that describes the reaction.

To see how a chemical equation can be used to obtain mole-to-mole relationships, consider the equation that describes the burning of octane, C_8H_{18}, in oxygen, O_2, to give carbon dioxide and water vapour:

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$$

This equation can be interpreted on a molecular scale as follows: for every 2 molecules of liquid octane that react with 25 molecules of oxygen gas, 16 molecules of carbon dioxide gas and 18 molecules of water vapour are produced.

We can also interpret the equation on a molar scale as follows; 2 moles of liquid octane react with 25 moles of oxygen gas to produce 16 moles of carbon dioxide gas and 18 moles of water vapour.

To use these relationships in a stoichiometry problem, the equation must be balanced. We must always check to see whether this is so for a given equation before we can use the coefficients in the equation to calculate stoichiometric ratios.

First, let us see how mole-to-mole relationships obtained from a chemical equation can be used to relate the amount of one substance to the amount of another when both substances are involved in a chemical reaction.

WORKED EXAMPLE 3.8

Stoichiometry of Chemical Reactions

What amount of sodium phosphate, Na_3PO_4, can be made from 0.240 mol of NaOH by the following reaction?

$$3NaOH(aq) + H_3PO_4(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(l)$$

Analysis

We use a similar approach to that used in worked example 3.4 but, in this case, we require the mole ratio between different compounds. We obtain this mole ratio directly from the stoichiometry of the balanced chemical equation.

Solution

We can see from the stoichiometric coefficients that 3 moles of NaOH will react to give 1 mole of Na_3PO_4. Therefore, if we start with 0.240 mol NaOH, we will obtain:

$$\frac{0.240\,\text{mol}}{3} = 0.0800\,\text{mol}\,Na_3PO_4$$

Is our answer reasonable?

There are really only two possible answers we could get to this problem — the correct one (0.0800 mol) and the incorrect one (0.720 mol), which would be obtained by multiplying rather than dividing by 3. Looking at the balanced chemical equation, we can see that the amount of Na_3PO_4 produced is less than the original amount of NaOH. In this case, our answer should be less than 0.240 mol, and it is.

PRACTICE EXERCISE 3.12

What amount of sulfuric acid, H_2SO_4, is needed to react completely with 0.366 mol of NaOH according to the following reaction?

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

PRACTICE EXERCISE 3.13

If 0.575 mol of CO_2 is produced by the combustion of propane, C_3H_8, what amount of oxygen is consumed? The balanced chemical equation is as follows:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

Mole Ratios in Chemical Reactions

We often need to relate mass of one substance to mass of another in a chemical reaction. Consider, for example, the reaction of glucose, $C_6H_{12}O_6$, one of the body's primary energy sources with oxygen. The body combines glucose and oxygen to give carbon dioxide and water. The balanced equation for the overall reaction is:

$$C_6H_{12}O_6(aq) + 6O_2(aq) \rightarrow 6CO_2(aq) + 6H_2O(l)$$

What mass of oxygen must the body take in to completely process 1.00 g of glucose (that is, 1.00 g $C_6H_{12}O_6$)?

The first thing we should notice about this problem is that we are relating amounts of *two different substances* in a reaction. The link between the amounts of substances is the mole-to-mole relationship between glucose and O_2 given by the chemical equation. In this case, the equation tells us that 1 mole of $C_6H_{12}O_6$ will react completely with 6 moles of O_2.

If we insert the mole-to-mole conversion between our starting point (1.00 g $C_6H_{12}O_6$) and the desired quantity (g O_2), we cut the problem into three simple steps:

$$1.00\,g\ C_6H_{12}O_6 \rightarrow \text{amount } C_6H_{12}O_6 \rightarrow \text{amount } O_2 \rightarrow \text{mass } O_2$$

We obtain the amount of $C_6H_{12}O_6$ from the mass of $C_6H_{12}O_6$ using the molar mass of $C_6H_{12}O_6$. We then obtain the amount of $C_6H_{12}O_6$ from the amount of O_2, using the stoichiometry of the balanced equation. Finally, we obtain the mass of O_2 from the amount of O_2 using the molar mass of O_2. If we have carried out these manipulations correctly, the answer should be 1.07 g O_2.

One of the most common mistakes made in stoichiometry problems like this is the incorrect determination and use of the mole ratios for substances in the reaction.

Consider the general chemical reaction:

$$aA + bB \rightarrow cC + dD$$

where *A*, *B*, *C* and *D* are reactants and products in the reaction, and *a*, *b*, *c* and *d* are the stoichiometric coefficients of each. For this reaction, the following *always* holds:

$$\frac{n_A}{a} = \frac{n_B}{b} = \frac{n_C}{c} = \frac{n_D}{d}$$

Applying this to the example above, we find that:

$$\frac{n_{C_6H_{12}O_6}}{1} = \frac{n_{O_2}}{6} = \frac{n_{CO_2}}{6} = \frac{n_{H_2O}}{6}$$

and, if we limit ourselves to the mole ratio between glucose and oxygen, we find:

$$\frac{n_{C_6H_{12}O_6}}{1} = \frac{n_{O_2}}{6}$$

Having calculated the amount of glucose, we know from the previous equation that this is equal to $n_{O2}/6$. We then rearrange this equation to make n_{O2} the subject:

$$n_{O_2} = 6n_{C_6H_{12}O_6}$$

and we find that we must *multiply* $n_{C_6H_{12}O_6}$ by 6 to obtain our answer.

WORKED EXAMPLE 3.9

Stoichiometric Mass Calculations

Metallic iron can be made by the thermite reaction, the spectacular reaction of aluminium with iron oxide, Fe_2O_3. So much heat is generated that the iron forms in the liquid state. The equation is:

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(l)$$

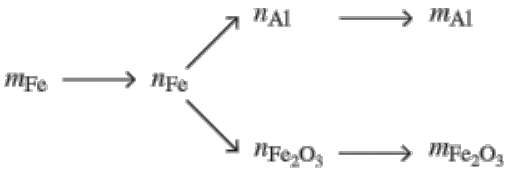
Assume that you need to produce 86.0 g of Fe in a welding operation.

What mass of both Fe_2O_3 and aluminium must be used for this operation, assuming all the Fe_2O_3 is converted to Fe? (M_{Fe} = 55.85 g mol^{-1}; M_O = 16.00 g mol^{-1}; M_{Al} = 26.98 g mol^{-1})

Analysis

We are asked to find the masses of Al and Fe_2O_3 required to prepare 86.0 g of Fe. We are given a mass of Fe (m) and the molar mass of Fe (M) so we can calculate the amount of Fe (n) using $M = \frac{m}{n}$. We then use the mole ratios in the balanced chemical equation to calculate the amounts of Al and Fe_2O_3. The final step is to use $M = \frac{m}{n}$ to obtain the masses from these amounts.

In summary:



Solution

Firstly, we calculate the amount of Fe in 86.0 g:

$$n = \frac{m}{M} = \frac{86.0\,\text{g}}{55.85\,\text{g mol}^{-1}} = 1.54\,\text{mol}$$

Using the stoichiometric coefficients from the balanced chemical equation, we can see that:

$$\frac{n\text{Al}}{2} = \frac{n_{Fe_2O_3}}{1} = \frac{n_{Al_2O_3}}{1} = \frac{n_{Fe}}{2}$$

$$n_{Fe_2O_3} = \frac{n_{Fe}}{2} = \frac{n_{Al}}{2}$$

Therefore, the formation of 2 moles of Fe requires 2 moles of Al and 1 mole of Fe_2O_3. In other words, we will require the same amount of Al, but half the amount of Fe_2O_3. Therefore:

$$n_{Al} = n_{Fe} = 1.54\,\text{mol}$$

$$n_{Fe_2O_3} = \frac{n_{Fe}}{2} = 0.770\,\text{mol}$$

Thus, $n_{Al} = n_{Fe}$. We then use $M = \frac{m}{n}$ to obtain the masses from these amounts:

$$m_{Al} = Mn = 26.98\,\text{g mol}^{-1} \times 1.54\,\text{mol} = 41.5\,\text{g}$$

$$m_{Fe_2O_3} = Mn = 159.70\,\text{g mol}^{-1} \times 0.770\,\text{mol} = 123\,\text{g}$$

Is our answer reasonable?

As the formation of Fe from Fe_2O_3 involves loss of oxygen from Fe_2O_3, we would expect the mass of Fe_2O_3 required to be greater than the mass of Fe produced. Given that 2 moles of Al give 2 moles of Fe, we would expect the mass of Al required to be less than the mass of Fe produced (86.0 g), as the molar mass of Al is less than that of Fe. Hence, our answers appear reasonable.

PRACTICE EXERCISE 3.14

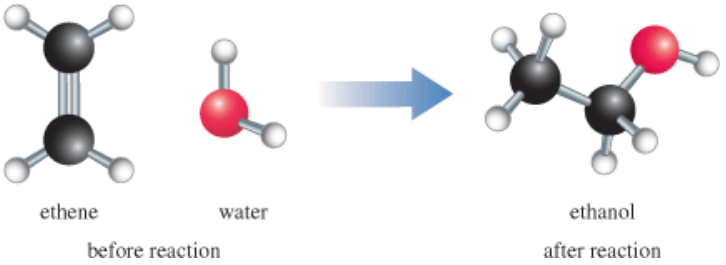
What mass of aluminium oxide is also produced when 86.0 g of Fe is formed by the reaction described in worked example 3.9?

Limiting Reagents

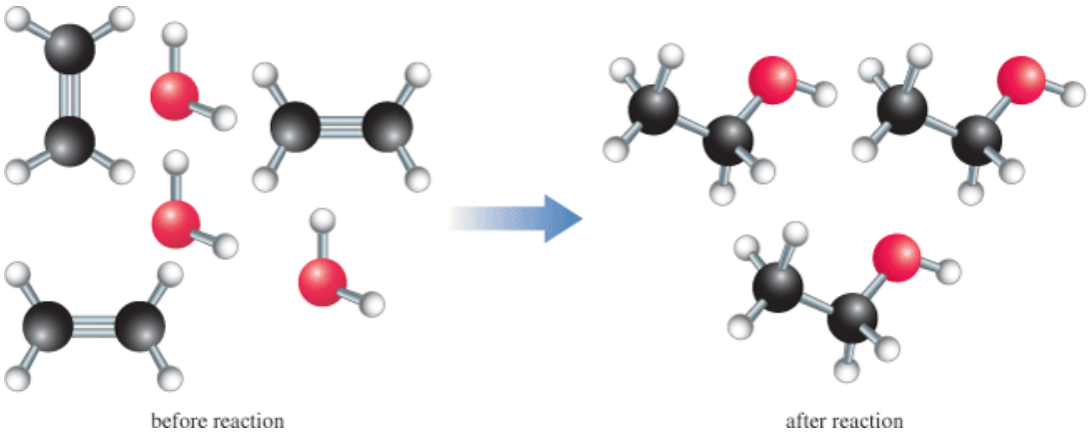
We have seen that balanced chemical equations can tell us how to mix reactants together in just the right proportions to get a certain amount of product. For example, ethanol, CH_3CH_2OH, is prepared industrially as follows:

$$\underset{\text{ethene}}{C_2H_4} + H_2O \rightarrow \underset{\text{ethanol}}{CH_3CH_2OH}$$

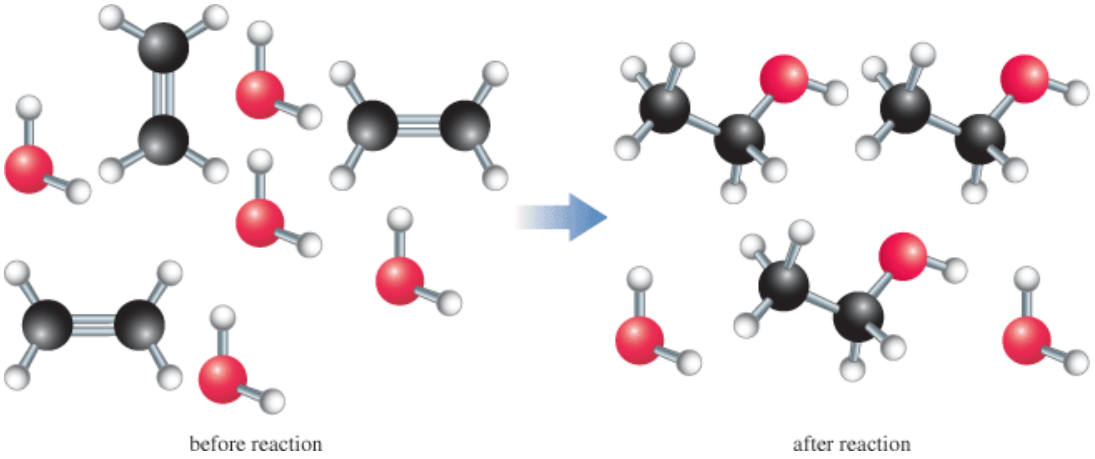
The equation tells us that 1 mole of ethene will react with 1 mole of water to give 1 mole of ethanol. We can also interpret the equation on a molecular level; every molecule of ethene that reacts requires 1 molecule of water to produce 1 molecule of ethanol:



If we have 3 molecules of ethene reacting with 3 molecules of water, 3 ethanol molecules are produced:



What happens if we mix 3 molecules of ethene with 5 molecules of water? The ethene will be completely used up before all the water, and the product mixture will contain 2 unreacted water molecules, as shown below.



This situation can be a problem in the manufacture of chemicals because we waste one of our reactants (water, in this case) and also obtain a product that is contaminated with unused reactant. Conversely, this can be used to advantage in situations where one of the reactants is cheap and easily recoverable. As we will see in chapter 9, we can sometimes force reactions to favour the formation of products by adding an excess of one of the reactants. An example of this is the preparation of margarine from the reaction of H_2 with animal or vegetable oils — use of excess H_2 makes the oil the limiting reagent and ensures complete conversion of the oil to margarine, and the excess H_2 can be easily recovered and reused.

In the reaction mixture at the bottom of the previous page, ethene is called the **limiting reagent** because it limits the amount of product (ethanol) that can form. Water is called an **excess reagent** because we have more of it than is needed to completely consume all the ethene.

To predict the amount of product we may theoretically obtain in a reaction, we need to know which of the reactants is the limiting reagent. In the previous example, we saw that we needed only three H_2O molecules to react with three C_2H_4 molecules; we had five H_2O molecules, so H_2O is present in excess and C_2H_4 is the limiting reagent.

Once we have identified the limiting reagent, it is possible to calculate the amount of product that might form and the amount of excess reagent that would be left over.

WORKED EXAMPLE 3.10

Limiting Reagent

Gold(III) hydroxide, $Au(OH)_3$, is used for electroplating gold onto other metals. It can be made by the following reaction:

$$2KAuCl_4(aq) + 3Na_2CO_3(aq) + 3H_2O(l) \rightarrow 2Au(OH)_3(s) + 6NaCl(aq) + 3CO_2(g)$$

To prepare a fresh supply of $Au(OH)_3$, a chemist at an electroplating plant mixed 20.00 g of $KAuCl_4$ with 25.00 g of Na_2CO_3 (both dissolved in a large excess of water).

What is the maximum mass of $Au(OH)_3$ that can form? ($M_{Na_2Co_3} = 105.99\ g\ mol^{-1}$; $M_{KAuCl_4} = 377.88 g\ mol^{-1}$; $M_{Au(OH)_3} = 247.99 g\ \ mol^{-1}$)

Analysis

We are asked to determine the maximum mass of $Au(OH)_3$ that can be formed. We are given masses (m) of both $KAuCl_4$ and Na_2CO_3 and their molar masses (M). This allows us to calculate the amounts of both $KAuCl_4$ and Na_2CO_3 using $M = \frac{m}{n}$. We then have to use the ratios of amounts to stoichiometric coefficients in the balanced chemical equation to determine if either $KAuCl_4$ or Na_2CO_3 is present in excess. The other substance would then be the limiting reagent.

Solution

Begin by calculating the amounts of $KAuCl_4$ and Na_2CO_3 using $M = \frac{m}{n}$:

$$\begin{aligned} M &= \frac{m}{n} \\ n &= \frac{m}{M} \\ n_{Na_2CO_3} &= \frac{m}{M} = \frac{25.00\,g}{105.99\,g\,mol^{-1}} = 2.359 \times 10^{-1}\,mol \\ n_{KAuCl_4} &= \frac{m}{M} = \frac{20.00\,g}{377.88\,g\,mol^{-1}} = 5.293 \times 10^{-2}\,mol \end{aligned}$$

We know, from the stoichiometry of the reaction, that 2 moles of $KAuCl_4$ require 3 moles of Na_2CO_3 for complete reaction. In other words:

$$\frac{n_{Na_2CO_3}}{3} = \frac{n_{KAuCl_4}}{2}$$

If we find that this is the case, then the reactants are present in exactly the correct stoichiometric amounts. If the ratios are unequal, the *smaller* number indicates the limiting reagent. In the experiment, we use:

$$\begin{aligned} \frac{n_{Na_2CO_3}}{3} &= \frac{2.359 \times 10^{-1}\,mol}{3} = 0.078\,63\,mol \\ \frac{n_{KAuCl_4}}{2} &= \frac{5.293 \times 10^{-2}\,mol}{2} = 0.026\,47\,mol \end{aligned}$$

This means that we have too much Na_2CO_3, so $KAuCl_4$ is the limiting reagent. The amount of $KAuCl_4$ now determines the amount of $Au(OH)_3$ that can be formed. To calculate how much $Au(OH)_3$ will be formed, we again use the stoichiometric coefficients from the balanced chemi cal equation. We see that 2 moles of $KAuCl_4$ will form 2 moles of $Au(OH)_3$ so:

$$n_{Au(OH)_3} = n_{KAuCl_4} = 5.293 \times 10^{-2}\,mol$$

Converting this amount of $Au(OH)_3$ to mass gives:

$$m = Mn = 247.99\,g\,mol^{-1} \times (5.293 \times 10^{-2}\,mol) = 13.13\,g$$

Therefore, using the reaction conditions given, we obtain a maximum of 13.13 g of $Au(OH)_3$.

Is our answer reasonable?

The main thing in calculations of this type is to get the mole ratios correct and, indeed, to interpret them correctly. We can

see that the molar mass of $KAuCl_4$ is more than three times that of Na_2CO_3. Since we are using a larger mass of Na_2CO_3 in the reaction, we will have a significantly larger amount of Na_2CO_3 than $KAuCl_4$, and our calculations bear this out. The molar mass of $Au(OH)_3$ is about two-thirds that of $KAuCl_4$ and, given that their mole ratio in the balanced chemical equation is 1 : 1, we would expect the mass of $Au(OH)_3$ to be about two-thirds the initial mass of $KAuCl_4$, which it is. The answer is reasonable.

PRACTICE EXERCISE 3.15

In an industrial process for producing nitric acid, the first step is the reaction of ammonia with oxygen at high temperature in the presence of a platinum gauze to form nitrogen monoxide as follows:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

What is the maximum mass of nitrogen monoxide that can form from an initial mixture of 30.00 g of NH_3 and 40.00 g of O_2?

Percentage Yield

In most chemical syntheses, the amount of a product actually isolated falls short of the calculated maximum amount. Losses occur for several reasons. Some are mechanical, such as materials sticking to glassware. In some reactions, losses occur by the evaporation of a volatile product. In others, a solid product separates from the solution as it forms because it is largely insoluble. The solid is removed by filtration. What stays in solution, although relatively small, contributes to some loss of product.

One of the common causes of obtaining less than the stoichiometric amount of a product is the occurrence of a reaction or reactions that compete with the **main reaction**. A **competing reaction** produces a **by-product**, i.e. a substance other than the product that we want to obtain. (*Note:* A second product of the main reaction is also called a by-product; however, it does not reduce the yield.) The synthesis of phosphorus trichloride from P and Cl_2, for example, gives some phosphorus pentachloride as well, because PCl_3 can react further with Cl_2.

$$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l) \quad \text{(main reaction)}$$
$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s) \quad \text{(competing reaction)}$$

The competition is between newly formed PCl_3 and unreacted phosphorus for chlorine. Another cause of lower than theoretical yields is a reversible reaction, where the forward and backward reactions occur concurrently.

The **theoretical yield** of a product is what would be obtained if the maximum amount of product was formed and no losses occurred. It is calculated based on the balanced chemical equation and the amounts of the reactants available. The **actual yield** of the product is simply how much has been isolated in practice. Chemists calculate the **percentage yield** of product to describe how successful the preparation was. The percentage yield is the actual yield calculated as a percentage of the theoretical yield:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Both the actual and theoretical yields must, of course, be in the same units.

It is important to realise that the actual yield is an experimentally determined (rather than calculated) quantity. The theoretical yield is always a calculated quantity based on a chemical equation and the amounts of the reactants available.

WORKED EXAMPLE 3.11

Calculating a Percentage Yield

A chemist set up a synthesis of phosphorus trichloride, PCl_3, by mixing 12.0 g of P with 35.0 g of Cl_2 and obtained 42.4 g of PCl_3. The equation for the reaction is:

$$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l)$$

Calculate the percentage yield of this compound. ($M_P = 30.97\ g\ mol^{-1}$; $M_{Cl_2} = 70.90\ g\ mol^{-1}$; $M_{PCl_3} = 137.32\ g\ mol^{-1}$)

Analysis

We are asked to calculate a percentage yield. We are given masses of all three components in the reaction and their molar masses (M). This means we can calculate the amounts of all three using $M = \frac{m}{n}$. To calculate the percentage yield, we must first decide on which reactant to base our calculations. We must calculate the amounts of each before we can make that decision. If we find that one of the reactants is a limiting reagent, the percentage yield is based on that reactant. To calculate the percentage yield, we must first calculate the theoretical yield: in other words, how much product would have been formed if the reaction went to completion. We do all of this using $M = \frac{m}{n}$ and the stoichiometry of the balanced chemical equation.

Solution

We begin by calculating the amounts of both P and Cl_2 used.

$$n_{\mathrm{P}} = \frac{m}{M} = \frac{12.0\,\mathrm{g}}{30.97\,\mathrm{g\,mol^{-1}}} = 3.87 \times 10^{-1}\,\mathrm{mol}$$

$$n_{\mathrm{Cl_2}} = \frac{m}{M} = \frac{35.0\,\mathrm{g}}{70.90\,\mathrm{g\,mol^{-1}}} = 4.94 \times 10^{-1}\,\mathrm{mol}$$

From the balanced chemical equation, we know that P reacts with Cl_2 in the mole ratio 2 : 3. Therefore, for complete reaction, theoretically:

$$\frac{n_{\mathrm{Cl_2}}}{3} = \frac{n_{\mathrm{P}}}{2}$$

The experimental ratios are 0.494 mol/3 = 0.165 for Cl_2 and 0.387 mol/2 = 0.194 for P. This means that we do not have sufficient Cl_2 to react with all the P present, so Cl_2 is the limiting reagent. We now base our subsequent calculations on this. From the balanced chemical equation, we know that:

$$\frac{n_{\mathrm{Cl_2}}}{3} = \frac{n_{\mathrm{PCl_3}}}{2}$$

Therefore, 0.165 mol $\mathrm{Cl_2} = n_{\mathrm{PCl_3}} / 2$, so $n_{\mathrm{PCl_3}} = 2(0.165\ \mathrm{mol}) = 0.330\ \mathrm{mol}$. Converting this to mass, we obtain:

$$m = Mn = 137.32\,\mathrm{g\,mol^{-1}} \times 0.330\,\mathrm{mol} = 45.3\,\mathrm{g}$$

The actual mass obtained was 42.4 g, so the percentage yield is given by:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{42.4\,\mathrm{g}}{45.3\,\mathrm{g}} \times 100\% = 93.6\%$$

Is our answer reasonable?

The obvious check is that the actual yield can never be more than the theoretical yield. So, on this score, our answer is reasonable. Again, the most common place where errors are made is in the use of the mole ratios. In this example, we must end up with *fewer* moles of *r* PCl_3 than Cl_2, so we must multiply n_{Cl2} by $\frac{2}{3}$, not $\frac{3}{2}$. We appear to have done the calculations correctly, so the answer is reasonable.

PRACTICE EXERCISE 3.16

Ethanol, CH_3CH_2OH, can be converted to acetic acid (the acid in vinegar), CH_3COOH, by the action of sodium dichromate, $Na_2Cr_2O_7$, in aqueous sulfuric acid according to the following equation:

$$3CH_3CH_2OH(aq) + 2Na_2Cr_2O_7(aq) + 8H_2SO_4(aq) \rightarrow 3CH_3OOH(aq) + 2Cr_2(SO_4)_3(aq) + 2Na_2SO_4(aq) + 11H_2O(l)$$

In one experiment, 24.0 g of CH_3CH_2OH, 90.0 g of $Na_2Cr_2O_7$ and a known excess of sulfuric acid was mixed, and 26.6 g of acetic acid was isolated. Calculate the percentage yield of CH_3COOH.

Another way to look at the yield of a reaction is to take into account the so-called atom efficiency. By this we mean that there is a difference between a reaction where most of the atoms of the starting material(s) end up forming the desired product and a reaction where a large fraction of the atoms in the starting material end up as unwanted by-products. There clearly is a trade-off between the percentage yield of a reaction and the atom efficiency. Concerns about pollution and cost certainly favour reactions (at least on the industrial scale) that produce the least amount of waste material.

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3.6 Solution Stoichiometry

Chemical reactions are most often carried out in solution because this allows intimate mixing of the reactants, which leads to more rapid reaction. A **solution** is a homogeneous mixture in which the atoms, molecules or ions of the components freely intermingle (see figure 3.10). When a solution forms, at least two substances are involved. One is called the solvent and all of the others are called solutes. The **solvent** is usually taken to be the component present in largest amount and is the medium into which the solutes are mixed or dissolved. Liquid water is a typical and very common solvent, but the solvent can actually be in any physical state — solid, liquid, or gas. Unless stated otherwise, we will assume that any solutions we mention are aqueous solutions, so that liquid water is understood to be the solvent.

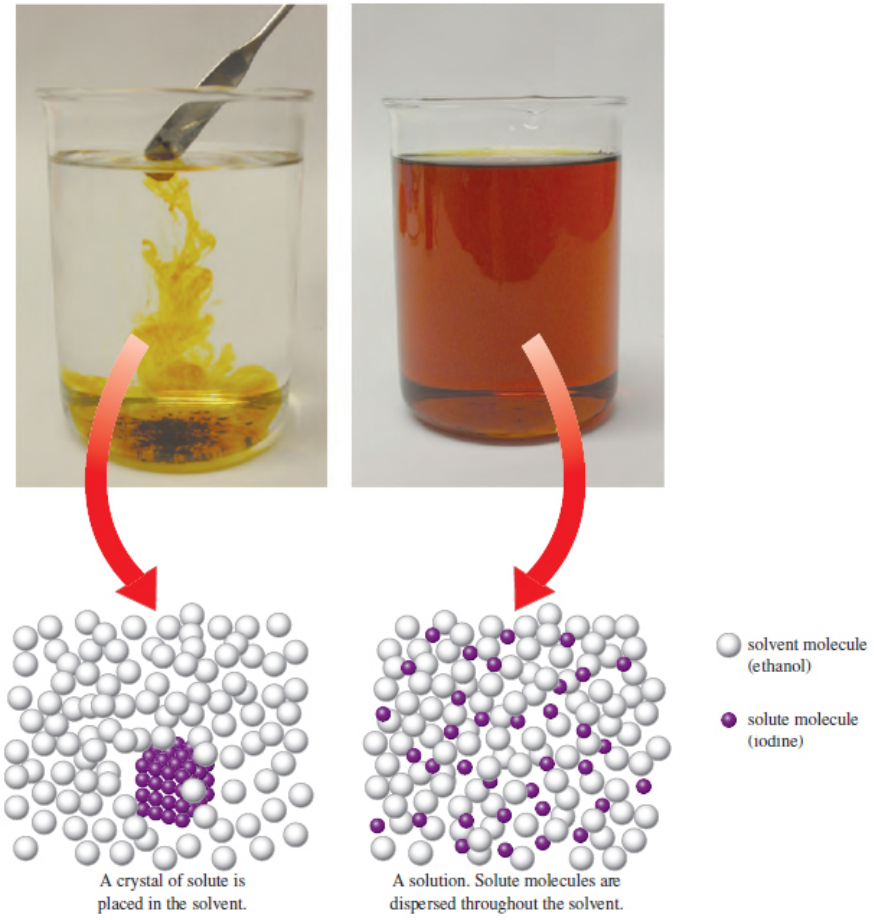


FIGURE 3.10 In the photo on the left, a crystal of iodine, I_2, that was added to a beaker containing ethanol started dissolving on its way to the bottom of the beaker, the purplish iodine crystal forming a reddish-brown solution. The photo on the right shows how after stirring the mixture with a spatula the solution takes on a homogeneous reddish-brown colour, due to the iodine molecules dissolved in the solvent as indicated in the schematic below the picture. Called 'tincture of iodine', such solutions were once widely used as antiseptics.

A **solute** is any substance dissolved in the solvent. It might be a gas, like the carbon dioxide dissolved in carbonated drinks. Some solutes are liquids, like the ethylene glycol dissolved in water to stop it from freezing in a car's radiator. Solids, of course, can be solutes, like the sugar dissolved in lemonade or the salt dissolved in sea water.

The Concentration of Solutions

We use the concentration of a solution to describe its composition. The **concentration** is defined as the amount of solute dissolved in a particular volume of solution. The concentration of a substance X is often represented as $[X]$. When the amount is given in moles and the volume in litres, it is called the **molarity** or molar concentration and has the units mol L^{-1} (often abbreviated m, not to be confused with the abbreviation for molar mass, M). The equation that defines concentration (c) is:

$$c = \frac{n}{V}$$

We stated earlier that there were only two equations needed to solve any stoichiometric problem. $M = \frac{m}{n}$ was the first, and this is the second. Again, we must commit this to memory, but it is easy to remember when we consider the units of concentration; mol L^{-1} implies amount divided by volume (in L).

Thus, a 1.00 L solution that contains 0.100 mol of NaCl has a molarity of 0.100 M, and we would refer to this solution as 0.100 *molar* NaCl or as 0.100 M NaCl. A 0.100 L solution containing 0.0100 mol of NaCl would have the same concentration because the *ratio* of amount of solute to volume of solution is the same.

$$\frac{0.100\,\text{mol NaCl}}{1.00\,\text{L NaCl}} = \frac{0.0100\,\text{mol NaCl}}{0.100\,\text{L NaCl}} = 0.100\,\text{M NaCl}$$

Concentration is particularly useful because it lets us obtain a given amount of a substance simply by measuring a volume of a previously prepared solution, and this measurement is quick and easy to do in the laboratory. If we had a stock supply of 0.100 M NaCl solution, for example, and we needed 0.100 mol of NaCl for a reaction, we would simply measure out 1.00 L of the solution because there is 0.100 mol of NaCl in this volume.

We need not (and seldom do) work with whole litres of solutions. It is the *ratio* of the amount of solute to the volume of solution, not the total volume, that matters. Suppose, for example, that we dissolved 0.0200 mol of sodium chromate, Na_2CrO_4, in sufficient solvent to give a final volume of 0.250 L. The

concentration of the solution would be found by:

$$c = \frac{n}{V} = \frac{0.0200\,\text{mol}}{0.250\,\text{L}} = 0.0800\,\text{M}$$

Such a solution can be accurately prepared in a *volumetric flask*, which is a narrow-necked container with an etched mark high on its neck. When filled 'up to the mark', the flask contains the volume given by the flask's label. Figure 3.11 shows how to use a 250 mL volumetric flask to prepare a solution of known concentration.

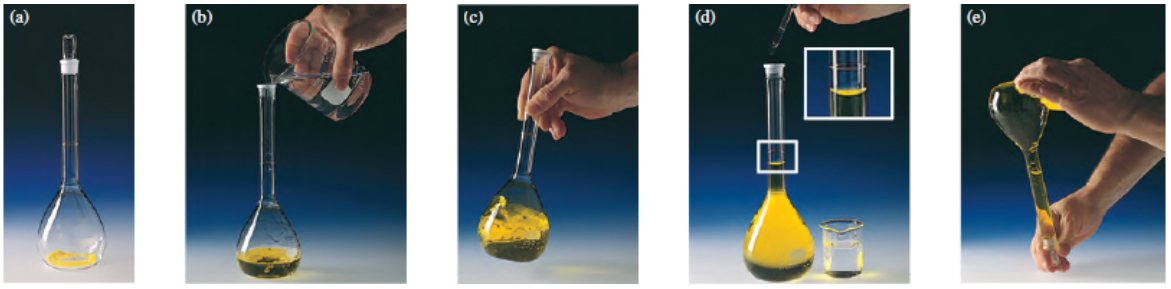


FIGURE 3.11 The preparation of a solution of known molarity:
(a) A 250 mL volumetric flask, one of a number of sizes available for preparing solutions. When filled to the line etched around its neck, this flask contains exactly 250 mL of solution. The flask here already contains a weighed amount of solute.
(b) Water is being added.
(c) The solute is brought completely into solution before the level is brought up to the narrow neck of the flask.
(d) More water is added to bring the level of the solution to the etched line or 'up to the mark'.
(e) The flask is stoppered and then inverted many times to mix its contents thoroughly.

Whenever we have to deal with a problem that involves an amount of a chemical and a volume of a solution of that substance, we will use the equation $c = \frac{n}{V}$.

WORKED EXAMPLE 3.12

Calculating the Concentration of a Solution

A student prepared a solution of NaCl by dissolving 1.461 g of NaCl in water and making up to the final volume of 250.0 mL in a volumetric flask to study the effect of dissolved salt on the rusting of an iron sample. What is the concentration of this solution?

Solution

Firstly, we convert the mass of NaCl to amount using:

$$\begin{aligned} \text{M} &= \frac{m}{n} \\ n &= \frac{m}{M} = \frac{1.461\,\text{g}}{58.44\,\text{g mol}^{-1}} \\ &= 2.500 \times 10^{-2}\,\text{mol} \end{aligned}$$

We then substitute the data into $c = \frac{n}{V}$ and solve for c:

$$\begin{aligned} c &= \frac{n}{V} = \frac{2.500 \times 10^{-2}\,\text{mol}}{0.2500\,\text{L}} \\ &= 1.000 \times 10^{-1}\,\text{mol L}^{-1} \end{aligned}$$

Therefore, the concentration of the NaCl solution is 1.000×10^{-1} mol L^{-1}.

Is our answer reasonable?

A 1 mol L^{-1} solution of NaCl would contain 58.44 g of NaCl in 1 litre, so a 0.1 mol L^{-1} solution would contain about 6 g in 1 L. We have 0.25 L, so we would expect about (0.25 × 6 g) = 1.5 g in 0.25 L, which is roughly what we have. The answer is certainly reasonable. An easy mistake to make in problems of this type is to forget to convert mL to L. Remember that the units of concentration must always come out as mol L^{-1} so, if the solution volume is given in mL, we must *divide* by 1000 to convert to L.

PRACTICE EXERCISE 3.17

As part of a study to determine if just the chloride ion in NaCl accelerates the rusting of iron, a student decided to see if iron rusted as

rapidly when exposed to a solution of Na_2SO_4. This solution was made by dissolving 3.550 g of Na_2SO_4 in water and making up the final volume to 100.0 mL in a volumetric flask. What is the concentration of this solution?

Notice that worked example 3.12 uses both $M = \frac{m}{n}$ and $c = \frac{n}{V}$. As we have stressed, with these two equations, there is no stoichiometric problem we cannot solve!

In the laboratory, we often must prepare a solution with a specific concentration. Usually, we select the volume of solution that we will make and then calculate how much solute must be used. Depending on the accuracy that you require for the concentration, you will need to use a balance that allows you to weigh your sample to the required number of significant figures. Figure 3.12 shows a range of balances and glassware used in the preparation of solutions of known concentration. Worked example 3.13 illustrates the kind of calculation required and also demonstrates the following useful relationship: *whenever we know both the volume and the concentration of a solution, we can calculate the amount of solute from* $c = \frac{n}{V}$.

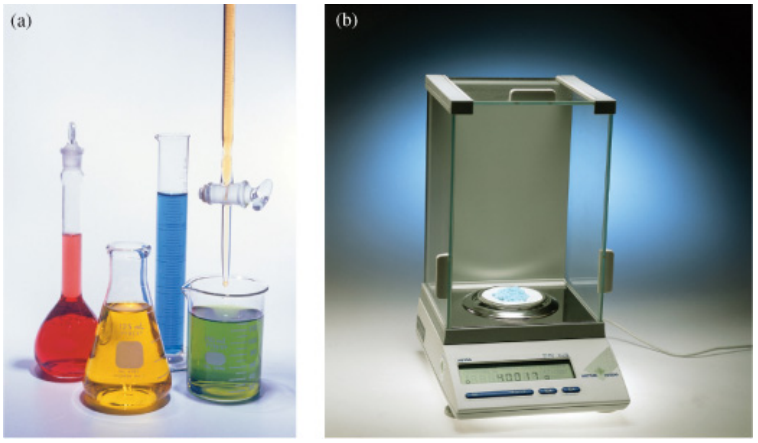


FIGURE 3.12 (a) Glassware that can be used for measuring volumes to different accuracies and (b) an analytical balance that can be read to 1×10^{-7} g.

WORKED EXAMPLE 3.13

Preparing a Solution of Known Concentration

Strontium nitrate, $Sr(NO_3)_2$, is used in fireworks to produce brilliant red colours like those shown in figure 3.13. What mass of strontium nitrate would a chemist need to prepare 250.0 mL of a 0.100 M $Sr(NO_3)_2$ solution? $\left(M_{Sr(NO_3)_2} = 211.64\ \text{g mol}^{-1}\right)$



FIGURE 3.13 The red colour in some fireworks is a result of the presence of strontium nitrate, $Sr(NO_3)_2$.

Analysis

We are asked to calculate a mass (m) of strontium nitrate and we are given the volume (V) and concentration (c) of a strontium nitrate solution, as well as the molar mass (M) of strontium nitrate. The concentration and volume will allow us to calculate the amount (n) of strontium nitrate using $c = \frac{n}{V}$, and we can then use this amount in the equation $M = \frac{m}{n}$ to calculate the mass of strontium nitrate.

Solution

We rearrange $c = \frac{n}{V}$ to solve for n:

$$\begin{aligned} n &= cV \\ &= 0.100\,\text{M} \times 0.2500\,\text{L} \\ &= 0.0250\,\text{mol} \\ &= 2.50 \times 10^{-2}\,\text{mol} \end{aligned}$$

We can now use $M = \frac{m}{n}$ to obtain the mass:

$$\begin{aligned} m = Mn &= 211.64\,\text{g mol}^{-1} \times (2.50 \times 10^{-2}\,\text{mol}) \\ &= 5.29\,\text{g} \end{aligned}$$

Therefore, the chemist would require 5.29 g of $Sr(NO_3)_2$ to prepare the solution.

Is our answer reasonable?

In 1 litre of 0.100 M $Sr(NO_3)_2$, there would be 0.1 mol of $Sr(NO_3)_2$, about 20 g. Therefore, in 0.25 L of this solution, we would have roughly (0.25 × 20 g) = 5 g. The answer, 5.29 g, is close to this, so it makes sense.

PRACTICE EXERCISE 3.18

What mass of $AgNO_3$ is needed to prepare 250 mL of 0.0125 M $AgNO_3$ solution?

Diluting a Solution

It is not always necessary to begin with a solute in pure form to prepare a solution with a known concentration. The solute can already be dissolved in a solution of relatively high concen tration, often called the stock solution, and this can be *diluted* with the same pure solvent to make a solution of the desired lower concentration. Dilution is accomplished by adding more solvent to the solution, which causes the concentration (the amount per unit volume) to decrease (figure 3.14). The choice of apparatus used depends on the precision required. If high precision is necessary, pipettes and volumetric flasks are used (figure 3.12a). If we can do with less precision, we might use graduated cylinders instead. Worked example 3.14 shows how we can use $c = \frac{n}{V}$ to calculate the final concentration of a diluted solution.

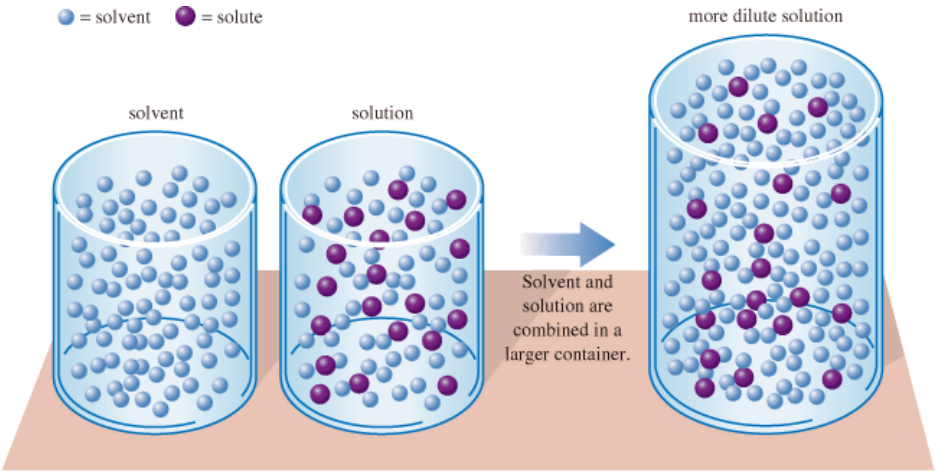


FIGURE 3.14 Diluting a solution. When solvent is added to a solution, the solute particles become more spread out and the solution becomes more dilute. The concentration of the solute in the solution becomes lower, while the total amount of solute remains constant.

WORKED EXAMPLE 3.14

Preparing a Solution of Known Concentration by Dilution

How could we prepare 100.0 mL of 0.0400 M $K_2Cr_2O_7$ from a solution of 0.200 M $K_2Cr_2O_7$?

Analysis

We are asked how to dilute a concentrated solution to give a solution of a particular concentration. We know both the volume (V) and the concentration (c) of the final solution, so use of $c = \frac{n}{V}$ will allow us to calculate n from these data. As we know the concentration of the initial solution, and we have calculated the required n, $c = \frac{n}{V}$ will allow us to calculate V, the volume of the initial solution required.

Solution

We are going to use $c = \frac{n}{V}$ twice, to calculate two different things. Firstly, we calculate $n_{K_2Cr_2O_7}$ in our final solution:

$$\begin{aligned} n = cV &= 0.0400\,\text{mol L}^{-1} \times 0.1000\,\text{L} \\ &= 4.00 \times 10^{-3}\,\text{mol} \end{aligned}$$

This is the amount of $K_2Cr_2O_7$ that, when dissolved in 100.0 mL, will give a concentration of 0.0400 M. We now turn our attention to the initial solution and use this calculated amount, in conjunction with the concentration, to calculate V, the volume of the initial solution required.

$$v = \frac{n}{c} = \frac{4.00 \times 10^{-3}\,\text{mol}}{0.200\,\text{mol L}^{-1}} = 0.0200\,\text{L}$$

Therefore, we take 20.0 mL of the original solution, pour it into a 100.0 mL volumetric flask and make it up to the mark with water to get a 0.0400 M solution of $K_2Cr_2O_7$ (figure 3.15).

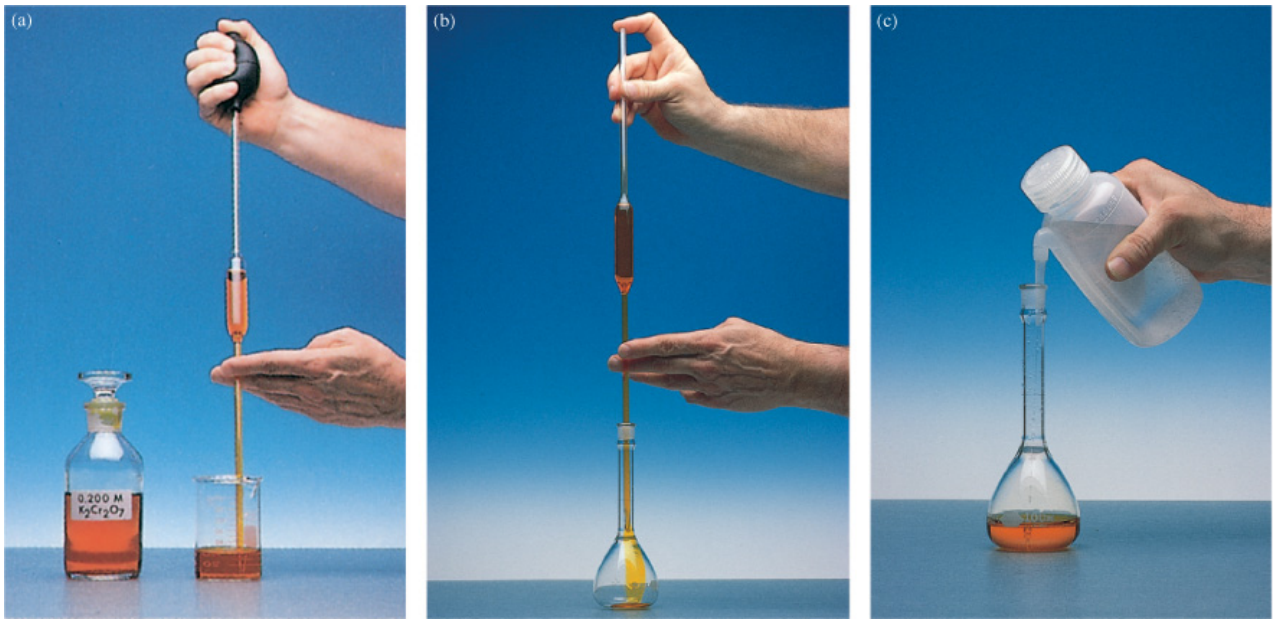


FIGURE 3.15 Preparing a solution by dilution:
(a) The calculated volume of the more concentrated solution is withdrawn from the stock solution by means of a volumetric pipette.
(b) The solution is allowed to drain entirely from the pipette into the volumetric flask.
(c) Water is added to the flask, the contents are mixed and the final volume is brought up to the mark on the narrow neck of the flask.

Is our answer reasonable?

Think about the magnitude of the dilution, from 0.2 M to 0.04 M. Notice that the concentrated solution is five times as concentrated as the dilute solution (5 × 0.04 = 0.2). To reduce the concentration by a factor of five requires that we increase the volume by a factor of five, and we see that 100 mL is 5 × 20 mL. The answer appears to be correct.

In a dilution, the amount of substance in the concentrated solution is the same as in the diluted solution. This allows us to use a shortcut for the calculation that we carried out in worked example 3.14.

If we define c_1 and V_1 as the concentration and volume of the initial solution and c_2 and V_2 as those of the final solution, because n is the same in both solutions we can write $n = c_1V_1$ and $n = c_2V_2$. As the amount, n, is the same for both solutions, we can then cancel out n, to give the equation $c_1V_1 = c_2V_2$. If we know the initial concentration and the final volume and concentration we can solve for the initial volume:

$$V_1 = \frac{c_2}{c_1} \times V_2$$

That is, if we multiply the final volume by the ratio of final to initial concentration, we obtain the required volume of the initial solution. For worked example 3.14, we could write:

$$V_1 = \frac{c_2}{c_1} \times V_2 = \frac{0.0400\,\text{M}}{0.200\,\text{M}} \times 0.1000\,\text{L} = 0.0200\,\text{L}$$

PRACTICE EXERCISE 3.19

How could 0.1 mL of 0.125 M H_2SO_4 solution be made from a 0.500 M H_2SO_4 solution?

Applications of Solution Stoichiometry

When we deal quantitatively with reactions in solution, we often work with volumes of solutions and concentrations.

WORKED EXAMPLE 3.15

Stoichiometry Involving Reactions in Solution

Before the advent of digital cameras, silver bromide, AgBr, was used extensively in photographic film. This compound is essentially insoluble in water, and one way to prepare it is to mix solutions of the water-soluble compounds, silver nitrate and calcium bromide (see figure 3.16).

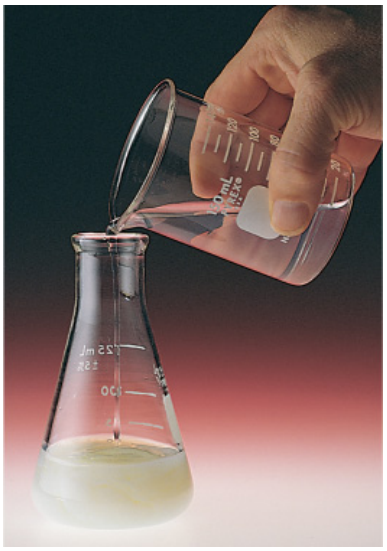


FIGURE 3.16 Addition of $CaBr_2(aq)$ to $AgNO_3(aq)$ results in precipitation of creamy white AgBr(s).

Suppose we wished to prepare AgBr by the following precipitation reaction:

$$2AgNO_3(aq) + CaBr_2(aq) \rightarrow 2AgBr(s) + Ca(NO_3)_2(aq)$$

What volume of 0.125 M $CaBr_2$ solution would be required to react completely with 50.0 mL of 0.115 M $AgNO_3$?

Analysis

We are asked to calculate a volume of $CaBr_2$ solution, and we are given the volume (V) and concentration (c) of a $AgNO_3$ solution. We can calculate the amount (n) of $AgNO_3$ using $c = \frac{n}{V}$. We are also given a balanced chemical equation, and we will need to use this to obtain the mole ratio between $AgNO_3$ and $CaBr_2$. We then use the stoichiometric coefficients from the balanced chemical equation to calculate n_{CaBr_2}. Finally, we will use $c = \frac{n}{V}$ along with the concentration of the $CaBr_2$ solution to calculate the volume of the initial solution required.

Solution

We start by calculating n_{AgNO3}:

$$\begin{aligned} c &= \frac{n}{V} \\ n &= cV = 0.115\,\text{mol}\,\text{L}^{-1} \times (50.0 \times 10^{-3}\,\text{L}) \\ &= 5.75 \times 10^{-3}\,\text{mol} \end{aligned}$$

From the balanced chemical equation, we know that 2 moles of $AgNO_3$ will react with 1 mole of $CaBr_2$. Therefore:

$$n_{CaBr_2} = \frac{n_{AgNO_3}}{2} = \frac{5.75 \times 10^{-3}\,\text{mol}}{2} = 2.88 \times 10^{-3}\,\text{mol}$$

We now know n_{CaBr_2} and the concentration of the $CaBr_2$ solution, so we can substitute these values into $c = \frac{n}{V}$ to calculate V, the volume of the $CaBr_2$ solution required.

$$V = \frac{n}{c} = \frac{2.88 \times 10^{-3}\,\text{mol}}{0.125\,\text{mol L}^{-1}} = 0.0230\,\text{L} = 2.30 \times 10^{-2}\,\text{L}$$

Therefore, 23.0 mL of the $CaBr_2$ solution will react completely with 50.0 mL of the 0.115 M $AgNO_3$ solution.

Is our answer reasonable?

The molarities of the two solutions are about the same, but only 1 mole of $CaBr_2$ is needed for every 2 moles of $AgNO_3$. Therefore, the volume of $CaBr_2$ solution needed (23.0 mL) should be about half the volume of $AgNO_3$ solution taken (50.0 mL), which it is.

PRACTICE EXERCISE 3.20

What volume of 0.124 M NaOH is required to react completely with 15.4 mL of 0.108 M H_2SO_4 according to the following equation?

$$2NaOH(aq) + H_2SOH_4(aq) \rightarrow NaSO_4(aq) + 2H_2O(l)$$

Stoichiometry of Solutions Containing Ions

In worked example 3.15, we used an equation involving ionic compounds to solve a stoichiometry problem. Ionic compounds dissociate into their constituent ions if they dissolve in water and this can have important consequences in stoichiometric calculations involving such solutions. For example, in worked example 3.15, we used calcium bromide, $CaBr_2$, as a reactant. Suppose we are working with an aqueous solution labelled '0.10 M $CaBr_2$'. This means there is 0.10 mole of $CaBr_2$ dissolved in each litre of this solution **dissociated** into Ca^{2+} and Br^- ions.

$$CaBr_2(s) \rightarrow Ca^{2+}(aq) + 2Br^-(aq)$$

From the stoichiometry of the dissociation, we see that 1 mole of $Ca^{2+}(aq)$ and 2 moles of $Br^-(aq)$ are formed from each mole of $CaBr_2(s)$. Therefore, 0.10 mole of $CaBr_2(s)$ will yield 0.10 mole of $Ca^{2+}(aq)$ and 0.20 moles of $Br^-(aq)$. In 0.10 M $CaBr_2$, then, the concentration of $Ca^{2+}(aq)$ is 0.10 M and the concentration of $Br^-(aq)$ is 0.20 M. Notice that the concentration of a particular ion equals the concentration of the salt multiplied by the number of ions of that kind in the formula of the salt.

We use the term 'dissolution' to describe the process of a solute dissolving in a solvent, and it is important that you understand the difference between the terms 'dissolution' and 'dissociation'. When an ionic compound undergoes dissolution (dissolves) in a solvent, it undergoes dissociation into its constituent ions. We showed the equation for this process with reference to $CaBr_2(s)$ above, and assumed that the salt dissociates fully. However, dissociation reactions do not necessarily do that, and the extent of such reactions depends on the nature of the ionic compound. We will assume 100% dissociation of all ionic compounds in the remaining examples in this chapter. We will investigate partial dissociation in chapter 10.

Initially you may find it difficult to know exactly which ionic species dissolve in water and which ones do not, but with experience you will be able to make reasonable assessments. In the first instance a table of solubility rules can be a great help. Table 3.1 summarises the rules for the solubilities of many common ionic compounds and you may find it helpful to be familiar with these.

TABLE 3.1 Solubility of common binary ionic compounds in water

If the anion is	the compound is usually	except for
F^-	soluble	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+} (Al^{3+})
Cl^-	soluble	Ag^+ and Hg_2^{2+} (Pb^{2+})
Br^-	soluble	Ag^+ and Hg_2^{2+} (Hg^{2+} and Pb^{2+})
I^-	soluble	Ag^+, Hg^{2+}, Hg_2^{2+} and Pb^{2+}
NO_3^-	soluble	none
SO_4^{2-}	soluble	Sr^{2+}, Ba^{2+}, Hg_2^{2+} and Pb^{2+} (Ag^+ and Ca^{2+})
CH_3COO^-	soluble	none (Ag^+ and Hg_2^{2+})

OH^-	insoluble	Li^+, Na^+, K^+ and Ba^{2+} (Ca^{2+} and Sr^{2+})
SO_3^{2-}	insoluble	Li^+, Na^+, K^+, NH_4^+ and Mg^{2+}
PO_4^{3-}	insoluble	Na^+, K^+ and NH_4^+
CO_3^{2-}	insoluble	Li^+, Na^+, K^+ and NH_4^+
$C_2O_4^{2-}$	insoluble	Li^+, Na^+, K^+ and NH_4^+

Note: For the purposes of this table, insoluble compounds are arbitrarily deemed to have molar solubilities of less than 1×10^{-2} M in water, slightly soluble compounds have molar solubilities in water between 1×10^{-1} M and 1×10^{-2} M, while soluble compounds have molar solubilities greater than 1×10^{-1} M in water. Cations in parentheses form slightly soluble compounds with the specified anion. Most oxides and sulfides are insoluble in water; apparent exceptions to this rule (e.g. Li_2O and MgS) are generally complicated by hydrolysis reactions and are therefore not listed.

Note that, in worked example 3.15, we wrote the balanced chemical equation as the molecular equation:

$$2AgNO_3(aq) + CaBr_2(aq) \rightarrow 2AgBr(s) + Ca(NO_3)_2(aq)$$

We can also write this in terms of the ions present as the ionic equation:

$$2Ag^+(aq) + 2NO_3^-(aq) + Ca^{2+}(aq) + 2Br^-(aq) \rightarrow 2AgBr(s) + Ca^{2+}(aq) + 2NO_3^-(aq)$$

The net reaction that occurred was:

$$2Ag^+(aq) + 2Br^-(aq) \rightarrow 2AgBr(s)$$

and the NO_3^- and Ca^{2+} took no part in the reaction, remaining simply as aqueous ions throughout. We call such ions **spectator ions**. Balanced ionic equations written without the inclusion of spectator ions are called **net ionic equations**. That is, net ionic equations show only those ions that participate in the reaction.

WORKED EXAMPLE 3.16

Calculating the Concentrations of Ions in a Solution

What are the concentrations of the ions in a 0.20 M solution of $Al_2(SO_4)_3(aq)$?

Analysis

The concentrations of the ions are determined by the concentration of the salt and its stoichiometry. We need to write a balanced chemical equation for the dissolution of the salt in water; from this, we can determine the concentration of each ion in the solution using the given concentration of the salt.

Solution

When $Al_2(SO_4)_3$ dissolves, it dissociates as follows:

$$Al_2(SO_4)_3(s) \rightarrow 2Al^{3+}(aq) + 3SO_4^{2-}(aq)$$

Each mole of $Al_2(SO_4)_3$ yields 2 moles of Al^{3+} ions and 3 moles of SO_4^{2-} ions on dissolution, assuming complete dissociation. Therefore, if we consider 1 litre of solution, the 0.20 mol of $Al_2(SO_4)_3$ will yield 0.40 mol Al^{3+} and 0.60 mol SO_4^{2-}. Hence, the concentrations of the ions in the solution will be 0.40 M Al^{3+} and 0.60 M SO_4^{2-}.

PRACTICE EXERCISE 3.21

What are the molar concentrations of the ions in 0.40 M $FeCl_3(aq)$?

PRACTICE EXERCISE 3.22

In an aqueous solution of Na_3PO_4, the PO_4^{3-} concentration was determined to be 0.250 M. What was the sodium ion concentration in the solution?

We have seen that a net ionic equation is convenient for focusing on the net chemical change in reactions involving ions. Let us study some examples that illustrate how such equations can be used in stoichiometric calculations.

WORKED EXAMPLE 3.17

Stoichiometry Calculations Using Net Ionic Equations

When aqueous solutions of $AgNO_3$ and $CaCl_2$ are mixed, a white precipitate of AgCl(s) is formed (see figure 3.17). The net ionic equation for the formation of this precipitate is:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

What volume of 0.100 M $AgNO_3$ solution is needed to react completely with 25.0 mL of 0.400 M $CaCl_2$ solution to form AgCl(s)?

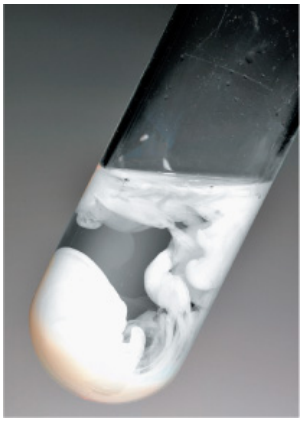


FIGURE 3.17 A solution of $AgNO_3$(aq) is added to a solution of $CaCl_2$(aq), producing a precipitate of AgCl(s).

Analysis

We are asked to calculate a volume of $AgNO_3$ solution. The volume (V) and concentration (c) of the $CaCl_2$ solution given in the question allow us to calculate n_{CaCl2} and hence n_{Cl^-} using $c = \frac{n}{V}$. From the stoichiometry of the reaction, we can then determine the required n_{Ag^+}. We can then calculate the required volume using the given concentration of the $AgNO_3$ solution.

Solution

We are given a volume and a concentration of the $CaCl_2$ solution, so we substitute these values into $c = \frac{n}{V}$.

$$n_{CaCl_2} = cV = 0.400\,\text{mol L}^{-1} \times (25.0 \times 10^{-3}\,\text{L}) = 1.00 \times 10^{-2}\,\text{mol}$$

We know that 1 mole of $CaCl_2$ will give 2 moles of Cl^- on dissolution in water (assuming complete dissociation), so:

$$n_{Cl^-} = 2 \times (1.00 \times 10^{-2}\,\text{mol}) = 2.00 \times 10^{-2}\,\text{mol}$$

The stoichiometry of the balanced chemical equation for the reaction of Ag^+ and Cl^- shows that 1 mole of Cl^- will react with 1 mole of Ag^+. Therefore, we can say that:

$$n_{Ag^+} = n_{Cl^-} = 2.00 \times 10^{-2}\,\text{mol}$$

Before we calculate the required volume, we need to look at the stoichiometry of $AgNO_3$. Because 1 mole of $AgNO_3$ will give us 1 mole of Ag^+ when dissolved in solution:

$$n_{Ag^+} = n_{AgNO_3}$$

Now we obtain:

$$V = \frac{n}{c} = \frac{2.00 \times 10^{-2}\,\text{mol}}{0.100\,\text{mol L}^{-1}} = 0.200\,\text{L}$$

Thus, we require 200 mL of 0.100 M $AgNO_3$ solution.

Is our answer reasonable?

Silver ions react with chloride ions in a 1 : 1 ratio. $CaCl_2$ solution is four times the concentration of the $AgNO_3$ solution and, as 1 mole of $CaCl_2$ dissolves to give 2 moles of Cl^-, the Cl^- concentration in this solution is eight times the concentration of the $AgNO_3$ solution. Therefore, we would expect a volume of $AgNO_3$ solution eight times the volume of the $CaCl_2$ solution. As 8 × 25 = 200, our answer appears correct.

PRACTICE EXERCISE 3.23

What volume of 0.500 M KOH is needed to react completely with 60.0 mL of a 0.250 M $FeCl_2$ solution to precipitate $Fe(OH)_2$?

Earlier in this chapter (pp. 86–8), we learned how to recognise and solve limiting reagent problems. Similar problems can be encountered when working with net ionic equations.

WORKED EXAMPLE 3.18

Calculation Involving the Stoichiometry of An Ionic Reaction

A suspension of $Mg(OH)_2$ in water is sometimes used as an antacid. It can be made by adding NaOH to a solution containing Mg^{2+}. Suppose that 40.0 mL of a 0.200 M NaOH solution is added to 25.0 mL of a 0.300 M $MgCl_2$ solution. The net ionic equation for the reaction is:

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$$

What mass of $Mg(OH)_2$ will be formed, and what will the concentrations of the ions in the solution be after the reaction is complete? ($M_{Mg(OH)2}$ = 58.33 g mol^{-1})

Analysis

We are asked to calculate the mass of $Mg(OH)_2$ and the concentrations of ions in solution at the end of the reaction. We are given concentrations (c) and volumes (V) of both the NaOH and $MgCl_2$ solutions, which allow us to calculate amounts (n) of these using $c = \frac{n}{V}$. We are also given the molar mass (M) of $Mg(OH)_2$, which allows us to use $M = \frac{m}{n}$ to calculate the mass (m) of $Mg(OH)_2$. This problem is similar to worked example 3.17, but slightly more complex. We must calculate the amounts of Mg^{2+} and OH^- present initially, and work out which of these will be limiting. We then proceed in the same way as we have done in other limiting reagent problems, using $M = \frac{m}{n}$ to calculate the mass of $Mg(OH)_2$ formed. We obtain the concentrations of the ions left in solution by difference.

Solution

We begin by calculating the amounts of both NaOH(aq) and $MgCl_2$(aq), and then calculating $n_{Mg^{2+}}$ and n_{OH^-} from these.

$$n_{NaOH} = cV = 0.200\,\text{mol L}^{-1} \times \left(40.0 \times 10^{-3}\,\text{L}\right) = 8.00 \times 10^{-3}\,\text{mol}$$

As 1 mole of NaOH gives 1 mole of OH^- on dissolution in water:

$$n_{OH^-} = n_{NaOH} = 8.00 \times 10^{-3}\,\text{mol}$$

Similarly:

$$n_{MgCl_2} = cV = 0.300\,\text{mol L}^{-1} \times (25.0 \times 10^{-3}\,\text{L}) = 7.50 \times 10^{-3}\,\text{mol}$$

Since 1 mole of $MgCl_2$ gives 1 mole of Mg^{2+} on dissolution in water:

$$n_{Mg^{2+}} = n_{MgCl_2} = 7.50 \times 10^{-3}\,\text{mol}$$

Looking at the balanced chemical equation, we see that 1 mole of Mg^{2+} will react with 2 moles of OH^-; so $n_{Mg^{2+}} = n_{OH^-} / 2$ for complete reaction. Therefore, we would require 1.50 × 10^{-2} mol of OH^-, but we have only 8.00 × 10^{-3} mol, meaning that OH^- is the limiting reagent. Therefore, from the balanced chemical equation, 8.00 × 10^{-3} mol OH^- will react with 4.00 × 10^{-3} mol Mg^{2+} to give 4.00 × 10^{-3} mol $Mg(OH)_2$. We can obtain the mass of this amount using $M = \frac{m}{n}$ and the given molar mass of $Mg(OH)_2$.

$$m = Mn = 58.33\,\text{g mol}^{-1} \times (4.00 \times 10^{-3}\,\text{mol}) = 0.233\,\text{g}$$

Therefore, the reaction forms 0.233 g $Mg(OH)_2$(s).

We still have to calculate the concentrations of the ions in solution at the end of the reaction. The ions present will be Mg^{2+}, Cl^- and Na^+. We have already calculated the amount of NaOH as 8.00 × 10^{-3} mol, so $n_{Na^+} = 8.00 \times 10^{-3}\,\text{mol}$. The final volume of the solution is 65.0 mL (40.0 mL of NaOH solution plus 25.0 mL of $MgCl_2$ solution), so:

$$c_{Na^+} = \frac{n}{V} = \frac{8.00 \times 10^{-3}\,\text{mol}}{65.5 \times 10^{-3}\,\text{L}} = 0.123\,\text{mol L}^{-1}$$

We have also calculated the amount of $MgCl_2$ as 7.50 × 10^{-3} mol, and, as 1 mole of $MgCl_2$ gives 2 moles of Cl^- on dissolution in water, $n_{Cl^-} = 2n_{MgCl_2} = 1.50 \times 10^{-2}\,\text{mol}$. We can then obtain the concentration from:

$$c_{Cl^-} = \frac{n}{V} = \frac{1.50 \times 10^{-2}\,\text{mol}}{65.0 \times 10^{-3}\,\text{L}} = 0.231\,\text{mol L}^{-1}$$

We will assume that all of the OH^- in solution has precipitated as $Mg(OH)_2$ so the final concentration of OH^- will be 0.00 mol L^{-1} (in fact, in chapter 10, we will see that a very small amount of OH^- will remain in solution, but not enough to make a significant difference to our calculation here). The final concentration we need to calculate is that of Mg^{2+}. This is slightly more involved than the others, as we need to remember that some of the Mg^{2+} has been precipitated as $Mg(OH)_2$. Earlier, we calculated the initial amount of Mg^{2+} as 7.50 × 10^{-3} mol. We also calculated that 4.00 × 10^{-3} mol of Mg^{2+} has precipitated as $Mg(OH)_2$, so we can obtain the amount of Mg^{2+} in solution by difference.

$$n_{Mg^{2+}\text{ in solution}} = (7.50 \times 10^{-3}\,\text{mol}) - (4.00 \times 10^{-3}\,\text{mol}) = 3.50 \times 10^{-3}\,\text{mol}$$

Therefore, the concentration of Mg^{2+} in solution is:

$$c_{Mg^{2+}} = \frac{n}{V} = \frac{3.50 \times 10^{-3}\,\text{mol}}{65.0 \times 10^{-3}\,\text{L}} = 5.38 \times 10^{-2}\,\text{mol L}^{-1}$$

Is our answer reasonable?

This was a fairly complex problem and there are no simple calculations we can make to verify our answers. However, there are a couple of key steps we might double-check. First, we can check that we have identified the limiting reagent correctly. In the previous calculation, we selected Mg^{2+} and determined if there was enough OH^- to react with it. As a check, let us look at OH^- to see if there is enough Mg^{2+}. We began with 8 × 10^{-3} mol of OH^-, which requires half that amount of Mg^{2+} (4 × 10^{-3} mol Mg^{2+}) to react completely. The amount of Mg^{2+} available (7.5 × 10^{-3}

mol) is more than enough, so Mg^{2+} will be left over and OH^- is limiting. Our analysis confirms that we have selected the correct limiting reagent.

Another place to be careful is in the calculation of the final concentrations of the ions in the reaction mixture. Whenever we add one aqueous solution to another, the mixture will have a final volume that is the sum of the volumes of the two solutions combined. When calculating the concentrations of anything in the final mixture, we have to use the final combined volume of the mixture. We see that we have taken this into account, so we can feel confident we've done this part of the calculation correctly.

PRACTICE EXERCISE 3.24

What amount of $BaSO_4$ will form if 20.0 mL of 0.600 M $BaCl_2$ is mixed with 30.0 mL of 0.500 M $MgSO_4$? Determine the concentration of each ion in the final reaction mixture.

The worked examples in this chapter so far have specified the reactants and products involved. There will be occasions when we do not know the composition of one of these, but stoichiometry can still help to determine the amount of a particular element in an unknown compound. The calculations required for these kinds of problems are not new; they are simply applications of the stoichiometric calculations we have already learned.

WORKED EXAMPLE 3.19

Calculation Involving an Unknown Compound

A compound used as an insecticide contains carbon, hydrogen and chlorine. Reactions were carried out on a 1.340 g sample of the compound that converted all of its chlorine to chloride ions dissolved in water. This aqueous solution was treated with an excess of $AgNO_3$ solution, and the AgCl precipitate was collected and then weighed. Its mass was 2.709 g. What was the percentage by mass of Cl in the original insecticide sample? (M_{Cl} = 35.45 g mol^{-1}; M_{AgCl} = 143.32 g mol^{-1})

Analysis

We are asked to calculate a percentage by mass. We are given the mass (m) and molar mass (M) of AgCl so we can calculate the amount of AgCl using $M = \frac{m}{n}$. We can obtain the rest of the necessary data using mole ratios. The important point to understand in this problem is that all the chlorine in the AgCl that was collected originated from the insecticide sample. The strategy, therefore, is to determine the mass of Cl in 2.709 g of AgCl. We then assume that this is the mass of chlorine in the original 1.340 g sample of insecticide and calculate the percentage Cl as follows:

$$\%\,\text{Cl by mass} = \frac{\text{mass of Cl in sample}}{\text{mass of sample}} \times 100\%$$

Solution

We begin by calculating the amount of AgCl using $M = \frac{m}{n}$.

$$n_{AgCl} = \frac{m}{M} = \frac{2.709\,\text{g}}{143.32\,\text{g mol}^{-1}} = 1.890 \times 10^{-2}\,\text{mol}$$

As 1 mole of AgCl contains 1 mole of Cl, the amount of Cl in the original insecticide sample must be 1.890 × 10^{-2} mol. We calculate the mass of this amount using $M = \frac{m}{n}$.

$$m = Mn = 35.45\,\text{g mol}^{-1} \times 1.890 \times 10^{-2}\,\text{mol} = 0.6700\,\text{g}$$

We can now calculate the %Cl by mass.

$$\%\,\text{Cl by mass} = \frac{\text{mass of Cl in sample}}{\text{mass of sample}} = \frac{0.6700\,\text{g}}{1.340\,\text{g}} \times 100\% = 50.00\%$$

Is our answer reasonable?

Let us consider the molar masses of AgCl and Cl (143.32 g mol^{-1} and 35.45 g mol^{-1}, respectively). If we round these to 140 and 35, we can say that AgCl is approximately 25% of Cl by mass (35/140 = 0.25). Approximately 3 g of AgCl was obtained; 25% of 3 g equals 0.75 g of Cl, which is close to the value we obtained. The original sample weighed 1.34 g, which is nearly twice 0.75 g (the mass of Cl), so an answer of 50% Cl by mass seems reasonable.

PRACTICE EXERCISE 3.25

A sample of a mixture containing $CaCl_2$ and $MgCl_2$ weighed 2.000 g. The sample was dissolved in water, and H_2SO_4 was added until the precipitation of $CaSO_4$ was complete. The $CaSO_4$ was filtered, dried completely and weighed. A total of 0.736 g of $CaSO_4$ was obtained. What amount of Ca^{2+} was in the original 2.000 g sample?

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SUMMARY

Chemical Equations

A chemical reaction is the formation of new substances (products) from one or more starting materials (reactants). A chemical equation is a before-and-after description of a chemical reaction. A qualitative analysis is concerned only with which substances are present. A quantitative analysis is concerned with the amounts of all the various substances. Stoichiometry is concerned with the relative amounts of products and reactants in a reaction. Stoichiometric coefficients are written in front of formulae in chemical equations to indicate the number of specified entities of each kind among the reactants and products. A balanced chemical equation has the same number of atoms of each kind in the products and reactants, thus conforming to the law of conservation of mass. The physical states of reactants and products can be shown in chemical equations using (s) for solid, (l) for liquid and (g) for gas. We use (aq) to indicate an aqueous solution (that is, when a substance is dissolved in water).

Balancing Chemical Equations

A chemical equation is balanced when all atoms present among the reactants are also somewhere among the products. To balance an equation, we first write the unbalanced equation and then adjust the stoichiometric coefficients to get equal numbers of each kind of atom on each side of the arrow.

The Mole

The mole (mol) is the base SI unit for amount. It is the amount of any substance with the same number of atoms or molecules as there are atoms in exactly 12 g of ^{12}C. The Avogadro constant, N_A, is 6.022×10^{23} mol^{-1} and gives the number of specified entities in 1 mol of a substance. The molar mass, M, is the mass of 1 mol of a substance.

Empirical Formulae

The actual composition of a molecule is given by its molecular formula. An empirical formula gives the ratio of atoms, but in the smallest whole numbers, and it is generally the only formula we write for ionic compounds. The molar mass of a molecular compound is equal to that calculated from the compound's empirical formula or to a simple multiple of it. When the two calculated masses are the same, the molecular formula is the same as the empirical formula.

An empirical formula can be found from the masses of the elements obtained by the quantitative analysis of a known sample of the compound, or it can be calculated from the percentage composition (the percentage of an element in a compound is the same as the number of grams of the element in 100 g of the compound). If there is J% of X in $X_x Z_z$, then 100 g of $X_x Z_z$ contains J g of X. The amounts of X and Z can be calculated from the masses of X and Z. The subscripts in the empirical formula are obtained by adjusting these amounts to their corresponding whole-number ratios.

Stoichiometry, Limiting Reagents and Percentage Yield

A chemical formula is a tool for stoichiometric calculations, because its subscripts tell us the mole ratios in which the various elements are combined. In 1 mole of $X_x Z_z$, x moles of X are combined with z moles of Z.

A balanced equation is a tool for reaction stoichiometry because its coefficients disclose the stoichiometric relationships. All problems of reaction stoichiometry must be solved at the mole level of the substances involved. If masses are given, they must first be changed to amounts.

From the generic balanced equation $aA + bB \rightarrow cC + dD$, it follows that the mole ratios for exact

stoichiometric reaction are:

$$\frac{n_A}{a} = \frac{n_B}{b} = \frac{n_C}{c} = \frac{n_D}{d}$$

In cases where this equation does not hold, the reactant present in the smallest mole ratio is called the limiting reagent. The other reactant is called the excess reagent. The theoretical yield of a product can be no more than that permitted by the limiting reagent. Sometimes, competing reactions (side re actions) that produce by-products reduce the actual yield. The ratio of the actual yield to the theoretical yield, expressed as a percentage, is the percentage yield.

Solution Stoichiometry

A solution is a homogeneous mixture in which one or more solutes are dissolved in a solvent. Concentration is the ratio of the amount of solute to the volume of solution. Solutions of known concentration can be prepared by weighing accurate masses of compounds using an analytical balance and then making them up to a particular volume with solvent in a volumetric flask. Concentrated solutions of known concentration can be diluted quantitatively using volumetric glassware such as pipettes and volumetric flasks. Molarity is a useful concentration unit for any calculation involving the stoichiometry of reactions in solution. In ionic reactions, the concentrations of the ions in a solution of a salt can be derived from the molar concentration of the salt, taking into account the number of ions formed on dissolution of the salt. For reactions involving ions there are three possible ways to write reaction equations. A molecular equation uses the empirical formula for each compound to aid stoichiometric calculations. The ionic equation shows all the ions that are formed in solution, while the net ionic equation shows only those ions that are actually involved in the net reaction (i.e. excluding spectator ions).

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KEY CONCEPTS AND EQUATIONS

Chemical formula *(section 3.1)*

We use subscripts in a formula to establish atom ratios and mole ratios between the elements in the substance.

Balanced chemical equation *(section 3.2)*

We use coefficients to establish stoichiometric equivalencies that relate the amount of one substance to the amount of another in a chemical reaction. The coefficients also establish the ratios of reactants and products involved in the reaction.

The mole *(section 3.3)*

The mole provides the basis for determination of the amount of substance.

Avogadro constant (N_A) *(section 3.3)*

The Avogadro constant relates macroscopic quantities used in a laboratory to numbers of individual atomic-sized particles, such as atoms, molecules and ions.

Molar mass (M) *(section 3.3)*

Molar mass can be used to calculate the mass of 1 mole of any substance or to convert between amount and mass using $M = \frac{m}{n}$.

$M = \frac{m}{n}$ *(section 3.3)*

This equation represents the relationship between mass (m), amount (n) and molar mass (M).

Percentage composition *(section 3.4)*

We use percentage composition to represent the composition of a compound and as the basis for calculating the empirical formula. Comparing experimental and theoretical percentage compositions can help to establish the identity of a compound.

Theoretical, actual and percentage yields *(section 3.5)*

We use these values to estimate the efficiency of a reaction. Remember that theoretical yield is calculated from the limiting reagent using the balanced chemical equation. The percentage yield is given by the equation: percentage yield = (actual yield/theoretical yield) × 100%.

Balanced equations and mole ratios *(section 3.5)*

For the generic balanced equation:

$$aA + bB \rightarrow cC + dD$$

the mole ratios for exact stoichiometric reaction are:

$$\frac{n_A}{a} = \frac{n_B}{b} = \frac{n_C}{c} = \frac{n_D}{d}$$

$c = \frac{n}{V}$ *(section 3.6)*

This equation represents the relationship between concentration (c), amount (n) and volume (V).

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REVIEW QUESTIONS

Chemical Equations

3.1 What do we mean when we say a chemical equation is 'balanced'? Why do we balance chemical equations?

3.2 In a chemical reaction, what do we mean by the term 'reactants'? What do we mean by the term 'products'?

3.3 What do we call the numbers that are written in front of the formulae in a balanced chemical equation?

3.4 The combustion of a thin wire of magnesium metal, Mg, in an atmosphere of pure oxygen produces the brilliant light of a flashbulb, once commonly used in photography. After the reaction, a thin film of magnesium oxide is seen on the inside of the bulb. The equation for the reaction is:

$$2Mg + O_2 \rightarrow 2MgO$$

(a) State in words how this equation is read.

(b) Give the formulae of the reactants.

(c) Give the formula of the product.

(d) Rewrite the equation to show that Mg and MgO are solids and O_2 is a gas.

Balancing Chemical Equations

3.5 When given the *unbalanced* equation:

$$Na(s) + Cl_2(g) \rightarrow NaCl(s)$$

and asked to balance it, student A wrote:

$$Na(s) + Cl_2(g) \rightarrow NaCl_2(s)$$

and student B wrote:

$$2Na(s) + Cl_2(g) \rightarrow NaCl_2(s)$$

(a) Both equations are balanced, but which student is correct?

(b) Explain why the other student's answer is incorrect.

The Mole

3.6 Define the term 'mole'.

3.7 Why are moles used when all stoichiometry problems could be done using only atomic mass units?

3.8 What information is required to calculate the amount of a substance from a given mass of that same substance?

3.9 Give the equation that relates molar mass, amount and mass.

3.10 How would you estimate the number of atoms in a gram of iron, using atomic mass units?

3.11 Which contains more molecules: 2.5 moles of H_2O or 2.5 moles of H_2?

3.12 What amount of iron atoms is in 1 mol of Fe_2O_3? How many iron atoms are in 1 mol of Fe_2O_3?

3.13 Why is the expression '1.0 mol of oxygen' ambiguous?

Empirical Formulae

3.14 In general, what fundamental information, obtained from experimental measurements, is required to calculate the empirical formula of a compound?

3.15 Why is the changing of subscripts not allowed when balancing a chemical equation?

3.16 Give a step-by-step procedure for estimating the mass of *A* required to completely react with 10

moles of *B*, given the following information:

i. *A* and *B* react to form A_5B_2.

ii. *A* has a molar mass of 100.0 g mol^{-1}.

iii. *B* has a molar mass of 200.0 g mol^{-1}.

iv. There are 6.022×10^{23} molecules of *A* in 1 mole of *A*. Which of these pieces of information was not needed?

Stoichiometry, Limiting Reagents and Percentage Yield

3.17 What information is required to determine the mass of sulfur that would react with 1 gram of arsenic?

3.18 A mixture of 0.020 mol of Mg and 0.020 mol of Cl_2 reacted completely to form $MgCl_2$ according to the equation:

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$

(a) What information describes the *stoichiometry* of this reaction?

(b) What information gives the *scale* of the reaction?

3.19 In a report to a supervisor, a chemist described an experiment in the following way: '0.0800 mol of H_2O_2 decomposed into 0.0800 mol of H_2O and 0.0400 mol of O_2'. Express the chemistry and stoichiometry of this reaction by a conventional chemical equation.

Solution Stoichiometry

3.20 Give the equation that relates concentration, volume and amount.

3.21 What is the definition of 'molarity'? Show that the ratio of millimoles (mmol) to millilitres (mL) is equivalent to the ratio of moles to litres.

3.22 What are spectator ions?

3.23 When a solution labelled 0.50 M HNO_3 is diluted with water to give 0.25 M HNO_3, what happens to the amount of HNO_3 in the solution?

3.24 Solutions A and B are labelled '0.10 M $CaCl_2$' and '0.20 M $CaCl_2$', respectively. Both solutions contain the same amount of $CaCl_2$. If solution A has a volume of 50 mL, what is the volume of solution B?

3.25 What is the difference between a qualitative analysis and a quantitative analysis?

3.26 The following equation shows the formation of cobalt(II) hydroxide, a compound used to improve the drying properties of lithographic inks:

$$CO^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + 2OH^-(aq) \rightarrow CO(OH)_2(s) + 2Na^+(aq) + 2Cl^-(aq)$$

Which are the spectator ions? Write the net ionic equation.

3.27 Why is the following equation not balanced? Find the errors and fix them.

$$3CO^{3+} + 2HPO_4^{2-} \rightarrow CO_3(PO_4)_2 + 2H^+$$

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REVIEW PROBLEMS

3.28 Consider the balanced equation:

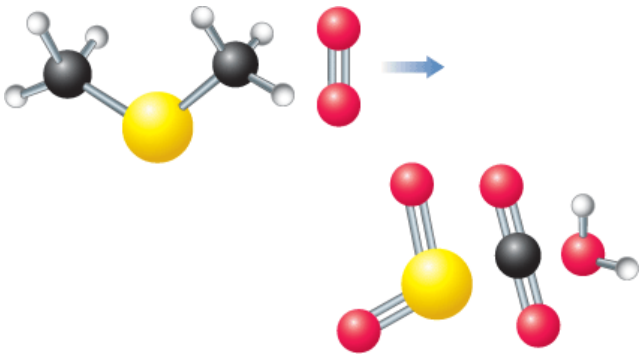
$$2Fe(NO_3)_3 + 3Na_2CO_3 \rightarrow Fe_2(CO_3)_3 + 6NaNO_3$$

(a) How many atoms of Na are on each side of the equation?

(b) How many atoms of C are on each side of the equation?

(c) How many atoms of O are on each side of the equation?

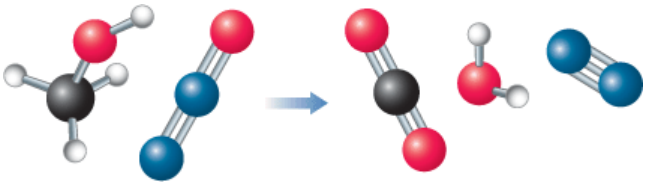
3.29 When sulfur impurities in fuels burn, they produce pollutants such as sulfur dioxide, a major contributor to acid rain. The following is a ball-and-stick model of a typical reaction.



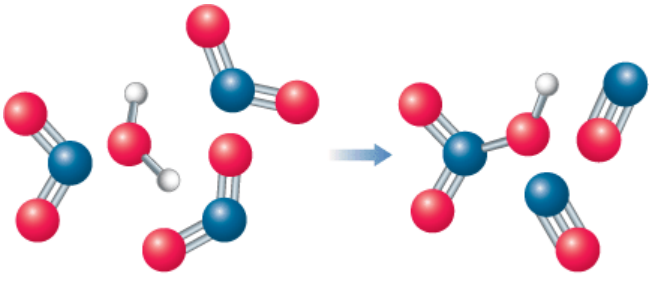
On the left are reactant molecules and on the right are product molecules in a chemical reaction. Write the balanced chemical equation for this reaction, using the stoichiometric coefficients that give the smallest whole number of product molecules

3.30 Write the equation that expresses in acceptable chemical shorthand the following statement: 'Iron can be made to react with molecular oxygen, O_2, to give iron oxide with the formula Fe_2O_3.'

3.31 Race car drivers can get extra power by burning methyl alcohol with nitrous oxide. Below on the left are the reactant molecules and on the right are product molecules of the chemical reaction. Write the balanced chemical equation for this reaction, using the stoichiometric coefficients that give the smallest whole number of product molecules.



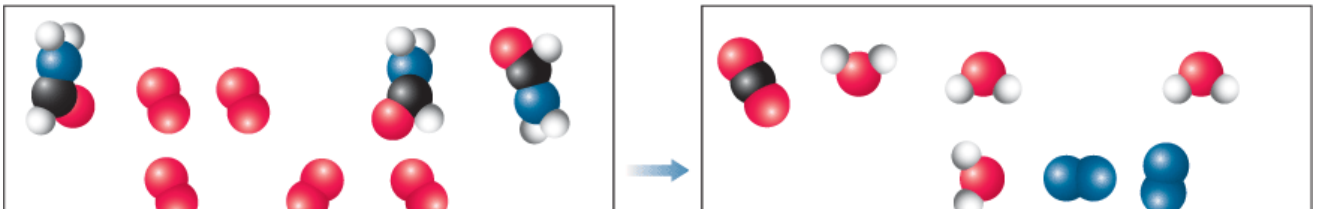
3.32 Is the following chemical equation balanced? This reaction is used for the production of nitric acid, HNO_3, and is one of the reactions responsible for acid rain.



$$3NO_2 + H_2O \rightarrow HNO_3 + 2NO$$

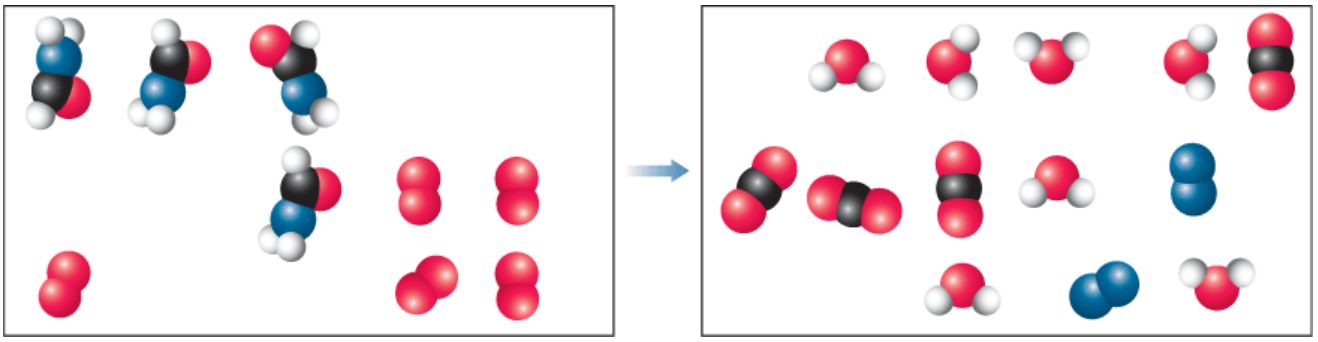
If the equation is not balanced, find coefficients that would make it balanced.

3.33 Write the balanced chemical equation for the chemical reaction depicted by the space-filling models below.





3.34 Write the balanced chemical equation for the chemical reaction depicted by the space-filling models below.



3.35 Balance the following equations:

(a) $Ca(OH)_2 + HCl \rightarrow CaCl_2 + H_2O$

(b) $NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$

(c) $AgNO_3 + CaCl_2 \rightarrow Ca(NO_3)_2 + AgCl$

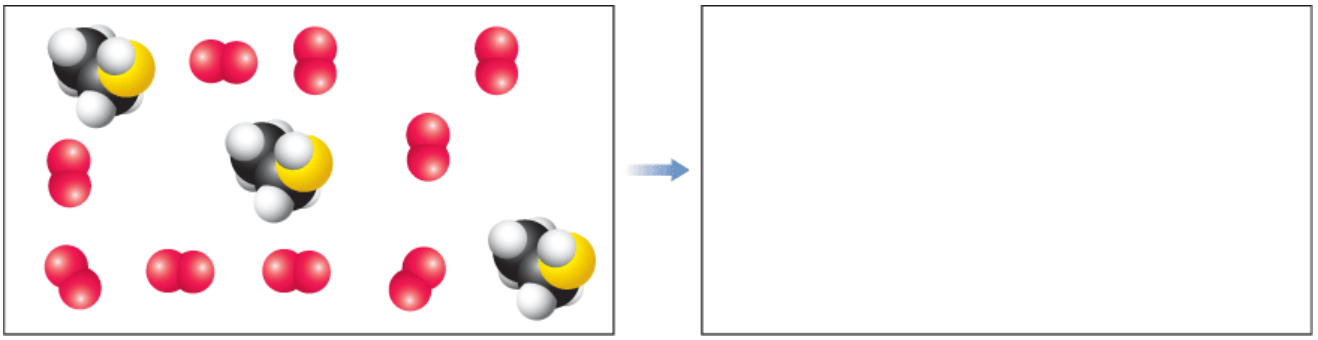
(d) $C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$

(e) $Fe_2O_3 + C \rightarrow Fe + CO_2$

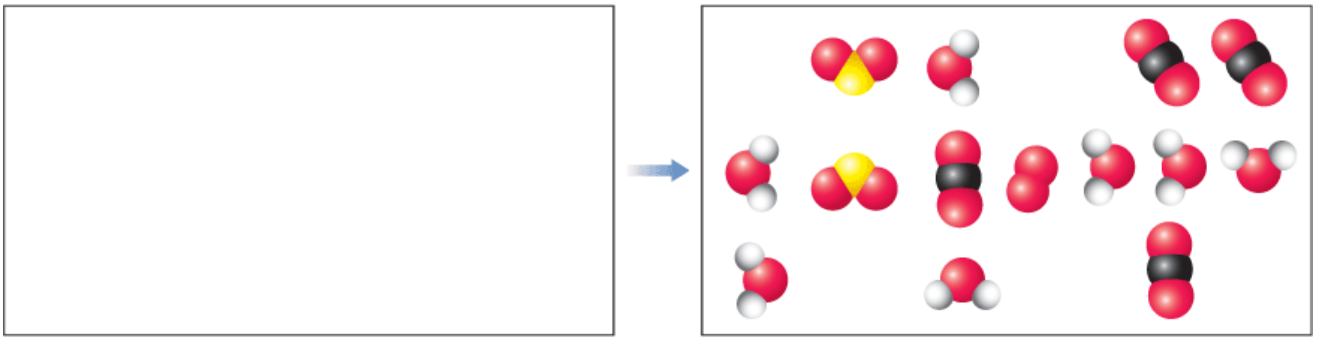
3.36 Given the balanced chemical equation

$$2C_2H_5SH(g) + 9O_2(g) \rightarrow 4CO_2(g) + 2SO_2(g) + 6H_2O(g)$$

determine the number of molecules of SO_2 that would be formed starting from the actual number of molecules of C_2H_5SH and O_2 shown below.



3.37 Using the balanced chemical equation from question 3.35, which of C_2H_5SH or O_2 was the limiting reagent if the product distribution for the reaction was that shown below?



3.38 In what smallest whole-number ratio must N and O atoms combine to make dinitrogen tetroxide, N_2O_4? What is the mole ratio of the elements in this compound?

3.39 What amount of sodium atoms corresponds to 1.56×10^{21} atoms of sodium?

3.40 What amount of Al atoms are needed to combine with 1.58 mol of O atoms to make aluminium oxide, Al_2O_3?

3.41 What amount of H_2 and N_2 can be formed by the decomposition of 0.145 mol of ammonia, NH_3?

3.42 What amount of UF_6 would have to be decomposed to provide enough fluorine to prepare 1.25 mol of CF_4? (Assume sufficient carbon is available.)

3.43 Quantitative analysis of a 0.896 g sample of sodium pertechnetate found 0.111 g of sodium and 0.477 g of technetium. The remainder was oxygen. Calculate the empirical formula of sodium pertechnetate. (Radioactive sodium pertechnetate is used as a brain-scanning agent in medicine.)

3.44 The composition of a dry-cleaning fluid, composed of only carbon and chlorine, was found to be 14.5% C and 85.5% Cl (by mass). What is the empirical formula of this compound?

3.45 When 0.684 g of an organic compound containing only carbon, hydrogen and oxygen was burned in oxygen, 1.312 g CO_2 and 0.805 g H_2O was obtained. What is the empirical formula of the compound?

3.46 A sample of a compound of mercury and bromine with a mass of 0.389 g was found to contain 0.111 g bromine. Its molar mass was found to be 561 g mol^{-1}. What are its empirical and molecular formulae?

3.47 Determine the mass in grams of each of the following:

(a) 1.35 mol Fe,

(b) 24.5 mol O,

(c) 0.876 mol Ca.

3.48 What is the mass, in grams, of 2.00×10^{12} atoms of potassium?

3.49 What amount of nickel is in 17.7 g of Ni?

3.50 Calculate the molar mass of each of the following:

(a) $NaHCO_3$,

(b) $K_2Cr_2O_7$,

(c) $(NH_4)_2CO_3$,

(d) $Al_2(SO_4)_3$,

(e) $CuSO_4.5H_2O$.

3.51 Calculate the mass in grams of each of the following:

(a) 1.25 mol $Ca_3(PO_4)_2$,

(b) 0.625 mol $Fe(NO_3)_3$,

(c) 0.600 mol C_4H_{10},

(d) 1.45 mol $(NH_4)_2CO_3$.

3.52 Calculate the amount of the compound in each of the following samples:

(a) 21.5 g $CaCO_3$,

(b) 1.56 g NH_3,

(c) 16.8 g $Sr(NO_3)_2$,

(d) 6.98 µg Na_2CrO_4.

3.53 What mass of a fertiliser made of pure $(NH_4)_2CO_3$ would be required to supply 1 kg of nitrogen to the soil?

3.54 Calculate the percentage composition by mass of all elements in each of the following:

(a) NaH_2PO_4,

(b) $NH_4H_2PO_4$,

(c) $(CH_3)_2CO$,

(d) $CaSO_4$,

(e) $CaSO_4 \cdot 2H_2O$.

3.55 What mass of O is combined with 7.14×10^{21} atoms of N in the compound N_2O_5?

3.56 Chlorine is used by textile manufacturers to bleach cloth. Excess chlorine is destroyed by its reaction with sodium thiosulfate, $Na_2S_2O_3$, as follows:

$$Na_2S_2O_3(aq) + 4Cl_2(g) + 5H_2O(l) \rightarrow 2NaHSO_4(aq) + 8HCl(aq)$$

(a) What amount of $Na_2S_2O_3$ is needed to react with 0.12 mol of Cl_2?

(b) What amount of HCl can form from 0.12 mol of Cl_2?

(c) What amount of H_2O is required for the reaction of 0.12 mol of Cl_2?

(d) What amount of H_2O reacts if 0.24 mol HCl is formed?

3.57 The following reaction is used to extract gold from pretreated gold ore:

$$2Au(CN)_2^-(aq) + Zn(s) \rightarrow 2Au(s) + Zn(CN)_4^{2-}(aq)$$

(a) What mass of Zn is needed to react with 0.11 mol of $Au(CN)_2^-$?

(b) What mass of Au can form from 0.11 mol of $Au(CN)_2^-$?

(c) What mass of $Au(CN)_2^-$ is required for the reaction of 0.11 mol of Zn?

3.58 The incandescent white of a fireworks display is caused by the reaction of phosphorus with O_2 to give P_4O_{10}.

(a) Write the balanced chemical equation for the reaction.

(b) What mass of O_2 is needed to combine with 6.85 g of P?

(c) What mass of P_4O_{10} can be made from 8.00 g of O_2?

(d) What mass of P is needed to make 7.46 g of P_4O_{10}?

3.59 Oxygen gas can be produced in the laboratory by decomposition of hydrogen peroxide, H_2O_2:

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

What mass of O_2 can be produced from 1.0 kg of H_2O_2?

3.60 The reaction of powdered aluminium and iron(III) oxide:

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(l)$$

produces so much heat that the iron that forms is molten. Because of this, the reaction is used when laying railway tracks to provide molten steel to weld steel rails together. Suppose that, in one batch of reactants, 4.20 mol of Al was mixed with 1.75 mol of Fe_2O_3.

(a) Which reactant, if either, was the limiting reagent?

(b) Calculate the mass of iron that can be formed from this mixture of reactants.

3.61 Silver nitrate, $AgNO_3$, reacts with iron(III) chloride, $FeCl_3$, to give silver chloride, AgCl, and iron(III) nitrate, $Fe(NO_3)_3$. A solution containing 18.0 g of $AgNO_3$ was mixed with a solution containing 32.4 g of $FeCl_3$. What mass of which reactant remains after the reaction is complete?

3.62 Barium sulfate, $BaSO_4$, is made by the following reaction:

$$Ba(NO_3)(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$$

An experiment was begun with 75.00 g of $Ba(NO_3)_2$ and an excess of Na_2SO_4. After collecting and drying the product, 64.45 g of $BaSO_4$ was obtained. Calculate the theoretical yield and percentage yield of $BaSO_4$.

3.63 The potassium salt of benzoic acid (potassium benzoate, C_6H_5COOK), can be made by the action of potassium permanganate, $KMnO_4$, on toluene, $C_6H_5CH_3$, as follows:

$$C_6H_5CH_3 + 2KMnO_4 \rightarrow KC_6H_5COO + 2MnO_2 + KOH + H_2O$$

If the yield of potassium benzoate cannot realistically be expected to be more than 71%, what is the minimum mass of toluene needed to achieve this yield while producing 11.5 g of potassium benzoate?

3.64 Calculate the concentration of a solution prepared by dissolving:

(a) 4.00 g of NaOH in 100.0 mL of solution

(b) 16.0 g of $CaCl_2$ in 250.0 mL of solution

(c) 14.0 g of KOH in 75.0 mL of solution

(d) 6.75 g of HO_2CCO_2H in 500 mL of solution.

3.65 Calculate the mass of each solute needed to make each of the following solutions.

(a) 125 mL of 0.200 M NaCl(aq)

(b) 250 mL of 0.360 M $C_6H_{12}O_6$(aq) (glucose)

(c) 250 mL of 0.250 M H_2SO_4(aq)

3.66 If 25.0 mL of 0.56 M H_2SO_4 is diluted to a volume of 125 mL, what is the concentration of the resulting solution?

3.67 To what volume must 25.0 mL of 18.0 M H_2SO_4 be diluted to produce 1.50 M H_2SO_4(aq)?

3.68 Calculate the amounts of each of the ions in the following solutions.

(a) 35.0 mL of 1.25 M KOH(aq)

(b) 32.3 mL of 0.45 M $CaCl_2$(aq)

(c) 50.0 mL of 0.40 M $AlCl_3$(aq)

3.69 Calculate the concentrations of each of the ions in:

(a) 0.25 M $Cr(NO_3)_2$(aq),

(b) 0.10 M $CuSO_4$(aq),

(c) 0.16 M Na_3PO_4(aq),

(d) 0.075 M $Al_2(SO_4)_3$(aq).

3.70 In a solution of $Al_2(SO_4)_3$(aq), the Al^{3+} concentration is 0.12 M. What mass of $Al_2(SO_4)_3$ is in 50.0 mL of this solution?

3.71 What volume of 0.25 M $NiCl_2$(aq) solution is needed to react completely with 20.0 mL of 0.15 M Na_2CO_3(aq) solution? What mass of $NiCO_3$ will be formed? The reaction is:

$$Na_2CO_3(aq) + NiCl_2(aq) \rightarrow NiCO_3(s) + 2NaCl(aq)$$

3.72 What volume of 0.150 M $FeCl_3$(aq) solution is needed to react completely with 20.0 mL of 0.0450 M $AgNO_3$(aq) solution? What mass of AgCl will be formed? The net ionic equation for the reaction is:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

3.73 Consider the reaction of aluminium chloride with silver acetate. What volume of 0.250 M $AlCl_3$(aq) would be needed to react completely with 20.0 mL of 0.500 M $AgOOCCH_3$(aq) solution? The net ionic equation for the reaction is:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

3.74 Suppose that 25.0 mL of 0.440 M NaCl(aq) is added to 25.0 mL of 0.320 M $AgNO_3$(aq).

(a) What amount of AgCl would precipitate?

(b) Determine the concentration of each of the ions in the reaction mixture after the reaction.

3.75 A mixture is prepared by adding 25.0 mL of 0.185 M Na_3PO_4(aq) to 34.0 mL of 0.140 M $Ca(NO_3)_2$(aq).

(a) What mass of $Ca_3(PO_4)_2$ will be formed?

(a) What mass of $CaSO_4$ will be formed?

(b) Determine the concentration of each of the ions in the mixture after reaction.

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ADDITIONAL EXERCISES

3.76 Write the net ionic equations for the following reactions. Include the designations for the states — solid, liquid, gas and aqueous solution. (For any substance soluble in water, assume that it is used as an aqueous solution.)

(a) $CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$

(b) $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$

(c) $FeS + 2HBr \rightarrow H_2S + FeBr_2$

(d) $2KOH + SnCl_2 \rightarrow 2KCl + Sn(OH)_2$

3.77 A 0.113 g sample of a mixture of sodium chloride and sodium nitrate was dissolved in water, and enough silver nitrate solution was added to precipitate all of the chloride ions. The mass of silver chloride obtained was 0.277 g. What mass percentage of the sample was sodium chloride?

3.78 In an experiment, 40.0 mL of 0.27 0 M $Ba(OH)_2(aq)$ was mixed with 25.0 mL of 0.330 M $Al_2(SO_4)_3(aq)$.

(a) Write the net ionic equation for the reaction that takes place.

(b) What is the total mass of precipitate that forms?

(c) What are the molar concentrations of the ions that remain in the solution after the reaction is complete?

3.79 What volume of 0.10 M HCl(aq) must be added to 50.0 mL of 0.40 M HCl(aq) to give a final solution that has a molarity of 0.25 M?

3.80 Answer the following questions about an insecticide with the chemical formula $C_{12}H_{11}NO_2$.

(a) What amount of carbon atoms is there in 8.3 g of the compound?

(b) What mass of oxygen is there in 4.5 g of the compound?

(c) The label on a 75 mL bottle of garden insecticide states that the solution contains 0.010% insecticide and 99.99% inert ingredients. What amount and how many molecules of the insecticide are in the bottle? (Assume that the density of the solution is 1.00 g mL^{-1}.)

(d) The instructions on the bottle of insecticide in (c) are to dilute the insecticide by adding 1.0 mL of the solution to 4.0 litres of water. If you spray 60 litres of the diluted insecticide mixture on your rose garden, What amount of the active ingredient is dispersed?

3.81 Solution A is prepared by dissolving 90.0 g of Na_3PO_4 in enough water to make 1.5 L of solution. Solution B is 2.5 L of 0.705 M $Na_2SO_4(aq)$.

(a) What is the molar concentration of Na_3PO_4 in solution A?

(b) What volume of solution A contains 2.50 g of Na_3PO_4?

(c) A 50.0 mL sample of solution B is mixed with a 75.00 mL sample of solution A. Calculate the concentration of Na^+ ions in the final solution.

3.82 Police officers confiscate a packet of white powder that they believe contains heroin. Purification by a forensic chemist yields a 38.70 mg sample for combustion analysis. This sample produces 97.46 mg CO_2 and 20.81 mg H_2O on complete combustion. A second sample is analysed for its nitrogen content, which is 3.8%. Show by calculations whether these data are consistent with the formula for heroin, $C_{21}H_{22}NO_5$.

3.83 When an unknown compound is burned completely in O_2, 1.23 g of CO_2 and 97.02 g of H_2O is recovered. What additional information is needed before the molecular formula of the unknown compound can be determined?

3.84 A sulfur-containing ore of copper releases sulfur dioxide when heated in air. A 5.26 g sample of the ore releases 2.12 g of SO_2 on heating. Assuming that the ore contains only copper and sulfur, what is the empirical formula?

3.85 The mineral turquoise has the formula $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$.

(a) What mass of aluminium is in a 7.25 g sample of turquoise?

(b) How many phosphate ions are in a sample of turquoise that contains 5.50×10^{-3} g of oxygen?

(c) What is the charge of the copper ion in turquoise?

3.86 A chemist needs a solution that contains aluminium ions, sodium ions and sulfate ions. In the laboratory she finds a large volume of 0.355 M sodium sulfate solution and a bottle of solid $Al_2(SO_4)_3 \cdot 18H_2O$. The chemist puts 250 mL of the sodium sulfate solution and 5.13 g of aluminium sulfate hydrate in a 500 mL volumetric flask. The flask is made up to the mark with water. Determine the molarity of aluminium ions, sodium ions and sulfate ions in the solution.

3.87 Adenosine triphosphate (ATP) is used to generate chemical energy in plant and animal cells. The molecular formula of ATP is $C_{10}H_{16}N_5O_{13}P_3$. Answer the following questions about ATP.

(a) What is the percentage composition by mass of each element in ATP?

(b) How many P atoms are in 1.75 μg of ATP?

(c) If a cell consumes 3.0 pmol of ATP, what mass has it consumed?

(d) What mass of ATP contains the same number of atoms of H as the number of N atoms in 37.5 mg of ATP?

3.88 The waters of the oceans contain many elements in trace amounts. Rubidium, for example, is present at the level of 2.2 nM (nanomolar). How many ions of rubidium are present in 1.00 L of sea water? How many litres would have to be processed to recover 1.00 kg of rubidium, assuming the recovery process was 100% efficient?

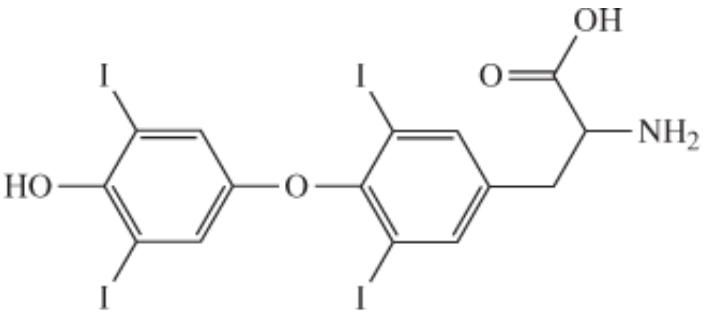
3.89 Vitamin B_{12} is a large molecule called cobalamin. There is 1 atom of cobalt in each molecule of vitamin B_{12}, and the mass percentage of cobalt is 4.34%. Calculate the molar mass of cobalamin.

3.90 Element *E* forms a compound with the formula ECl_5. Elemental analysis shows that the compound is 85.13% chlorine by mass. Identify element *E*.

3.91 Pure acetic acid, CH_3COOH, has a concentration of 17.4 M. A laboratory worker measured out 100.0 mL of pure acetic acid and added enough water to make 500.0 mL of solution. A 75.0 mL portion of the acetic acid solution was then mixed with enough water to make 1.50 L of dilute solution. What was the final molarity of acetic acid in the dilute solution?

3.92 A worker in a biological laboratory needed a solution that was 0.30 M in sodium acetate, $NaOOCCH_3$, and 0.15 M in acetic acid, CH_3COOH. On hand were stock solutions of 5.0 M sodium acetate and 5.0 M acetic acid. Describe how the worker prepared 1.5 L of the desired solution.

3.93 The thyroid gland produces hormones that help regulate body temperature, metabolic rate, reproduction, synthesis of red blood cells and more. Iodine must be present in the diet to produce these thyroid hormones. Iodine deficiency leads to sluggishness and weight gain, and can cause severe problems in the development of a foetus. One thyroid hormone is thyroxine, with the chemical formula $C_{15}H_{11}I_4NO_4$. What mass of thyroxine can be produced from 210 mg of iodine atoms, the amount a typical adult consumes per day? How many molecules is this?



thyroxine
$C_{15}H_{11}I_4NO_4$

3.94 A sample of a component of petroleum was subjected to combustion analysis. An empty vial of mass 2.7534 g was filled with the sample, after which the vial plus sample had a mass of 2.8954 g. The sample was burned and the resulting CO_2 and H_2O were collected in separate traps. Before combustion, the CO_2 trap had a mass of 54.4375 g and the H_2O trap had a mass of 47.8845 g. At the end of the analysis, the CO_2 trap had a new mass of 54.9140 g and the H_2O trap had a new mass of 47.9961 g. Determine the empirical formula of this component of petroleum.

3.95 Aluminium sulfate is used in the manufacture of paper and in the water purification industry. In the solid state, aluminium sulfate is a hydrate with the formula $Al_2(SO_4)_3 \cdot 18H_2O$.

(a) What mass of sulfur is there in 0.570 moles of solid aluminium sulfate?

(b) How many water molecules are there in a 5.1 g sample of solid aluminium sulfate?

(c) What amount of sulfate ions is there in a sample of solid aluminium sulfate that contains 12.5 moles of oxygen atoms?

(d) An aqueous solution of aluminium sulfate contains 1.25% aluminium by mass and has a density of 1.05 g mL^{-1}. What is the molarity of aluminium ions in the solution?

3.96 In the Haber synthesis of ammonia, N_2 and H_2 react at high temperature, but they never react completely. In a typical reaction, 24.0 kg of H_2 and 84.0 kg of N_2 react to produce 68 kg of NH_3. Find the theoretical yield, the percentage yield and the masses of H_2 and N_2 that remain unreacted, assuming that no other products form.

3.97 Silicon tetrachloride is used in the electronics industry to make elemental silicon for computer chips. Silicon tetrachloride is prepared from silicon dioxide, graphite and chlorine gas according to the equation:

$$SiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow SiCl_4(l) + 2CO(g)$$

If the reaction achieves 95.7% yield, how much silicon tetrachloride can be prepared from 75.0 g of each starting material, and how much of each reactant remains unreacted?

3.98 Silver jewellery is usually made from silver and copper alloys. The amount of copper in an alloy can vary considerably. The finest quality alloy is sterling silver, which is 92.5% silver by mass. To determine the composition of a silver–copper alloy, a jeweller dissolved 0.135 g of metal shavings in 50 mL of concentrated nitric acid and then added 1.00 M KCl solution until no more precipitate formed. Filtration and drying yielded 0.156 g of AgCl precipitate. What was the mass composition of the silver alloy?

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KEY TERMS

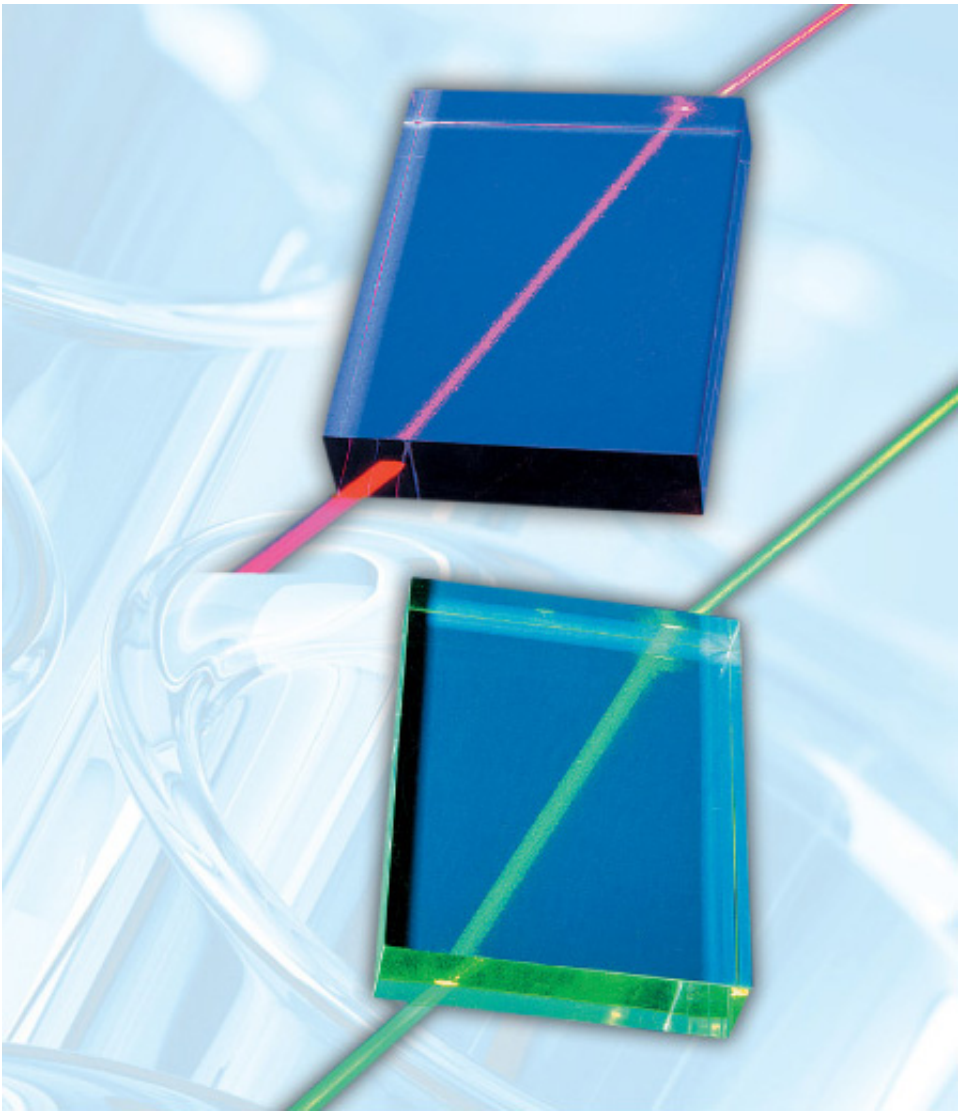
actual yield
amount of substance
Avogadro constant (N_A)
balanced chemical equation
by-product
chemical equation
chemical reaction
combustion
competing reaction
concentration
dissociation
elemental analysis
empirical formula
excess reagent
limiting reagent
main reaction
mass percentage composition
molar mass (M)
molarity (c)
mole
molecular formula
net ionic equation
percentage by mass
percentage yield
product
qualitative analysis
quantitative analysis
reactant
reversible reaction
solute
solution
solvent
spectator ion
stoichiometric coefficients
stoichiometry
theoretical yield

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CHAPTER

4 Atomic Energy Levels

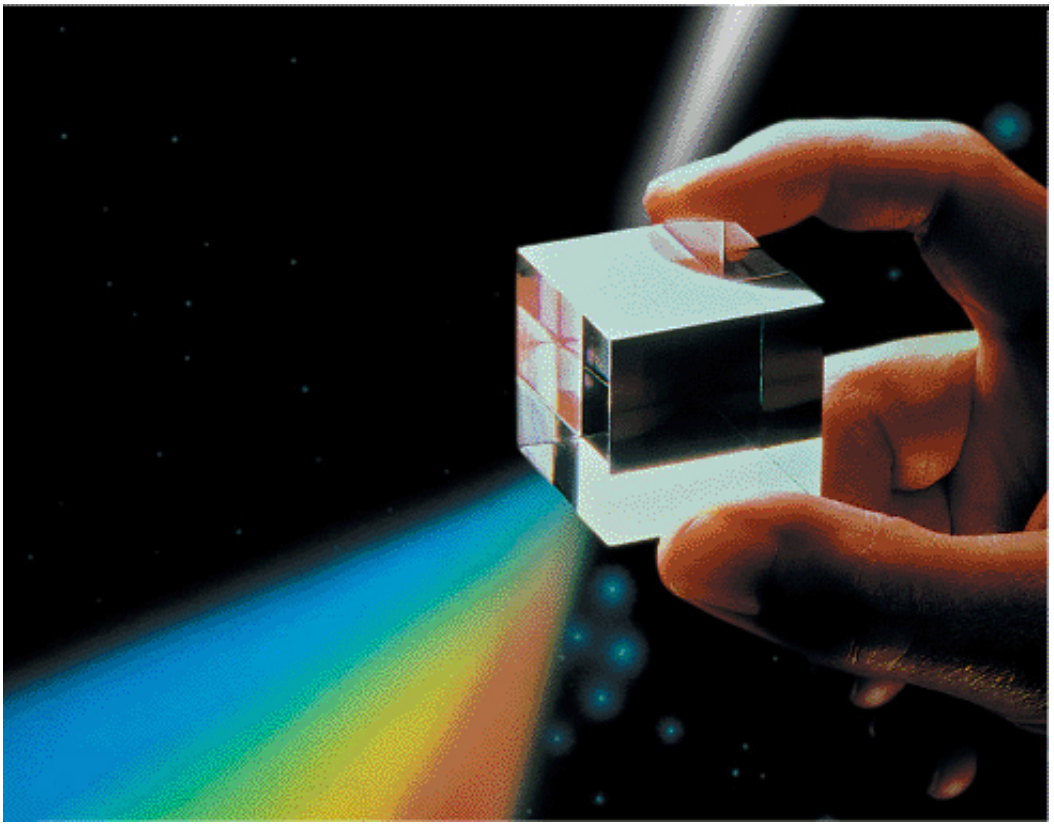
In the right combination, atoms and light combine to create one of the most remarkable tools of modern technology, the laser. Laser light is more highly organised than normal light. Laser light is mono chromatic (has a single wavelength) and is highly directional, whereas conventional light sources typically produce disperse light of many wavelengths. The pictures on this page demonstrate these differences. In the top two figures we see red and green laser light with wavelengths of 650 and 532 nm, respectively pass through a prism. While the light is diffracted, there is no splitting into different colours, as we see for white light in the bottom figure. This confirms that laser light consists of only one wavelength while normal white light comprises many wavelengths. Many of the applications of lasers take advantage of the high degree of organisation.



Lasers are also used in, for example, DVD scanners, eye surgery and fibre optics communications. Lasers have also become versatile tools for scientific research. For example, finely tuned lasers have been used to deposit vapour-phase atoms on solid surfaces in regular patterns. The ability to manipulate individual atoms is likely to have important

applications in nanotechnology.

Every laser is based on the interactions between light and atoms or molecules. In this chapter, we describe the properties of atoms and light and the energy changes that accompany the interactions between them. Then we describe the properties of electrons bound to atoms and how these contribute to atomic structure. We explore the details of orbital energies and relate them to the ordering of atoms that leads to the familiar form and structure of the periodic table. Orbital energy levels have consequences that are far reaching. Orbital energies determine the stability of atoms and how atoms react. The periodic table is based on orbital energy levels and provides the foundation for interpreting patterns of chemical behaviour related to an element's position in the table.



KEY TOPICS

4.1 Characteristics of atoms
4.2 Characteristics of light
4.3 Properties of electrons
4.4 Quantisation and quantum numbers
4.5 Atomic orbital electron distributions and energies
4.6 Structure of the periodic table
4.7 Electron configurations
4.8 Periodicity of atomic properties
4.9 Ions and chemical periodicity

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4.1 Characteristics of Atoms

We introduced the concept of the atom in chapter 1, and stated that it was the fundamental building block of all matter. In this chapter, we will investigate the properties of atoms in more detail. We will start by outlining the basic characteristics of atoms; we read about many of these characteristics in chapter 1.

Atoms possess mass, most of which, as Rutherford showed, is concentrated in the nucleus. The nucleus of an atom is small and positively charged, and all nuclei, except that of the hydrogen atom ^{1}H, consist of both positively charged protons and neutral neutrons. The positive charge of the nucleus is exactly balanced by negatively charged electrons, which occupy the region of space around the nucleus. A neutral atom contains equal numbers of protons and electrons. Atoms occupy volume, the majority of which is taken up by the electron cloud. The chemical properties of elements are determined to a large extent by both their atomic size and their number of accessible (valence) electrons. Finally, atoms can attract one another, and, as a result, can combine to form molecules.

This chapter examines in detail how both the number of electrons and their specific arrangement influence chemical properties. Since there are similarities between the properties of light and electrons, and light is an essential tool for probing the properties of electrons, we will begin our discussion by describing light and its interaction with atoms.

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4.2 Characteristics of Light

The most useful tool for studying the structure of atoms is **electromagnetic radiation**. What we call **light** is one form of this radiation, with other forms including radiowaves, microwaves and X-rays. We need to know about the fundamental properties of light to understand what electromagnetic radiation reveals about atomic structure.

Wave-like Properties of Light

Light has wave-like properties. A wave is a regular oscillation in some particular property, such as the up-and-down variation in position of water waves. Water waves vary with time. A surfer waiting for a 'big one' bobs up and down as 'small ones' pass by. Light waves vary with time too, in a more regular manner than water waves. This variation is characterised by the wave's **frequency (ν)**, which is the number of wave crests passing a point in space in 1 second (so the unit is s^{-1}, also designated hertz or Hz). Water waves also vary in height as you move away from the beach; that is, the height of the wave varies with position. Light waves vary in space in a manner illustrated in figure 4.1. This variation in space is characterised by the **wavelength (λ)**, which is the distance between successive wave crests. Wavelengths are measured in units of length, such as metres or nanometres. As we will see below, frequency and wavelength are not independent variables, but are inversely proportional to each other.

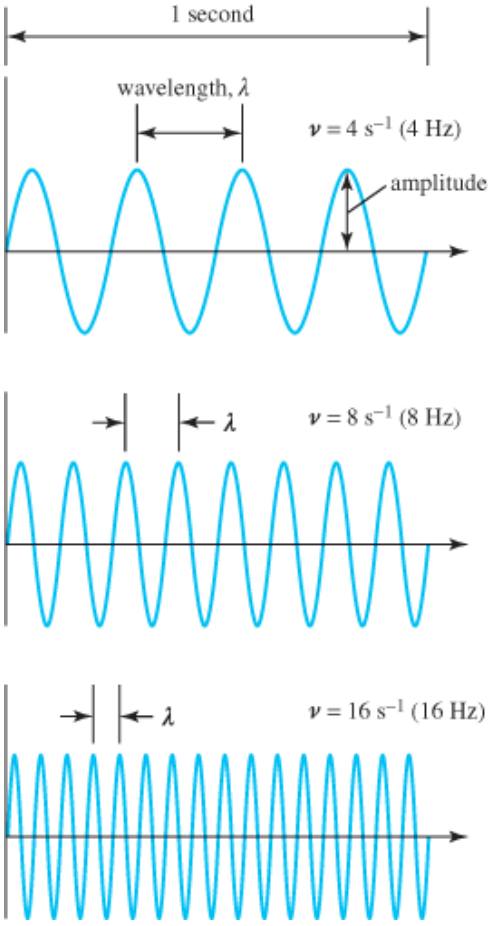


FIGURE 4.1 A light wave can be described by its wavelength or frequency. As wavelength increases, frequency decreases, and vice versa.

Amplitude is the maximum displacement of a wave from its centre. The amplitude of a light wave determines the **intensity** of the light. As figure 4.2 shows, a bright light is more intense than a dim one as its waves have higher amplitudes. It is important to note that the intensity of light is proportional to the square of its amplitude. The amplitude itself has no physical meaning because at any moment in time the amplitude of the wave can be negative or positive, while the square is always positive and equivalent to photon density.

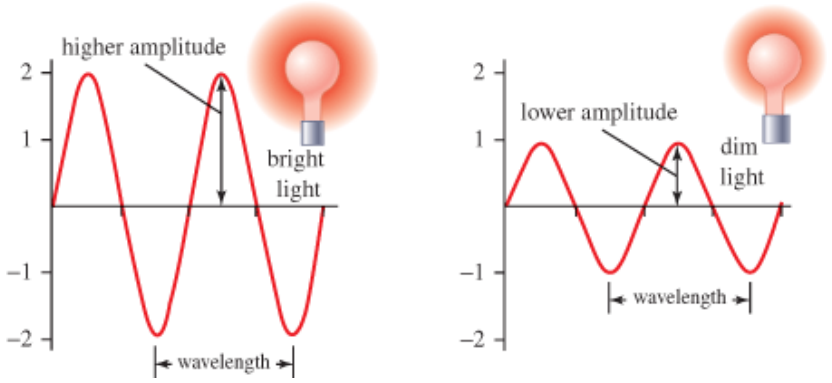


FIGURE 4.2 The amplitude of a light-wave determines the intensity of the light. A bright light is more intense and has a higher amplitude than a dim light.

Waves can also be described in terms of their phase. **Phase** refers to the starting position of a wave with respect to one wavelength. We can see that waves in figures 4.3a and 4.3b have the same amplitude and wavelengths, but different starting points. We say that the two waves have different phases. We can see this more clearly in figure 4.3c which shows the two waves superimposed. If they had the same phase (and the same amplitude and wavelength), they would line up perfectly. As we will see on p. 189, when waves interact, the outcome is influenced, among other things, by their relative phases.

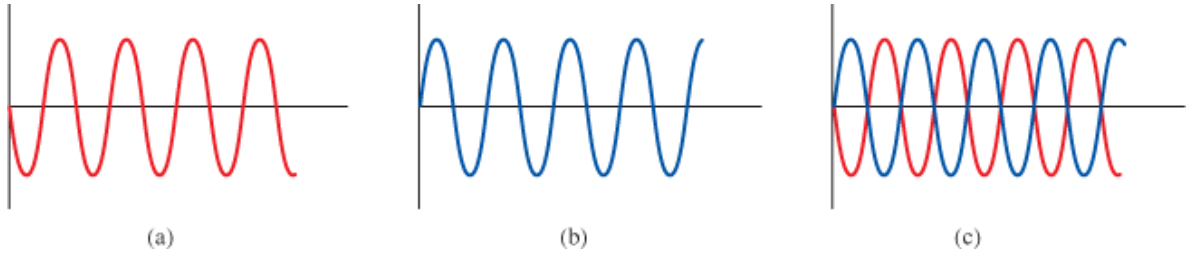


FIGURE 4.3 Phase refers to the starting position of a wave with respect to one wavelength. The waves in **(a)** and **(b)** have different phases; **(c)** shows an overlap of (a) and (b).

Light waves, and all other types of electromagnetic radiation, always move through a vacuum at the same speed. The speed of light is a fundamental constant, denoted by the symbol c: c = 2.997 924 58 × 10^8 m s^{-1} (we will round it to 2.998 × 10^8 m s^{-1}). For any wave, its frequency (ν) (in units of s^{-1}) multiplied by its wavelength (λ) (in units of m) equals its speed c (m s^{-1}), i.e.

$$c = \nu\lambda$$

WORKED EXAMPLE 4.1

Wavelength–frequency Conversion

An FM radio station transmits its signal at 88.1 MHz. What is the wavelength of the signal?

Analysis

The link between wavelength (λ) and frequency (ν) is given by $c = \nu\lambda$.

Solution

First, we summarise the data.

$$c = 2.998 \times 10^8 \text{ m s}^{-1} \quad \lambda = 88.1 \text{ MHz}$$

Next, we rearrange the equation to solve for wavelength.

$$c = \nu\lambda \quad \text{so} \quad \lambda = \frac{c}{\nu}$$

To obtain equivalent units, convert the frequency units from MHz to Hz. The prefix ‘M’ stands for ‘mega’, which is a factor of 10^6. Remember that Hz is equivalent to s^{-1}.

$$\lambda = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{88.1 \times 10^6 \text{ s}^{-1}} = 3.40 \text{ m}$$

Is our answer reasonable?

The wavelength of 3.40 m may seem rather long, but radio waves are known as long wavelength radiation. See figure 4.4 for a sense of the wavelengths of electromagnetic radiation.

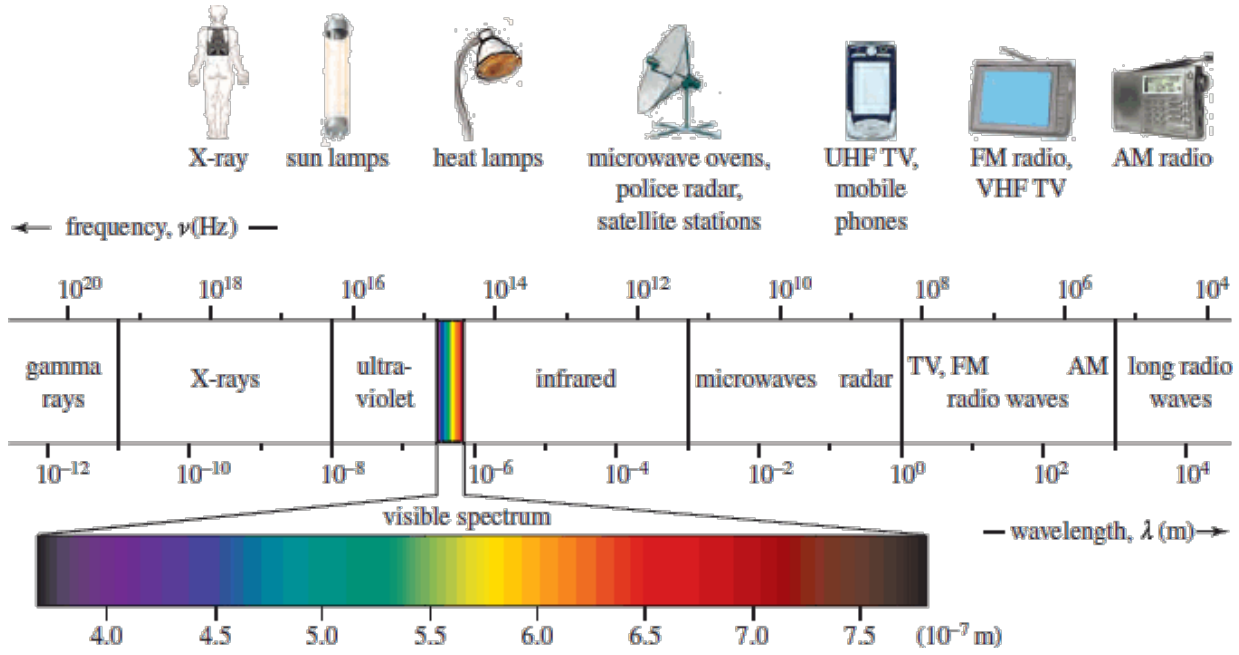


FIGURE 4.4 The electromagnetic spectrum, showing its various regions and the associated wavelengths and frequencies.

PRACTICE EXERCISE 4.1

What is the frequency of electromagnetic radiation that has a wavelength of 1.40 cm?

The wavelengths or frequencies of electromagnetic radiation cover an immense range. Figure 4.4 shows that the visible spectrum covers the wavelength range from about 380 nm (violet) to 780 nm (red). The centre of this range is yellow light, with a wavelength of about 580 nm and a frequency around 5.2×10^{14} s^{-1}. Although visible light is extremely important to living creatures for vision, the gamma ray, X-ray, ultraviolet, infrared, microwave and radio frequency portions of the electromagnetic spectrum also have diverse effects on, and uses in, our lives.

Radiation with short wavelengths, in the X-ray and gamma ray regions, can generate ions by removing electrons from atoms and molecules. These ions are highly reactive and can cause serious damage to the material that absorbs the radiation. However, under closely controlled conditions, X-rays are used in medical imaging, and gamma rays are used to treat cancer. The wavelength of ultraviolet (UV) radiation lies between that of X-rays and visible light. Ultraviolet radiation can also damage materials, especially in high doses. High rates of skin cancer in Australia and New Zealand are a direct result of exposure to damaging UV radiation in sunlight.

Radiation with long wavelengths falls in the infrared, microwave or radio frequency regions. Heat lamps make use of infrared radiation, microwave ovens cook with microwave radiation, and radio and television signals are transmitted by radio waves.

What we perceive as white light actually contains a range of wavelengths. This becomes apparent when sunlight passes through a prism (see p. 109) or through raindrops (which creates a rainbow as shown in figure 4.5). These objects diffract different wavelengths of light through different angles, so the light that passes through spreads out in space, with each wavelength appearing at its own characteristic angle.



FIGURE 4.5 Light rays bend as they pass through raindrops, causing white light to separate into its rainbow of colours.

Particle Properties of Light

Light carries energy. When our bodies absorb sunlight, for example, we feel warm because energy from the sunlight has been transferred to our skin. A phenomenon known as the **photoelectric effect** shows how the energy of light depends on its frequency and intensity. The photoelectric effect is the basis for many light-sensing devices, such as automatic door openers and camera exposure meters. Figure 4.6 illustrates a photoelectric experiment in which a beam of light strikes the surface of a metal. Under the right conditions, the light causes electrons to be ejected from the metal surface. A detailed study of the photoelectric effect reveals how the behaviour of these electrons is related to the characteristics of the light:

1. Below a characteristic threshold frequency, ν_0, no electrons are observed, regardless of the light's intensity.

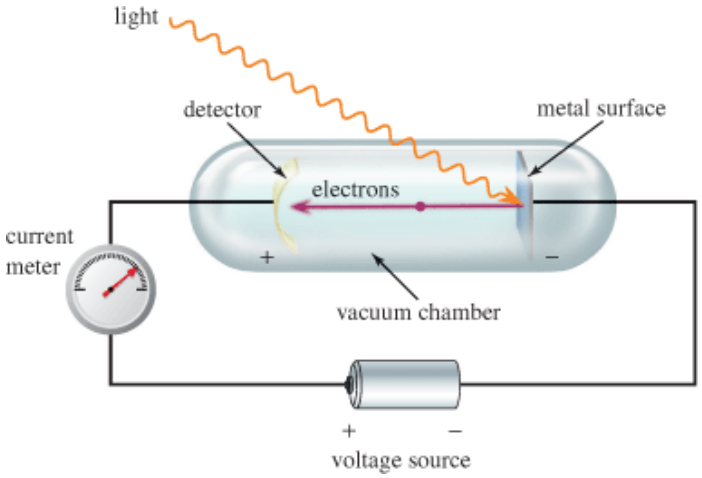


FIGURE 4.6 A diagrammatic view of the photoelectric effect. When light of a high enough frequency strikes a metal, electrons are ejected from the surface.

2. Above the threshold frequency, the maximum kinetic energy of ejected electrons increases linearly with the frequency of the light, as shown in figure 4.7. (Kinetic energy is a function of the electron's speed. We will learn more about kinetic energy with reference to gases in chapter 6.)

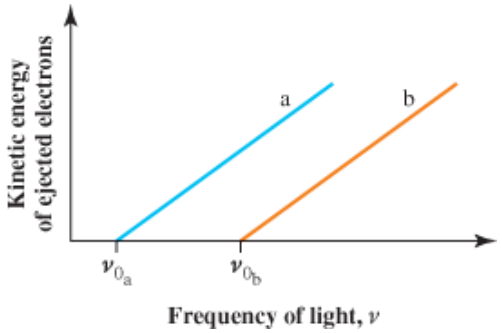


FIGURE 4.7 Variation in the maximum kinetic energy of electrons ejected from two different metal surfaces (a and b) as a function of the frequency of incoming light.

3. Above the threshold frequency, the *number* of emitted electrons increases with the light's intensity, but the *kinetic energy* per electron does not depend on the light's intensity.
4. All metals exhibit the same behaviour, but, as figure 4.7 shows, each metal has a different threshold frequency.

In 1905, Albert Einstein postulated that light comes in 'packets' or 'bundles', called **photons**. Each photon has an energy that is directly proportional to its frequency.

$$E_{\text{photon}} = h\nu_{\text{photon}}$$

In this equation, E is the energy of a photon of light and ν is its frequency. The proportionality constant between energy and frequency is known as **Planck's constant (h)** and has a value of 6.626 069 3(11) × 10^{-34} J s (we will use 6.626 × 10^{-34} J s). The 11 in parentheses refers to the uncertainty in the final digits; therefore, h = (6.626 069 3 ± 0.000 001 1) × 10^{-34} J s.

WORKED EXAMPLE 4.2

The energy of light

What is the energy of a photon of red light with a wavelength of 655 nm?

Analysis

This conversion problem requires two steps. We do not have an equation that will calculate E based on the data we have, but, by combining the two equations we do know, we can relate the energy of a photon to its frequency and wavelength.

Solution

First, we summarise the data.

$$h = 6.626 \times 10^{-34}\,\text{J s} \quad \lambda = 655\,\text{nm} \quad c = 2.998 \times 10^{8}\,\text{m s}^{-1}$$

Then we combine the equations into an equation that relates energy to wavelength.

$$E = h\nu \quad \text{and} \quad \nu = \frac{c}{\lambda} \quad \text{so} \quad E = \frac{hc}{\lambda}$$

Substituting our data, we find:

$$E_{\text{photon}} = \frac{\left(6.626 \times 10^{-34}\,\text{J s}\right)\left(2.998 \times 10^{8}\,\text{m s}^{-1}\right)}{655 \times 10^{-9}\,\text{m}}$$

$$= \frac{\left(6.626 \times 10^{-34}\,\text{J}\cancel{\text{ s}}\right)\left(2.998 \times 10^{8}\,\cancel{\text{m s}^{-1}}\right)}{655 \times 10^{-9}\,\cancel{\text{m}}} = 3.03 \times 10^{-19}\,\text{J}$$

Is our answer reasonable?

An energy of 10^{-19} J seems very small, but we must remember that this is the energy of a single photon. If we want to calculate the energy of a mole of these photons, we need to multiply our result by the Avogadro constant, i.e. $E_{\text{one mole of photons}} = E_{\text{photon}} \times N_A$ = (3.03 × 10^{-19} J) × (6.022 × 10^{23} mol^{-1}) = 182 × 10^{3} J mol^{-1} = 182 kJ mol^{-1}. This energy is comparable to the energies of chemical bonds.

PRACTICE EXERCISE 4.2

What is the energy of a photon with a wavelength of 254 nm (UV radiation)?

Einstein concluded that the energy of a photon that has the threshold frequency (v_0) corresponds to the binding energy of the electron. Energy beyond the threshold frequency increases the electron's kinetic energy as shown in figure 4.8. This can be described by:

$$\text{electron kinetic energy} = \text{photon energy} - \text{binding energy}$$
$$E_{\text{kinetic(electron)}} = h\nu - h\nu_0$$

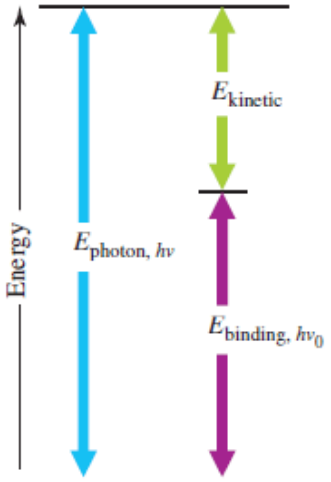


FIGURE 4.8 Diagram of the energy balance for the photoelectric effect.

Einstein's explanation accounts for the observed properties of the photoelectric effect. When the energy of the photon is less than $h\nu_0$ (low-frequency light), no electrons can escape from the metal surface, no matter how intense the light. When the energy of the photon is greater than $h\nu_0$, an electron is ejected and any excess energy is transferred to that electron as kinetic energy. The intensity of a light beam is a measure of the number of photons per unit time; light of a higher amplitude carries more photons than light of lower amplitude. The intensity of the light *does not* determine the amount of energy per photon. More photons striking the metal result in more electrons being ejected, but the energy of each photon and each electron is unchanged. Finally, the fact that each metal has its own characteristic threshold frequency suggests that electrons are bound more tightly to some metals than to others.

Chemistry Research

The Australian Synchrotron

Electromagnetic radiation in its many forms is frequently used to probe the nature of chemical compounds, whether they are employed as materials for electronic devices, newly developed drugs or anything in between. The intensity, coherence and wavelength of the available radiation strongly influence the detailed information that can be extracted and which is needed to advance chemistry in all its forms. Important properties of electromagnetic radiation can be maximised using a synchrotron source and, in this context, the opening of the Australian Synchrotron in Melbourne in 2007 has been a highlight for the advancement of Australasian science (figure 4.9). The opening of the facility has brought the synchrotron home, in a sense, since it was Australian physicist Sir Marcus Oliphant who is credited with the original idea for a proton synchrotron (the facility in Melbourne is actually an electron synchrotron). While scientists from our region have previously used synchrotrons around the globe (there are now about 50 of these facilities in the world), the synchrotron in Melbourne allows current and future Australian and New Zealand scientists unprecedented access to such a facility. Figure 4.10 shows a beamline scientist and two students from the University of Sydney aligning a sample on the powder diffraction beamline at the Australian Synchrotron. So far about 2000 scientists, mainly from Australia and New Zealand, have used beamlines at the Australian Synchrotron for their research. Many of these users are students working on their Honours or PhD theses, and one day you might use the facility yourself.



FIGURE 4.9 Aerial view of the Australian Synchrotron building located in Clayton, Victoria.
Australian Synchrotron

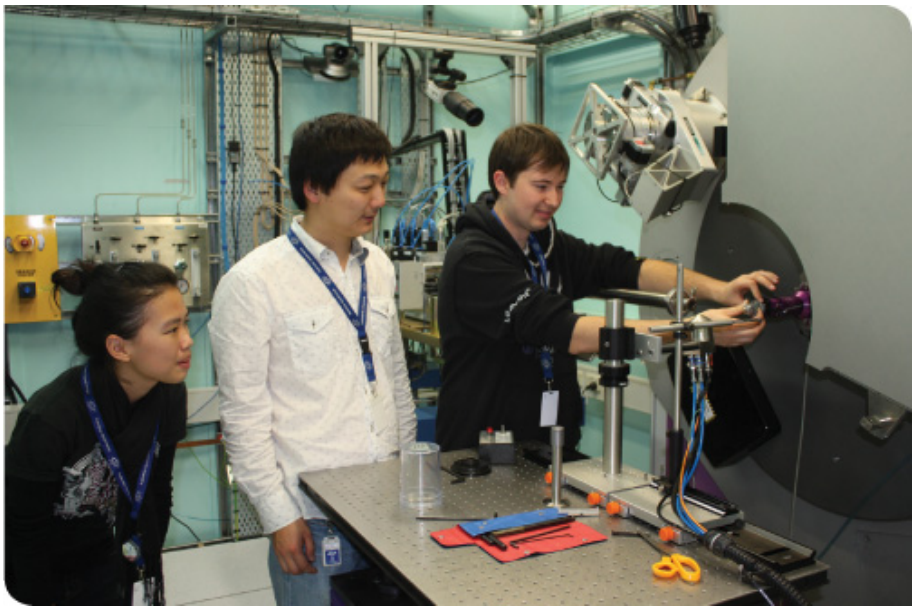


FIGURE 4.10 Beamline scientist (middle) helping postgraduate students using the Australian Synchrotron facilities to assist their studies.

Australian scientists have used synchrotrons for applications as diverse as establishing the presence of arsenic in the racehorse Phar Lap; understanding how some native plants immobilise heavy metals and hence can be used to remediate contaminated soils; studying the uptake of lead in teeth with a view to enhancing neonatal care around Broken Hill; designing drugs, including the anti-viral drug Relenza® by the Australian biotechnology company Biota; and developing copper-based anti-inflammatory drugs for treating arthritis in horses and dogs. Synchrotron radiation can also be used in less obvious areas such as studying the early stages of lung development in newborn tammar wallabies, in archaeology both to identify the origins of artefacts and to understand how they were made, as well as in food science to develop low-fat potato chips. Recent highlights of the work by many visiting scientists at the Australian Synchrotron include investigations of chemical compounds for the development of anti-cancer drugs, scanning an entire Arthur Streeton painting to identify individual brushstrokes of different colours based on the distribution of different elements on the canvas, and investigation of advanced materials for incorporation into re-chargeable Li–ion batteries.

In order to improve our understanding of synchrotron science we need to discuss the origin of the radiation. When electrons are forced to travel in a circular orbit at speeds approaching the speed of light, they emit radiation in the form of photons of various wavelengths, ranging from infrared to hard X-rays (wavelengths of 10^{-6} to 10^{-11} m, respectively, see figure 4.4). This radiation is called synchrotron radiation and is characterised by its high intensity (figure 4.11), making it very useful for studying the absorption, reflection and diffraction properties of matter. The generation of synchrotron radiation is not a trivial matter, and, as we have seen above, there is a limited number of facilities around the world in which synchrotron experiments can be carried out.

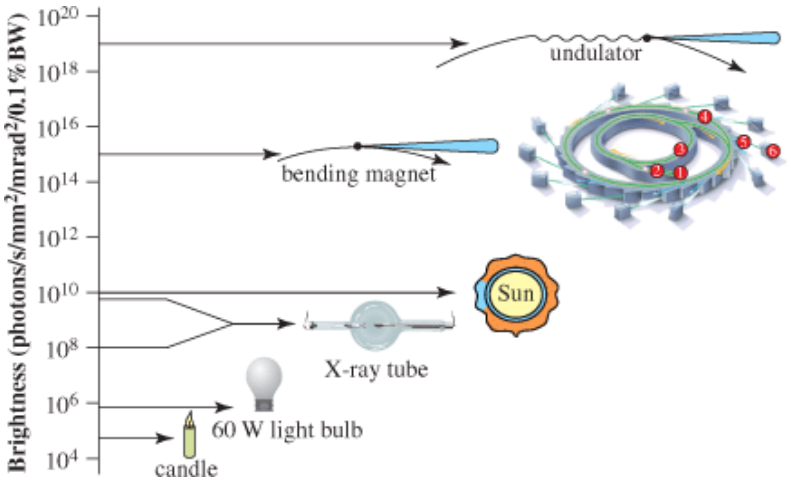


FIGURE 4.11 Comparison of brightness (intensity) of radiation from a range of sources.

Figure 4.12 shows a schematic of the Australian Synchrotron. Electrons are generated near the centre (electron gun) and accelerated to almost the speed of light by the linear accelerator (linac) and the booster ring. They are then transferred to the outer storage ring. The electrons are confined to the circular orbit by a series of bending magnets separated by straight sections. As the electrons are deflected through the magnetic field created by the bending magnets, they give off electromagnetic radiation, so that a beam of synchrotron radiation is produced at each bending magnet. These intense beams of white radiation (i.e. with a spectrum of wavelengths from infrared to hard X-rays) can be captured and directed to a beamline end station where a specific wavelength appropriate for a particular technique or specific experiment can be selected.

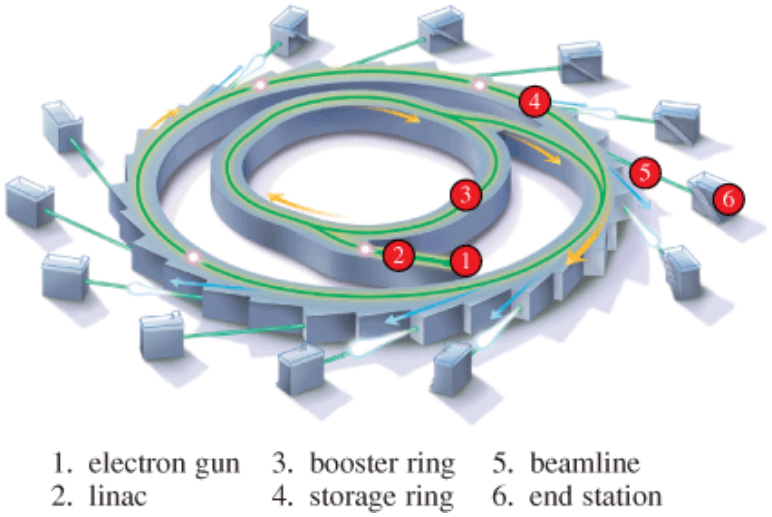


FIGURE 4.12 Schematic of the Australian Synchrotron.
Source: Illustrator Michael Payne. Image supplied courtesy of Australian Synchrotron.

At this stage the Australian Synchrotron has a total of nine beamlines, of which eight are operational. Each of these beamlines is dedicated to the specific purposes outlined in the table below.

Beamline name	Capabilities
Beamline 1 High-throughput protein crystallography	Dedicated facility for crystallography of large protein crystals, set up with robotic loading and centring, and for remote operation

Beamline 2 Protein microcrystal and small molecule diffraction	Facility with finely focused X-ray beam for determining the crystal structure and electron density maps of small, hard-to-crystallise proteins, nucleic acids, and for small molecules
Beamline 3 Powder diffraction	Versatile, high-resolution powder diffraction facility equipped with sample chambers for a wide range of in-situ experiments
Beamline 4 Small and wide angle X-ray scattering	Measurement of long-range order in complex molecules and materials
Beamline 5 X-ray absorption spectroscopy	Measurement of short and medium range order, bond lengths, coordination numbers and local coordination geometry, and the oxidation state of atoms from atomic number $Z = 20$ upwards
Beamline 6 Soft X-ray spectroscopy	As for beamline 5, for the light elements, $Z < 20$; also for the analysis of surfaces and thin films
Beamline 7 Infrared spectroscopy	Analysis of bonds in complex molecules, biological materials, minerals and band structures in certain semiconductors
Beamline 8 Microspectroscopy	For production of high-resolution maps of elemental distribution in a sample; also for determination of the oxidation state and coordination geometry of atoms in particles down to submicron size
Beamline 9 Imaging and medical therapy	Very flexible beamline for research into high-contrast imaging of objects from small animals through to engineering components; also for research into the physics and biophysics of cancer therapy techniques

The intensity of the radiation can be further increased by the use of ‘insertion devices’ in the straight sections of the ring. Th ere are two classes of insertion devices, multipole wigglers and undulators. Current (‘third-generation’) designs of synchrotrons aim to optimise the intensity that can be obtained from insertion devices. In particular, attention is given to the size and positioning of the straight sections that accommodate the insertion devices. The Australian Synchrotron is an advanced third-generation design. It accommodates the three different types of light sources (bending magnets, multipole wigglers and undulators) to enable a wide range of advanced experiments and measurements to be carried out.

Einstein's explanation of the photoelectric effect showed that light has some properties of particles. A complete description of light includes both wave-like and particle-like properties. When light interacts with a relatively large body such as a raindrop or a prism, its wave properties dominate the interaction. On the other hand, when light interacts with a small body such as an atom or an electron, particle properties dominate the interaction. Each view provides different information about the properties of light, and, when we think about light, we must think of *particle–waves* that combine both types of features.

Absorption and Emission Spectra

In the photoelectric effect, when photons strike a metal surface, the energy absorbed provides information about the binding energies of electrons to metal surfaces. When light interacts with free atoms, the interaction reveals information about electrons within individual atoms.

Light and Atoms

Attractive electrostatic forces hold an electron within an atom. Energy must be supplied to remove the electron from the atom. The lower the atom's energy state, the more energy is required to remove its electron. The energy required is measured relative to the energy of a free electron. We define the energy of a hypothetical free stationary electron to be zero. As figure 4.13 indicates, the kinetic energy of a freely moving electron is positive relative to this conventional zero point. In contrast, bound electrons are lower in energy than the hypothetical free stationary electron, so we assign them negative energy values.

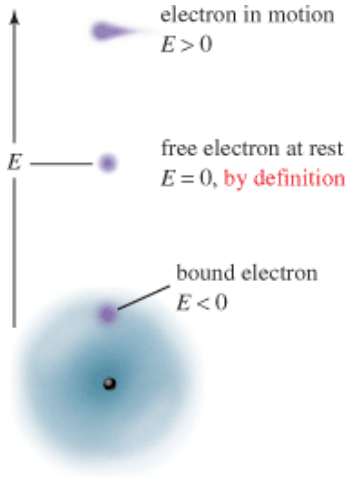


FIGURE 4.13 By convention, a free stationary electron has zero energy, and bound electrons have negative energies.

The absorption of photons by free atoms has two possible results, depending on the energy of the photon. When an atom absorbs a photon of sufficiently high energy, an electron is ejected (i.e. the atom ionises). This process is described later in this chapter. Here, we focus on the second type of result, in which the atom gains energy, but does not ionise. Instead, the atom moves from the lowest energy or **ground state** to a higher energy state called an **excited state**. As we saw in chapter 1, this process is called an electronic transition. Excited states are not stable and atoms in excited states subsequently give up their excess energy to return to lower energy states, and eventually the ground state. They lose their excess energy in collisions with other atoms or by emitting photons.

The key feature in the exchange of energy between atoms and light (photons) is that energy is conserved. This requires that the change in energy of the atom exactly equals the energy of the photon.

$$\Delta E_{\text{atom}} = \pm h\nu_{\text{photon}}$$

When an atom *absorbs* a photon, the atom gains the photon's energy, so ΔE_{atom} is positive. When an atom *emits* a photon, the atom loses the photon's energy, so ΔE_{atom} is negative. As an atom returns from an excited state to the ground state, it must lose exactly the amount of energy that it originally gained. However, excited atoms usually lose excess energy in several steps involving small energy changes, so the frequencies of emitted photons are often lower than those of absorbed photons.

WORKED EXAMPLE 4.3

Emission Energies

A sodium-vapour street lamp emits yellow light (figure 4.14) at a wavelength of 589 nm. What is the energy change for a sodium atom involved in this emission? How much energy is released per mole of sodium atoms?



FIGURE 4.14 Sodium-vapour lamps emit yellow light.

Analysis

This problem relates energies of photons to energy changes of atoms. The solution requires a conversion involving wavelength and energy.

Solution

Sodium atoms lose energy by emitting photons of light (λ = 589 nm). We can relate the wavelength of one of these photons to its energy.

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

Energy is conserved, so the energy of the emitted photon must exactly equal the energy lost by the atom.

$$\Delta E_{\text{atom}} = -E_{\text{photon}} = -\frac{hc}{\lambda}$$

The equality includes a negative sign because the atom *loses* energy.

To calculate the energy of a photon, we need the following data.

$$h = 6.626 \times 10^{-34}\,\text{J s} \quad c = 2.998 \times 10^{8}\,\text{m s}^{-1} \quad \lambda = 589\,\text{nm} = 589 \times 10^{-9}\,\text{m}$$

$$\Delta E_{\text{atom}} = -E_{\text{photon}} = -\frac{hc}{\lambda} = -\frac{(6.626 \times 10^{-34}\,\text{J s})\,(2.998 \times 10^{8}\,\text{m s}^{-1})}{589 \times 10^{-9}\,\text{m}}$$

$$= -3.37 \times 10^{-19}\,\text{J}$$

This calculation gives the energy change for one sodium atom emitting one photon. We multiply this value by the Avogadro constant to convert from energy per atom to energy per mole.

$$\Delta E_{\text{mol}} = (\Delta E_{\text{atom}})(N_A) = (-3.37 \times 10^{-19}\,\text{J})(6.022 \times 10^{23}\,\text{mol}^{-1})$$

$$= -2.03 \times 10^{5}\,\text{J mol}^{-1} = -203\,\text{KJ mol}^{-1}$$

Remembering that the negative sign simply means that the atom is losing energy, the actual energy released is the absolute value of this, i.e. 203 kJ mol^{-1}.

PRACTICE EXERCISE 4.3

Mercury lamps emit photons with a wavelength of 436 nm. Calculate the energy change of the mercury atoms in J atom^{-1} and kJ mol^{-1}.

Atomic Spectra

When a light beam passes through a tube containing a gas consisting of atoms of a single element, the atoms absorb specific frequencies of light characteristic of that element. As a result, the beam emerging from the sample tube has fewer photons at these specific frequencies. The frequencies with diminished intensity in the visible portion of the spectrum can be detected by passing the emerging light through a prism. The prism diffracts the light, with different frequencies diffracting through different angles. After leaving the prism, the beam strikes a screen, where the frequencies with diminished intensity appear as gaps or dark bands called 'lines', which are images of the slit. These are the frequencies of light absorbed by the atoms in the sample tube. The resulting pattern, shown schematically in figure 4.15, is called an **absorption spectrum**.

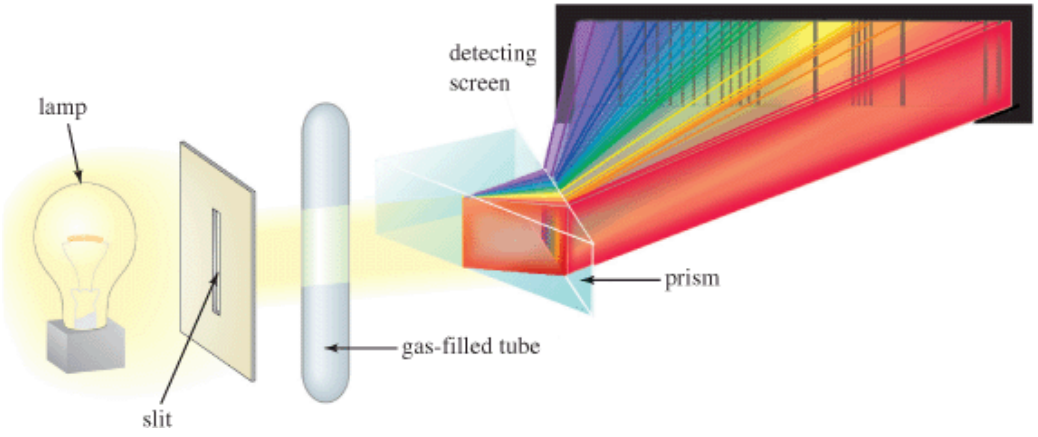


FIGURE 4.15 Schematic representation of an apparatus that measures the absorption spectrum of a monatomic gas. The gas in the tube absorbs light at specific wavelengths, called lines, so the intensity of transmitted light is low and, therefore, dark lines appear at these particular wavelengths.

An absorption spectrum is used to determine the frequencies of the photons that an atom *absorbs*. A similar experiment can measure the energies of the photons *emitted* by atoms in excited states. Figure 4.19 outlines the features of an apparatus that measures these emitted photons. An electrical discharge excites a collection of atoms from their ground state into higher energy states. These excited atoms then lose all, or part of, their excess energy by emitting photons. This emitted light can be analysed by passing it through a prism to give an **emission spectrum**. This is a plot of the intensity of light emitted as a function of frequency. The emission spectrum for atomic hydrogen, shown in figure 4.22, shows several sharp emission lines of high intensity. The frequencies of these lines correspond to photons emitted by the hydrogen atoms as they return to their ground state.

Each element has unique absorption and emission spectra. That is, each element has a set of characteristic frequencies of light that it can absorb or emit. It is important to note that figures 4.15, 4.19, 4.20 and 4.22 show only the visible portions of the absorption and emission spectra. Electronic transitions also take place in regions of the electromagnetic spectrum that the human eye cannot detect. Instruments allow scientists to observe electromagnetic radiation in these regions.

Chemical Connections

Photoelectron Spectroscopy

Dr Daniel Southam, Department of Chemistry, Curtin University

The relative energies of electrons within atoms can be measured using a suite of techniques called photoelectron spectroscopy (PES). PES exploits the photoelectric effect (see pp. 112–13) to measure the kinetic energy of ejected electrons from atoms and molecules. In PES, an atom is excited by a monochromatic beam of photons with a known energy (E_{photon}). The energy of the incident photon beam is well in excess of the ionisation energies of electrons within all valence and some core shells of many atoms. When an incident photon excites the atom or molecule, an electron absorbs energy and is ejected from its orbital (see figure 4.16). The ejected electrons are called *photoelectrons*.

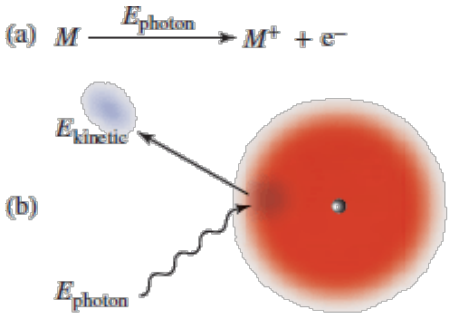


FIGURE 4.16 (a) The process of ionisation of an element *M* caused by the incident photon ejecting a photoelectron.
(b) An illustration of the atomic-scale process showing an incident photon exciting an electron which is ejected from the atom with a measurable kinetic energy.

The kinetic energy of the photoelectron can be compared with the energy of the incident photon to give its binding energy. The binding energy of each electron is characteristic not only of the atom and the orbital in which the electron resides, but also of the oxidation state of the atom or ion and the surrounding chemical bonding environment. PES gives strong experimental evidence for the quantised nature of the atom and the existence of atomic and molecular orbitals (see section 5.7). For example, in figure 4.17, the photoelectron spectra of elements from the second period of the periodic table confirms that, as the atomic number increases, the core 1*s* electrons also increase in energy. Their binding energies therefore increase, and they become more difficult to remove.

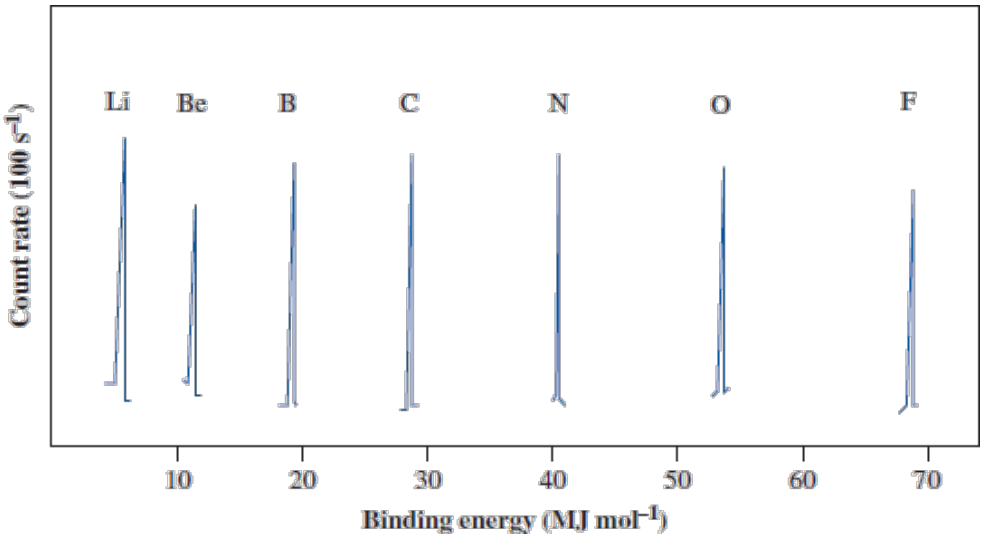
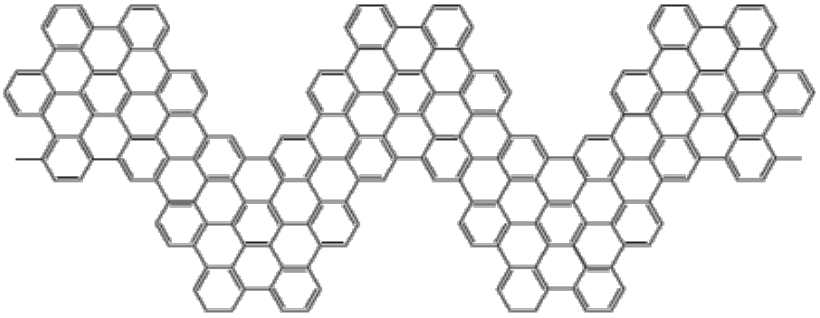


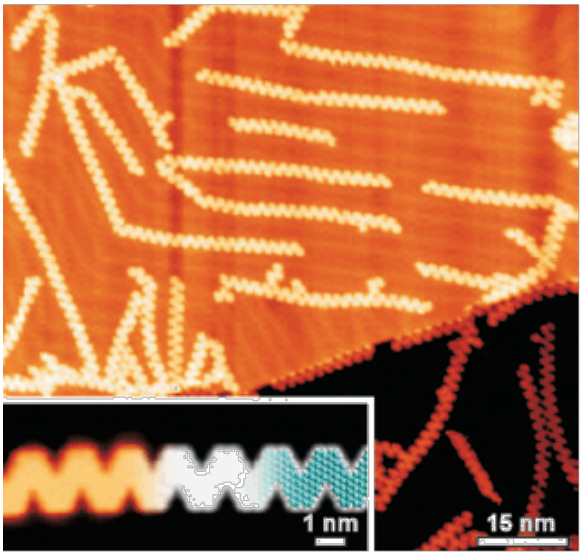
FIGURE 4.17 Photoelectron spectra of elements from the second period of the periodic table. The region of the spectra corresponding to ionisation of 1s electrons is shown for each element.

The incident photons used in PES are often derived from X-ray emissions of magnesium (˜121.0 MJ mol^{-1}) and aluminium (143.4 MJ mol^{-1}), making X-ray photoelectron spectroscopy (XPS; also called electron spectroscopy for chemical analysis, ESCA) the most frequently encountered technique of the suite. XPS is most often used for the analysis of surfaces, such as semiconductors, polymers, ceramics and metal alloys. XPS allows the quantitative determination of elemental abundance, and some instruments can achieve spatial elemental mapping, which is useful in a wide range of disciplines such as materials science and geology. A recent example displays the utility of XPS in modern scientific research. The investigators deposited atomically precise nanoribbons of graphene sheets in a chevron pattern onto a gold surface, as shown in figures 4.18a,b and used XPS to ensure that the graphene did not suffer any oxidation during this process. As shown in figure 4.18c, the carbon 1*s* peak has a chemical bonding environment characteristic of the absence of oxygen.

(a)



(b)


1 nm
15 nm

(c)

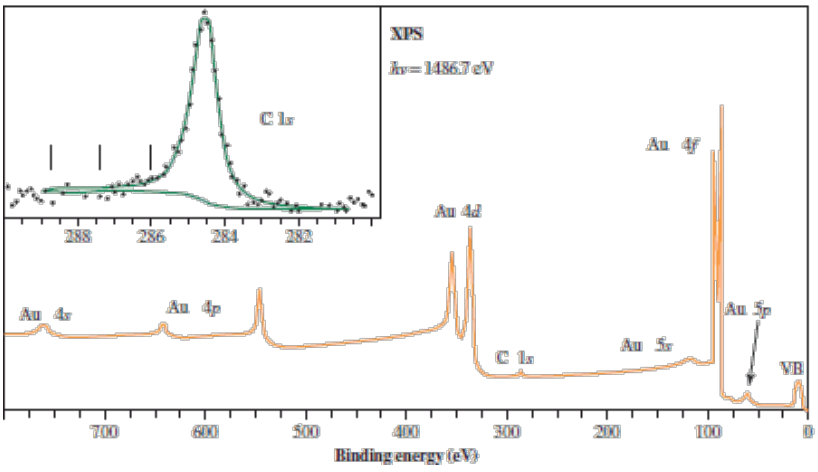

XPS
hν = 1486.7 eV
C 1s
288
286
284
282
Au 4f
Au 4d
Au 4s
Au 4p
C 1s
Au 5s
Au 5p
VB
700
600
500
400
300
200
100
0
Binding energy (eV)

FIGURE 4.18 (a) The chemical structure of a graphene nanoribbon,
(b) a scanning tunnelling micrograph (see chapter 1) illustrating deposition of nanoribbons on a gold surface and
(c) a photoelectron spectrum of the surface indicating the lack of oxidation of graphene.

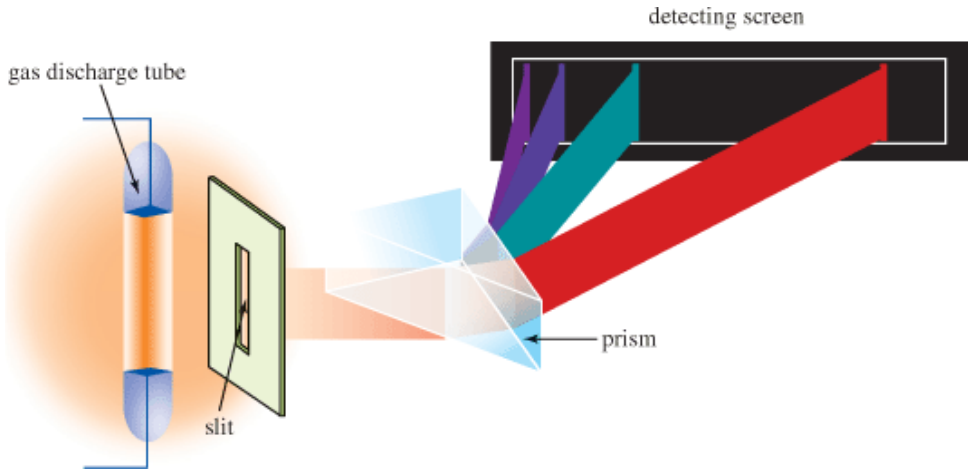


FIGURE 4.19 Schematic representation of an apparatus that measures the emission spectrum of a gaseous element. Emission lines appear bright against a dark background. The spectrum shown is the emission spectrum for hydrogen atoms.

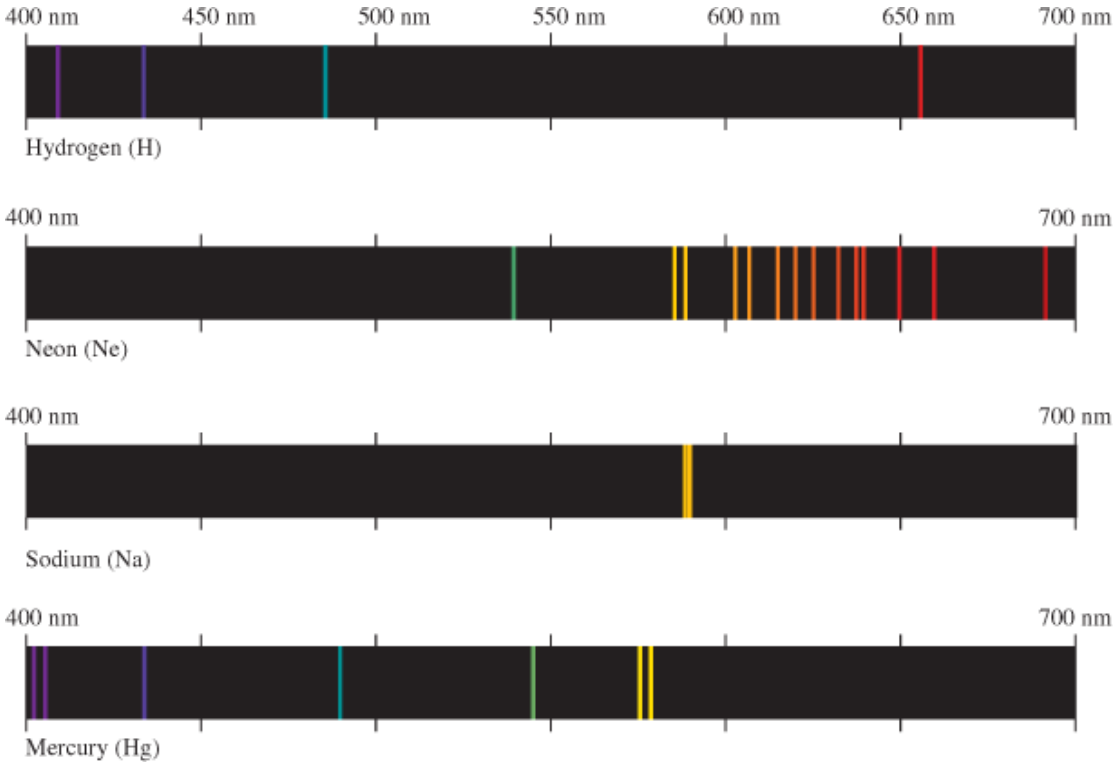


FIGURE 4.20 Emission patterns for hydrogen, neon, sodium and mercury. Each element has a unique emission pattern that provides valuable clues about its atomic structure.

Each frequency absorbed or emitted by an atom corresponds to a particular energy change for the atom. These characteristic patterns of energy gains and losses provide information about atomic structure. Figure 4.20 shows the emission spectra for selected atoms.

Quantisation of Energy

When an atom absorbs a photon of light of frequency v, the light beam loses energy equal to hv, and the atom gains that amount of energy. What happens to the energy that the atom gains? A clue is that, when the frequency of the incoming (or absorbed) light is high enough, it produces cations and free electrons. In other words, a photon with high enough energy

can cause an atom to lose one of its electrons, i.e. ionise. This implies that absorption of a photon results in an energy gain for an electron in the atom. Stated as an equation:

$$\Delta E_{\text{atom}} = \Delta E_{\text{electron}} = h\nu$$

The atomic spectra of most elements are complex and show little apparent regularity. However, in 1885, the Swiss mathematician and physicist Johann Balmer was able to propose a single equation that could describe the emission spectrum of the hydrogen atom. The equation was:

$$\nu_{\text{emission}} = (3.29 \times 10^{15}\,\text{s}^{-1})\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

in which n_1 and n_2 are integers (1, 2, 3 etc.). In 1913, the Danish physicist Niels Bohr used Einstein's postulate ($E = h\nu$) to interpret Balmer's observations. Combining the two equations, Bohr was able to describe the energy levels of the electron in the hydrogen atom with the following equation, where n is a positive integer.

$$E_n = -\frac{2.18 \times 10^{-18}\,\text{J}}{n^2}$$

The negative sign in the equation reflects the fact that bound electrons are lower in energy than a stationary free electron (with its energy defined as zero).

Bohr realised that the emission frequencies have specific values because the electron in a hydrogen atom is restricted to specific energies. Bohr's idea of restricted energy levels was revolutionary because scientists at that time thought that the electron in a hydrogen atom could have any energy. In contrast, Bohr interpreted the hydrogen emission spectrum to mean that electrons bound to atoms can have only certain specific energy values. He won the Nobel Prize in physics in 1922 for this interpretation. A property that cannot change continuously, and is restricted to specific values, is said to be **quantised**. The atomic energy levels of hydrogen (and other elements) are quantised. Each integer value of n describes one of the allowed energy levels of the hydrogen atom. For example, the energy of an electron in hydrogen's fourth level is:

$$E_4 = -\frac{2.18 \times 10^{-18}\,\text{J}}{4^2} = -1.36 \times 10^{-19}\,\text{J}$$

When an electron changes energy levels, the change is an electronic transition between quantised levels. When a hydrogen atom absorbs or emits a photon, its electron moves from one energy level to another. Thus, the change in energy (ΔE) of the atom is the energy difference between the two levels.

$$\Delta E_{\text{atom}} = E_{\text{final}} - E_{\text{initial}}$$

Photons always have positive energies, but energy changes (ΔE) can be positive or negative. When a photon is absorbed, an electron is promoted to a higher energy level, the atom gains energy and ΔE for the atom is positive.

$$E_{\text{absorbed photon}} = \Delta E_{\text{atom}}$$

When a photon is emitted, an electron falls from a higher energy level to a lower one, the atom loses energy and ΔE for the atom is negative.

$$E_{\text{emitted photon}} = -\Delta E_{\text{atom}}$$

We can combine these two equations by using absolute values.

$$E_{\text{photon}} = |\Delta E_{\text{atom}}|$$

WORKED EXAMPLE 4.4

Energy levels of the Hydrogen Atom

What is the energy change when the electron in a hydrogen atom undergoes a transition from the fourth energy level to the second energy level? What is the wavelength of the photon emitted?

Analysis

The question asks about energy and the wavelength of a photon emitted by a hydrogen atom. Wavelength is

related to energy, and photon energy is determined by the difference in energy between the two levels involved in the transition. In this case, the electron moves from the fourth to the second energy level. The energy difference between these two states is given by:

$$\Delta E_{\text{atom}} = E_{\text{final}} - E_{\text{initial}} = E_2 - E_4$$

Solution

As shown above, E_4 = -1.36 × 10^{-19} J. A similar calculation gives the energy of the second level.

$$E_2 = -\frac{2.18 \times 10^{-18}\ \text{J}}{2^2} = -5.45 \times 10^{-19}\ \text{J}$$

This energy change is negative because the atom loses energy. The energy difference between the two levels is:

$$\begin{aligned}\Delta E_{\text{atom}} &= E_{\text{final}} - E_{\text{initial}} = (-5.45 \times 10^{-19}\ \text{J}) - (-1.36 \times 10^{-19}\ \text{J}) \\ &= -4.09 \times 10^{-19}\ \text{J}\end{aligned}$$

The negative sign for the energy change is consistent with the atom losing energy. This lost energy appears as a photon with energy of:

$$E_{\text{photon}} = \left|\Delta E_{\text{atom}}\right| = \left|-4.09 \times 10^{-19}\ \text{J}\right| = 4.09 \times 10^{-19}\ \text{J}$$

To determine the wavelength of the photon, we use:

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

Solving for λ gives:

$$\begin{aligned}\lambda_{\text{photon}} &= \frac{hc}{E_{\text{photon}}} \\ &= \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{4.09 \times 10^{-19}\ \text{J}} = 486 \times 10^{-9}\ \text{m} = 486\ \text{nm}\end{aligned}$$

Is our answer reasonable?

The signs of the energies are consistent — the atom loses energy and the photon emitted has positive energy. From figure 4.4 (p. 112) we can see that light with a wavelength of 486 nm has a blue-green colour. Cross-checking against the emission spectrum of hydrogen (figure 4.20), we can see that it has such a blue-green line. Therefore, we can be confident that our answer is correct.

PRACTICE EXERCISE 4.4

What energy and wavelength must a photon have to excite a hydrogen atom from its ground state, i.e. n = 1, to the n = 4 level?

Energy Level Diagrams

Electronic transitions in atoms can be represented using an **energy level diagram** such as the one shown in figure 4.21b. Energy level diagrams are a concise way to summarise information about atomic energies. They show energy along the vertical axis and each energy state of the atom is represented by a horizontal line.

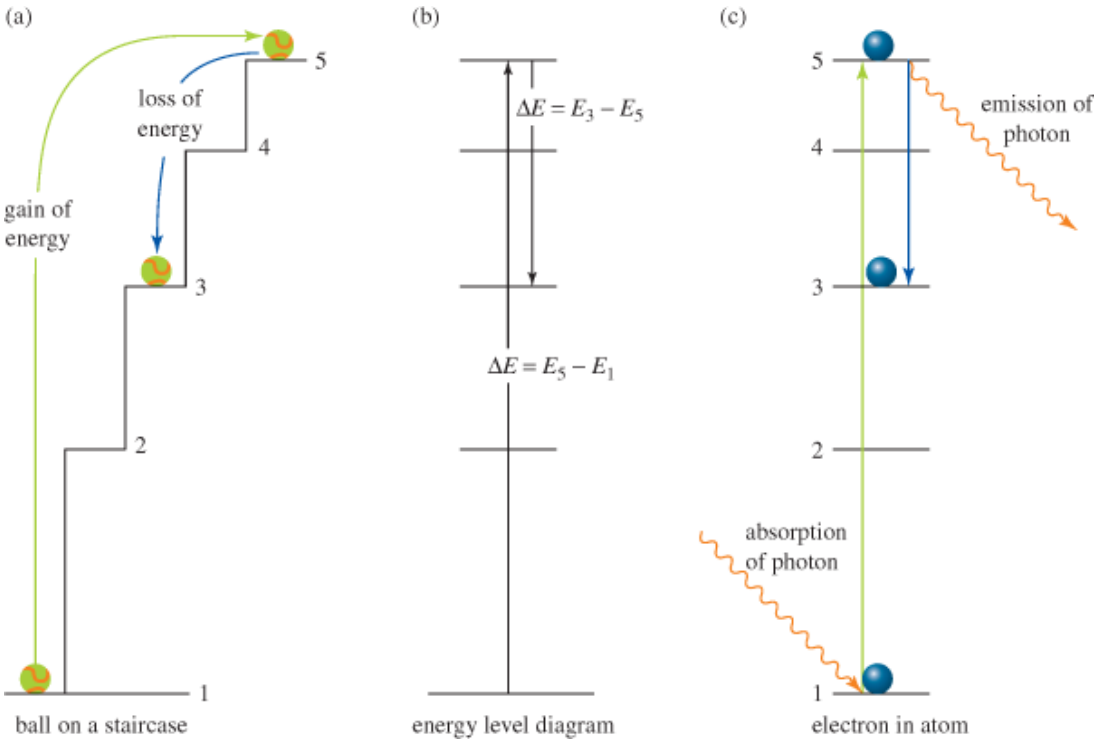


FIGURE 4.21

(a) A ball on a staircase shows some of the properties of quantised energy levels.

(b) Quantised energy levels can be depicted using an energy level diagram.

(c) Electronic transitions occur between quantised energy levels through either absorption or emission of photons.

We can begin to understand the quantum levels of an electron bound to an atom by picturing a ball on a staircase. As illustrated in figure 4.21, a ball may sit on any of the steps. To move a ball from the bottom of the staircase to step 5 requires the addition of a specific amount of energy, $\Delta E = E_5 - E_1$. If too little energy is supplied, the ball cannot reach this step. Conversely, if a ball moves down the staircase, it releases specific amounts of energy. If a ball moves from step 5 to step 3, it loses energy, $\Delta E = E_3 - E_5$. Although a ball may rest squarely on any step, it cannot be suspended between the steps. Electrons in atoms, like balls on steps, cannot exist 'between steps', but must occupy one of the specific, quantised energy levels. *Remember that this is an analogy; atomic energy levels are not at all similar to staircases except in being quantised*.

A hydrogen atom has a regular progression of quantised energy levels. Figure 4.22 shows the energy level diagram for hydrogen atoms; arrows represent some of the possible absorption and emission transitions. Notice that the energies of absorption from the lowest energy level are identical to the energies of emission to the lowest energy level. This means that the wavelengths of light absorbed in these upward transitions are identical to the wavelengths of light emitted in the corresponding downward transitions.

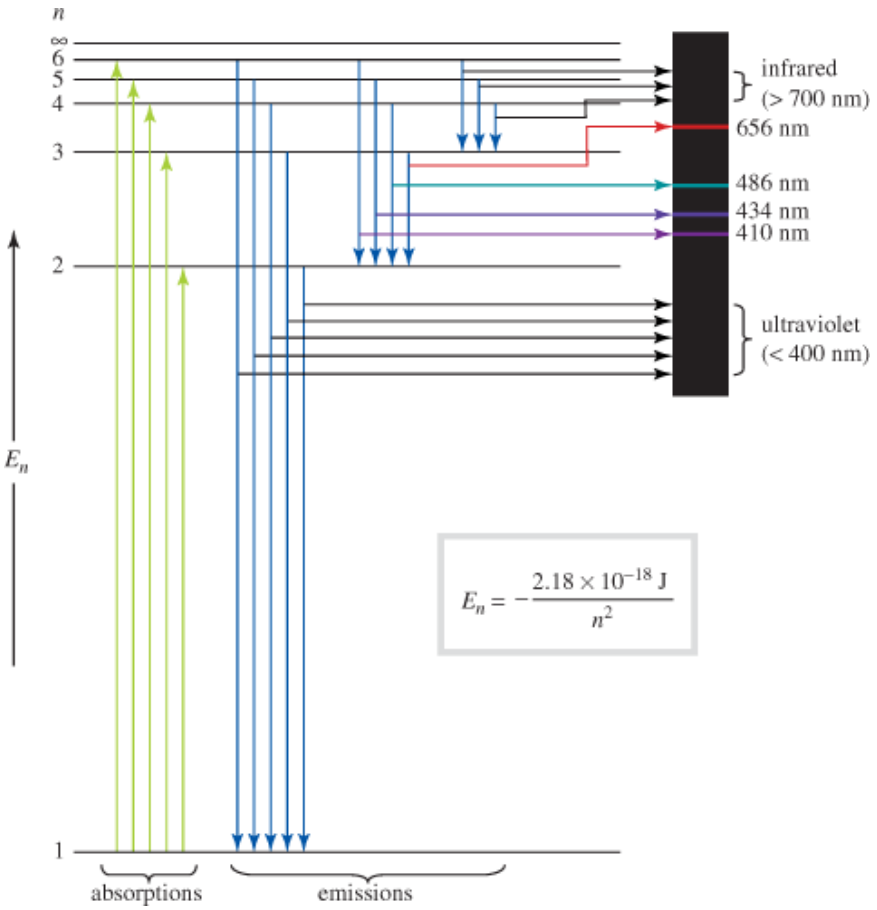


FIGURE 4.22 Energy levels for the hydrogen atom and some of the transitions that occur between levels, as well as the resulting emission spectrum. Upward arrows represent absorption transitions, and downward arrows represent emissions.

Elements other than hydrogen also have quantised energy levels, but as we will see later in this chapter they cannot be so simply described because they have more than one electron. In these cases, scientists use experimental values for observed absorption and emission lines to calculate the allowed energy levels for each different element.

WORKED EXAMPLE 4.5

Energy Level Diagrams

Ruby lasers use crystals of Al_2O_3. The crystals contain small amounts of Cr^{3+} ions, which absorb light between 400 and 560 nm. The excited-state ions lose some energy as heat. After losing heat, the Cr^{3+} ions return to the ground state by emitting red light with a wavelength of 694 nm.

(a) Calculate the energy in kJ mol^{-1} of the 500 nm radiation used to excite the Cr^{3+} ions.

(b) Calculate the energy in kJ mol^{-1} of the emitted light.

(c) Calculate the fraction of the excitation energy emitted as red photons and the fraction lost as heat.

(d) Draw an energy level diagram that summarises these processes.

Analysis

This problem asks about energies, light and ions. With multipart problems, the best strategy is to work through the parts one at a time. Parts (a) and (b) concern the link between light and energy as discussed earlier in this section. Once the transition energies have been determined, we can calculate the fraction of the excited-state energy lost as heat for part (c), and we can also draw an energy level diagram that shows how the levels are related for part (d).

Solution

We solve (a) using the following equations and the Avogadro constant.

$$E_{\text{photon}} = h\nu \quad \text{and} \quad c = \nu\lambda \quad \text{so} \quad E_{\text{photon}} = \frac{hc}{\lambda}$$

$$E_{\text{photon absorbed}} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{500 \times 10^{-9}\ \text{m}} = 3.97 \times 10^{-19}\ \text{J}$$

This is the energy change per ion. To calculate the change per mole, we multiply by the Avogadro constant. We also need to convert from J to kJ.

$$E_{\text{photon absorbed}} = (3.97 \times 10^{-19}\ \text{J})(6.022 \times 10^{23}\ \text{mol}^{-1}) = 239 \times 10^{3}\ \text{J mol}^{-1} = 239\ \text{KJ mol}^{-1}$$

Apply the same reasoning to (b). The result gives the energy of the red photon.

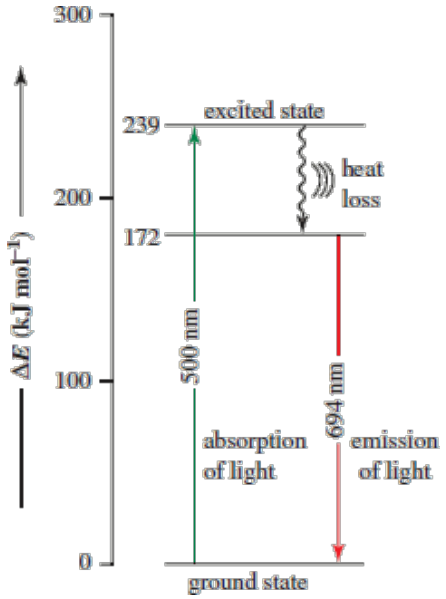
$$E_{\text{photon emitted}} = 172\ \text{kJ mol}^{-1}$$

To solve (c), remember that energy is conserved. The sum of the emitted heat and the emitted photon must equal the energy absorbed by the ion.

$$E_{\text{photon absorbed}} = E_{\text{photin emitted}} + E_{\text{heat emitted}}$$

Because 239 kJ mol^{-1} is absorbed and 172 kJ mol^{-1} is emitted, the fraction of the excitation energy re-emitted is $\frac{172}{239} = 0.720$. The fraction converted to heat is the difference between this value and 1.000, which is 0.280. In other words, 72.0% of the energy absorbed by the chromium ion is emitted as red light, and the other 28.0% is lost as heat.

Part (d) asks for an energy level diagram for this process. The electron starts in the ground state. On absorption of a photon, the electron moves to an energy level that is higher by 239 kJ mol^{-1}. The chromium ion loses 28.0% of its excited-state energy as heat as the electron moves to a level that is 172 kJ mol^{-1} above the ground state. Finally, emission of the red photon returns the Cr^{3+} ion to the ground state. The numerical values allow us to construct an accurate diagram.



Is our answer reasonable?

When Cr^{3+} ions absorb light, they are promoted to an energy level higher than the energy that they later emit. If calculations had shown that the emitted light had a larger energy than the absorbed light, the result would have been unreasonable because the system would violate the law of conservation of energy.

PRACTICE EXERCISE 4.5

After excitation in an electric discharge, an atom of Hg returns to the ground state by emitting two photons

with wavelengths of 436 nm and 254 nm. Calculate the excitation energy of the excited state in kJ mol^{-1}.

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4.3 Properties of Electrons

The energies of electrons in atoms play a central role in determining chemical behaviour. Several other properties of electrons also influence the physical and chemical characteristics of atoms and molecules. Some properties are characteristic of all electrons, but others arise only when electrons are bound to atoms or molecules. In this section, we describe the properties characteristic of all electrons.

Every electron has a mass of 9.109×10^{-31} kg and a charge of 1.602×10^{-19} C. Electrons have magnetic properties that arise from a property called spin, which we met briefly in chapter 1 and will describe in more detail in section 4.4.

The French physicist Louis de Broglie (1892–1987, Nobel Prize in physics, 1929) was the first to suggest that, like photons, electrons also display wave–particle duality, which means that they have both particle and wave properties.

Experiments had shown that a beam of light shining on an object exerts a pressure, which implies that a photon has momentum. Quantitative measurements of the pressure exerted by light showed that a simple equation relates the momentum of light (p) to its energy.

$$E = pc$$

As we have already described, light energy is also related to its wavelength.

$$E = h\nu = \frac{hc}{\lambda}$$

Combining these two energy expressions gives an expression relating p to λ.

$$pc = \frac{hc}{\lambda}$$

The speed of light cancels, leaving an equation that de Broglie suggested should apply to electrons and other particles as well as to photons.

$$p = \frac{h}{\lambda}$$

The momentum of a particle is the product of its mass and velocity (u), $p = mu$. Substituting this and solving for λ gives a form of the de Broglie equation that links the wavelength of a particle with its mass and velocity.

$$\lambda_{\text{particle}} = \frac{h}{mu}$$

De Broglie's theory predicted that electrons are wave-like. How might this be confirmed? Figure 4.23 shows examples of the characteristic intensity patterns displayed by waves. In figure 4.23a, water waves radiate away from two bobbing floats and form a standing pattern. In figure 4.23b, diffracted X-rays form a similar wave pattern. High-energy photons have passed through the regular array of atoms in a crystal, whose electron clouds scatter the photon waves. If electrons have wave properties, they should display regular wave patterns like these.

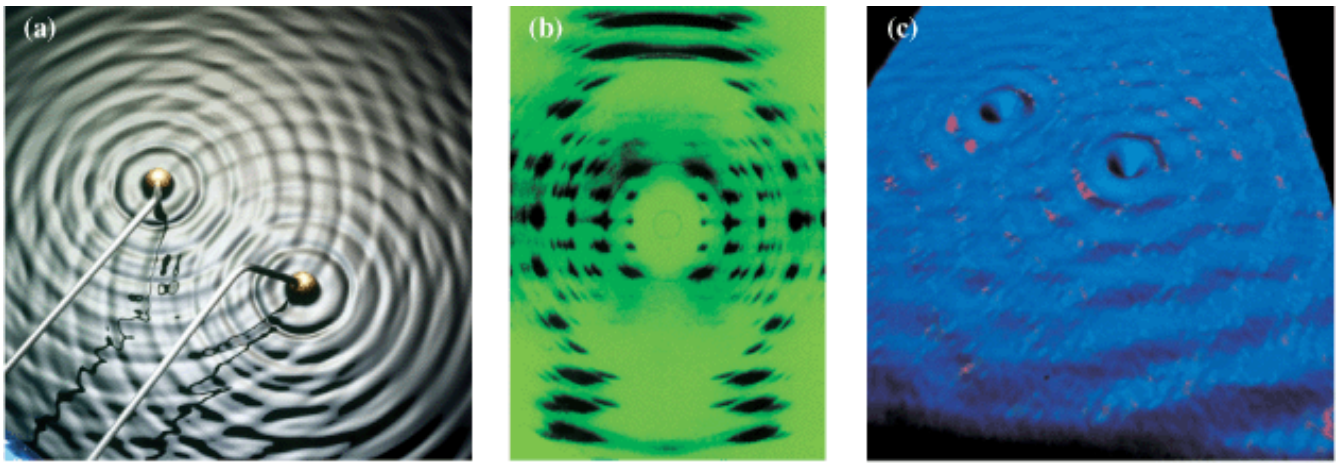


FIGURE 4.23 Examples of wave patterns:
(a) Floats produce standing water waves,
(b) X-rays generate wave interference patterns and
(c) protruding atoms on a metal surface generate standing electron waves.

In 1927, American physicists Clinton Davisson and Lester Germer, and British physicist George Thomson, separately carried out experiments in which they exposed metal films to electron beams with well-defined kinetic energies. Both experiments generated patterns like those shown in figure 4.23b, confirming the validity of the de Broglie equation for electron wavelengths. This established the wave nature of electrons. Davisson and Thomson were awarded the Nobel Prize in physics in 1937 for this discovery.

In recent years, scanning tunnelling electron microscopes have produced images of electron waves, an example of which appears in figure 4.23c. Here, two atoms on an otherwise smooth metal surface act like the floats in figure 4.23a, and cause the electrons in the metal to set up a standing wave pattern.

Both photons and electrons have wave and particle properties, but different equations describe their properties. Table 4.1 summarises the properties of photons and free electrons.

TABLE 4.1 Equations for photons and free electrons

Property	Photon equation	Electron equation
energy	$E = h\nu$	$E_{\text{kinetic}} = \frac{1}{2}mu^2$
wavelength	$\lambda = \frac{hc}{E}$	$\lambda = \frac{h}{mu}$
speed	$c = 2.998 \times 10^8\ \text{m s}^{-1}$	$u = \sqrt{\frac{2E_{\text{kinetic}}}{m}}$

h: Planck's constant; ν: frequency; m: mass; u: velocity

WORKED EXAMPLE 4.6

Wavelengths

The structure of a crystal can be studied by observing the wave interference patterns that result from passing particle–waves through the crystal. To generate well-defined patterns, the wavelength of the particle–wave must be similar to the distance between atoms in the crystal.

Determine the energy of a photon particle–wave beam with a wavelength of 0.25 nm and the energy of an electron particle–wave beam with this wavelength.

Analysis

This problem has two parts, one dealing with photons and the other with electrons. We are asked to relate the wavelengths of the particle–waves to their corresponding energies. Table 4.1 emphasises that photons and electrons have different relationships between energy and wavelength. Thus, we use different equations for the two calculations.

Solution

Photon energy is given by $E = h\nu = hc/\lambda$. We substitute and evaluate, being careful with units.

$$E_{\text{photon}} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{0.25 \times 10^{-9}\ \text{m}} = 7.9 \times 10^{-16}\ \text{J}$$

For an electron, we need to work with two equations. The de Broglie equation links the velocity of an electron with its wavelength.

$$\lambda_{\text{particle}} = \frac{h}{mu}$$

The kinetic energy equation links the velocity of an electron with its kinetic energy.

$$E_{\text{kinetic}} = \frac{1}{2}mu^2$$

Begin by determining the velocity of the electron, recalling from chapter 2 that 1 J = 1 kg m^2 s^{-2}.

$$u_{\text{electron}} = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{(9.109 \times 10^{-31}\ \text{kg})(0.25 \times 10^{-9}\ \text{m})} = 2.91 \times 10^{6}\ \text{m s}^{-1}$$

Next, use the velocity to find the kinetic energy of the electron.

$$E_{\text{kinetic}} = \frac{1}{2}mu^2 = \frac{(9.109 \times 10^{-31}\ \text{kg})(2.91 \times 10^{6}\ \text{m s}^{-1})^2}{2}$$
$$= 3.9 \times 10^{-18}\ \text{kg m}^2\ \text{s}^{-2} = 3.9 \times 10^{-18}\ \text{J}$$

Is our answer reasonable?

The energy of the photon is higher than the kinetic energy of the electron, which is reasonable since the electron has a mass.

PRACTICE EXERCISE 4.6

In a photoelectric-effect experiment, a photon with an energy of 1.25×10^{-18} J is absorbed, causing the ejection of an electron with a kinetic energy of 2.5×10^{-19} J. Calculate the wavelength (in nm) associated with each.

The de Broglie equation predicts that every particle has wave characteristics. The wave properties of subatomic particles such as electrons and neutrons play important roles in their behaviour, but for larger objects, such as table tennis balls or cars, they do not. The reason is the scale of the waves. For all except subatomic particles, the wavelengths involved are so short that we are unable to detect the wave properties.

WORKED EXAMPLE 4.7

Matter Waves

Calculate the wavelengths of an electron travelling at 1.00×10^5 m s^{-1} and a table tennis ball with a mass of 11 g travelling at 2.5 m s^{-1}.

Analysis

This problem deals with particle–waves that have mass. The de Broglie equation relates the mass and speed of an object to its wavelength.

Solution

For the electron: $m_{electron} = 9.109 \times 10^{-31}$ kg, $u = 1.00 \times 10^5$ m s^{-1}

$$\lambda_{electron} = \frac{h}{mu} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{(9.109 \times 10^{-31}\ \text{kg})(1.00 \times 10^5\ \text{m s}^{-1})} = 7.27 \times 10^{-9}\ \text{m}$$

For the table tennis ball: $m_{ball} = 11$ g, $u = 2.5$ m s^{-1}

$$\lambda_{ball} = \frac{h}{mu} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{(11 \times 10^{-3}\ \text{kg})(2.5\ \text{m s}^{-1})} = 2.4 \times 10^{-32}\ \text{m}$$

Is our answer reasonable?

The wavelength of the electron is in the order of the atomic size, which is consistent with the fact that electrons have particle–wave duality. The wavelength of the table tennis ball is extremely small, which is expected as we do not observe wave characteristics for the table tennis ball.

PRACTICE EXERCISE 4.7

Calculate the wavelength associated with a proton that is moving at a speed of 2.85×10^5 m s^{-1}.

The Heisenberg Uncertainty Principle

A particle occupies a particular location, but a wave has no exact position. A wave extends over some region of space. Because of their wave properties, electrons are always spread out rather than located in one particular place. As a result, *the position of a moving electron cannot be precisely defined*. We describe electrons as delocalised because their waves are spread out rather than pinpointed.

Mathematically, the position and momentum of a particle–wave are linked. Werner Heisenberg (1901–1976, Nobel Prize in physics, 1932), a German physicist, showed in the 1920s that the momentum and position of a particle–wave cannot be simultaneously determined. If a particular particle–wave can be pinpointed in a specific location, its momentum cannot be known accurately. Conversely, if the momentum of a particle–wave is known precisely, its location cannot be identified. Heisenberg summarised this uncertainty in what has become known as the **uncertainty principle**: the more accurately we know position, the more uncertain we are about momentum, and vice versa. Uncertainty is a feature of all objects, but it becomes important only for very tiny objects like electrons.

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4.4 Quantisation and Quantum Numbers

The properties of electrons mentioned so far (mass, charge, spin and wave nature) apply to all electrons. Electrons travelling freely in space, electrons moving in a copper wire and electrons bound to atoms all have these characteristics. Bound electrons, those held in a specific region of an atom by electrostatic forces, have additional important properties relating to their energies and the shapes of their waves. These additional properties can have only certain specific values, i.e. they are quantised.

As described in section 4.2, atoms of each element have unique, quantised electronic energy levels (see figures 4.21 and 4.22). This quantisation of energy is a property of bound electrons. The absorption and emission spectra of atoms consist of specific discrete energies because electrons undergo transitions from one bound state to another. In contrast, if an atom absorbs enough energy to remove an electron completely, the electron is no longer bound and can take on any amount of kinetic energy. *Bound* electrons have quantised energies; *free* electrons can have any amount of energy.

Experimental values for the quantised energies of atomic electrons can be calculated from absorption and emission spectra. The theory of quantum mechanics provides a mathematical explanation that links quantised energies to the wave characteristics of electrons. These wave properties of atomic electrons are described by the Schrödinger equation:

$$\hat{H}\psi = E\,\psi$$

where $\hat{H}$ is the Hamiltonian operator (containing terms for the kinetic and potential energy) for the system, E is the energy of the system and ψ is the wavefunction for the system. In particular, ψ is the amplitude of the electron's matter wave. As with light, the amplitude itself does not have any physical meaning, but its square represents the electron density distribution or probability of finding an electron. A wavefunction is a mathematical function that gives us information about an electron's position in an atom. The solution of the Schrödinger equation gives us both the energies and the associated wavefunctions of a chemical system. Despite its concise form, the Schrödinger equation can be solved *exactly* only for systems containing one electron.

The Schrödinger equation has solutions only for specific energy values because the energy of an atom is quantised. For each quantised energy value, the Schrödinger equation generates a wavefunction that describes how the electrons are distributed in space. A one-electron wavefunction is called an **orbital**. We will describe the properties of orbitals in section 4.5.

Each described property can be identified, or indexed, using a **quantum number**. These are numbers that specify the values of the electron's quantised properties. Each electron in an atom has three quantum numbers that specify its three variable properties: energy (or orbital size), angular momentum (or orbital shape) and orbital orientation. A fourth quantum number describes the spin of an electron. To describe an atomic electron completely, chemists specify a value for each of its four quantum numbers: the principal quantum number, azimuthal quantum number, magnetic quantum number and spin quantum number.

Principal Quantum Number (*n*)

The most important quantised property of an atomic electron is its energy. The quantum number that indexes energy for an atom or ion containing only a single electron is the **principal quantum number (*n*)**. For the simplest atom, hydrogen, we can use $E_n = \frac{-2.18 \times 10^{-18}\ \text{J}}{n^2}$ to calculate the energy of the electron if we know *n* (as seen in section 4.2). However, that equation applies only to the hydrogen atom or other one-electron, hydrogenic (hydrogen-like) ions (such as He^+ and Li^{2+}).

No known equation provides the exact energies of an atom that has more than one electron. Nevertheless, each electron in a multi-electron atom can be assigned a value of *n* that is a positive integer and which broadly correlates with the energy of the electron. The lowest energy for an atomic electron corresponds to *n* = 1, and each successively higher value of *n* describes a higher energy state. *The principal quantum number must be a positive integer: n* = 1, 2, 3 etc.

The principal quantum number also tells us something about the size of an atomic orbital, because the energy of an electron is correlated with its distribution in space. The higher the principal quantum number, the more energy the electron has and the greater is its average distance from the nucleus.

Summarising, the principal quantum number (*n*) can have any positive integer value. It indexes the energy of the electron and is correlated with orbital size. As *n* increases, the energy of the electron increases, its orbital gets bigger and the electron is less tightly bound to the atom.

Azimuthal Quantum Number (*l*)

A second quantum number indexes the angular momentum of an atomic orbital. This quantum number is the **azimuthal quantum number (*l*)**. The solutions for the Schrödinger equation and experimental evidence show that the electron distribution associated with orbitals can be described by a variety of shapes. Note that it is technically incorrect to talk about the 'shape' of an orbital itself. As we have seen, an orbital is merely a mathematical function. An orbital is the amplitude of an electron's three-dimensional matter wave. Because the amplitude can fluctuate between positive and negative values (just like any other wave), it has no physical meaning by itself. We can, however, talk about the shape of the electron distribution associated with a particular orbital, and this tells us where we are most likely to find an electron within this orbital.

We can categorise the shapes of objects, such as the soccer ball, rugby ball and four-leaf clover shown in figure 4.24, according to their preferred axes. A preferred axis is a line through the centre of mass of an object or shape, about which the shape can be aligned or distributed. A soccer ball has no preferred axis because its mass is distributed equally in all directions about its centre. A rugby ball has one preferred axis, with more mass along this axis than in any other direction. A four-leaf clover has two preferred axes, at right angles to each other. In an analogous fashion, electron density in an orbital can be concentrated along preferred axes.

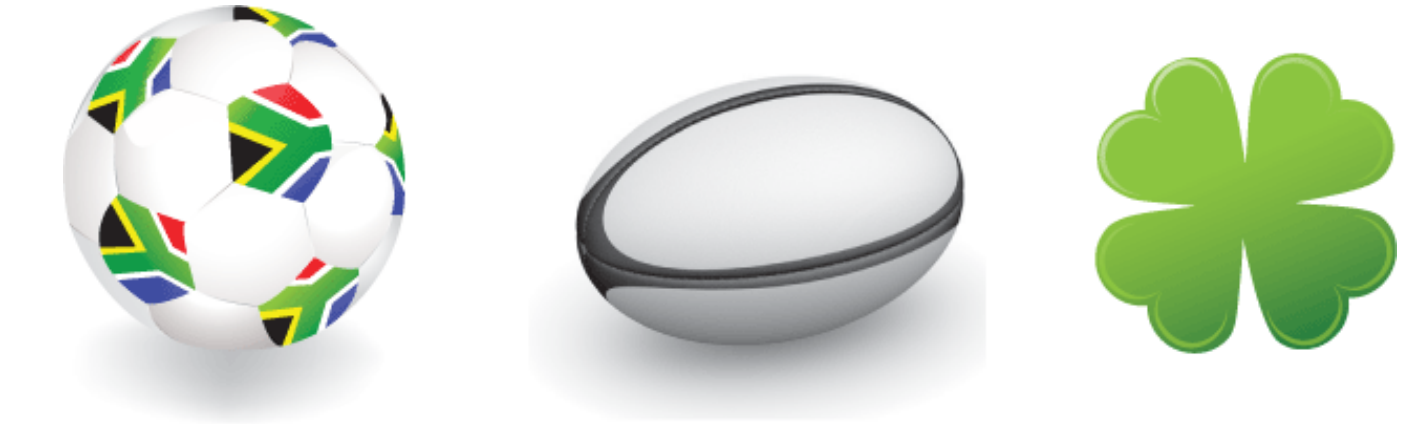


FIGURE 4.24 Some everyday objects have their masses concentrated along preferred axes. A soccer ball has no such axis, but a rugby ball has one and a four-leaf clover has two.

The value of *l* correlates with the number of preferred axes in a particular orbital and thereby identifies the shape of the electron distribution within the orbital. According to quantum theory, these shapes are highly restricted. These restrictions are linked to energy, so the value of the principal quantum number (*n*) limits the possible values of *l*. The smaller the value of *n* is, the more compact the orbital and the more restricted

its possible electron distributions. *The azimuthal quantum number (l) can be zero or any positive integer smaller than n:* $l = 0, 1, 2, \ldots, (n - 1)$; i.e. there are n values of l.

Historically, orbitals have been identified with letters rather than numbers. These letter designations correspond to the values of l as shown below.

Value of *l*	0	1	2	3	4
Orbital designation	*s*	*p*	*d*	*f*	*g*

An orbital is named by listing the numerical value for n, followed by the letter that corresponds to the numerical value for l. Thus, a 3*s* orbital has quantum numbers $n = 3$, $l = 0$. A 5*f* orbital has $n = 5$, $l = 3$. Notice that the restrictions on l mean that, when $n = 1$, l can be only zero. In other words, 1*s* orbitals exist, but there are no 1*p*, 1*d*, 1*f* or 1*g* orbitals. Similarly, there are 2*s* and 2*p* orbitals but no 2*d*, 2*f* or 2*g* orbitals.

Magnetic Quantum Number (m_l)

A sphere has no preferred axis, so it has no directionality in space. When there is a preferred axis, as for a rugby ball, figure 4.25 shows that the axis can point in many different directions relative to an *xyz* coordinate system. Thus, objects with preferred axes have directionality as well as shape.

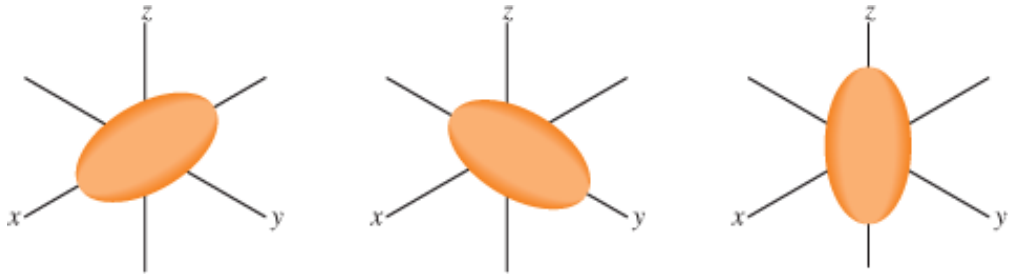


FIGURE 4.25 A rugby ball has directionality and shape. The figure shows three of the many ways in which a rugby ball can be oriented relative to a set of *x*-, *y*- and *z*-axes.

The electron distribution within an *s* orbital is spherical and has no directionality. Electron distributions in other orbitals are non-spherical and therefore have a directional dependence. Like energy and orbital electron distribution, this directional dependence is quantised. Unlike rugby balls, the electron distributions within *p*, *d* and *f* orbitals have restricted numbers of possible orientations. The **magnetic quantum number (m_l)** indexes these restrictions.

Just as orbital size (n) limits the number of preferred axes (l), the number of preferred axes (l) limits the possible orientations of the preferred axes (m_l). When $l = 0$, there is no preferred axis and therefore no preferred orientation, so $m_l = 0$ for *s* orbitals. One preferred axis ($l = 1$) can orient in any of three directions, giving three possible values for m_l: +1, 0 and -1. Two preferred axes ($l = 2$) can orient in any of five directions, giving five possible values for m_l: +2, +1, 0, -1 and -2. Each time l increases in value by one unit, two additional values of m_l become possible, and the number of possible orientations increases by two. *The magnetic quantum number (m_l) can be any positive or negative integer between 0 and l:* $m_l = 0, \pm1, \pm2, \ldots, \pm l$; i.e. there are $(2l + 1)$ values of m_l.

Spin Quantum Number (m_s)

As we saw in section 1.5, all electrons have a property called **spin**. This means that electrons can behave

in one of two ways when placed in a magnetic field. When a beam of silver atoms is passed through a magnetic field (similar to the experiment carried out by Otto Stern and Walter Gerlach in 1921, see figure 4.26), the atom beam is split, some atoms are deflected in one direction and the rest are deflected in the opposite direction. Since classical physics associates a spinning electric charge with a magnetic field, the experimental observation was explained by the Dutch physicists George Uhlenbeck and Samuel Gouldsmit with a property they called electron spin. (*Note:* (There is no physical evidence that an electron actually spins.) The fact that only two responses are observed demonstrates that spin is quantised. The **spin quantum number (m_s)** indexes this behaviour. The two possible values of m_s are $+\frac{1}{2}$ and $-\frac{1}{2}$.

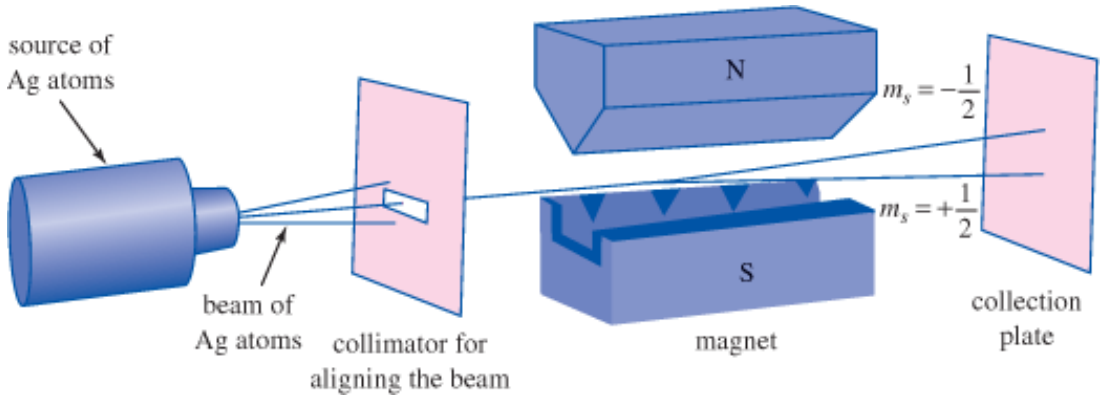


FIGURE 4.26 The Stern–Gerlach magnetic field experiment.

The Pauli Exclusion Principle

A complete description of an atomic electron requires a set of four quantum numbers: n, l, m_l and m_s, which must meet all the restrictions mentioned earlier, as summarised in table 4.2. Each electron in an atom has a unique set of quantum numbers; no two electrons in an atom have exactly the same set of quantum numbers. This was first postulated by the Austrian physicist Wolfgang Pauli (1900–1958, Nobel Prize in physics, 1945) and is known as the **Pauli exclusion principle**. The principle is derived from quantum mechanics and supported by all experimental evidence.

TABLE 4.2 Restrictions on quantum numbers for electrons in atoms

Quantum number	Restrictions	Range
n	positive integers	1, 2, …, ∞
l	positive integers less than n	0, 1, …, (n - 1)
m_l	integers between -l and l	-l, …, -1, 0, +1, …, +l
m_s	$-\frac{1}{2}$ or $+\frac{1}{2}$	$-\frac{1}{2}$, $+\frac{1}{2}$

The number of possible sets of quantum numbers increases rapidly as n increases. An atomic orbital is designated by its n and l values, such as 1s, 3d, 4p and so on. When $l > 0$, there is more than one orbital of each designation; that is, when $l = 1$, there are three p orbitals and for $l = 2$ there are five d orbitals. An electron in any orbital can have a spin quantum number (m_s) of either $+\frac{1}{2}$ or $-\frac{1}{2}$. Thus, there are many sets of valid quantum numbers. An electron in a 3p orbital, for example, can have any one of six valid sets of quantum numbers.

$$n=3, l=1, m_l=+1, m_s=+\frac{1}{2} \quad n=3, l=1, m_l=+1, m_s=-\frac{1}{2}$$
$$n=3, l=1, m_1=0, \quad m_s=+\frac{1}{2} \quad n=3, l=1, m_l=0, \quad m_s=-\frac{1}{2}$$
$$n=3, l=1, m_l=-1, m_s=+\frac{1}{2} \quad n=3, l=1, m_l=-1, m_s=-\frac{1}{2}$$

A direct consequence of the Pauli exclusion principle is that any orbital can contain a maximum of two electrons (we say that an orbital containing two electrons is full) and that the two electrons in a full orbital must be of opposite spin.

WORKED EXAMPLE 4.8

Valid Quantum Numbers

How many valid sets of quantum numbers exist for 4*d* orbitals? Give two examples.

Analysis

The question asks for the sets of quantum numbers that have $n = 4$ and $l = 2$. Each set must meet all the restrictions listed in table 4.2. The easiest way to see how many valid sets there are is to list all the valid quantum numbers.

Solution

Because this is a 4*d* orbital, *n* and *l* are specified and cannot vary. The other two quantum numbers, however, have several acceptable values. For each value of m_l, either value of m_s is acceptable, so the total number of possibilities is the product of the number of possible values for each quantum number. This is shown on the next page.

Quantum number	*n*	*l*	m_l	m_s
Possible values	4	2	2, 1, 0, -1, -2	$+\frac{1}{2}, -\frac{1}{2}$
Number of possible values	1	1	5	2

Possible sets of values for a 4*d* electron: (1)(1)(5)(2) = 10

There are 10 sets of quantum numbers that can describe a 4*d* orbital. Two of them are shown below.

$$n=4, \quad l=2, \quad m_l=1, \quad m_s=+\frac{1}{2}$$
$$n=4, \quad l=2, \quad m_l=-2, \quad m_s=-\frac{1}{2}$$

You should be able to list the other eight sets.

Is our answer reasonable?

If you write down all the possible sets, you will find that there are 10. Notice that there are always $2l + 1$ possible values of m_l and 2 possible values of m_s, so every *nd* set of orbitals has 10 possible sets of quantum numbers.

PRACTICE EXERCISE 4.8

Write all the valid sets of quantum numbers of the 5*p*

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4.5 Atomic Orbital Electron Distributions and Energies

The chemical properties of atoms are determined by the behaviour of their electrons. Because atomic electrons are described by orbitals, the interactions of electrons can be described in terms of orbital interactions. The two characteristics of orbitals that determine how electrons interact are their electron distributions in three-dimensional space and their energies.

Orbital Electron Distributions

Wave-like properties cause electrons to be smeared out rather than localised at an exact position. This smeared-out distribution can be described using electron density. Where electrons are most likely to be found, there is high electron density. Low electron density occurs in regions where electrons are less likely to be found. Each electron, rather than being a point charge, is a three-dimensional particle–wave that is distributed over space as an orbital. Orbitals describe the delocalisation of electrons. Moreover, when the energy of an electron changes, the size and shape of its distribution in space change as well. Each atomic energy level is associated with a specific three-dimensional atomic orbital.

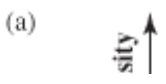
An atom that contains many electrons can be described by superimposing (adding together) the orbitals for all of its electrons to obtain the overall size and ‘shape’ of the atom.

The quantum numbers n and l determine the size and electron distribution of an orbital. As n increases, the size of the orbital increases, and, as l increases, the electron distribution of the orbital becomes more elaborate. These can be nodal planes or radial nodes, and the number of these depends on n and l; i.e. for every orbital, there are n - 1 nodes, of which l are nodal planes and the remainder are spherical (radial) nodes.

Orbital Depictions

We need ways to visualise electrons as particle–waves delocalised in three-dimensional space. Orbital pictures provide maps of how an electron wave is distributed in space. There are several ways to represent these three-dimensional maps. Each one shows some important orbital features, but none shows all of them. We use three different representations: electron density plots, electron density pictures and boundary surface diagrams.

An **electron density plot** represents the electron distribution in an orbital as a two-dimensional graph. These graphs show electron density along the y-axis and distance from the nucleus, r, along the x-axis. Figure 4.27a shows an electron density plot for the 2s orbital.



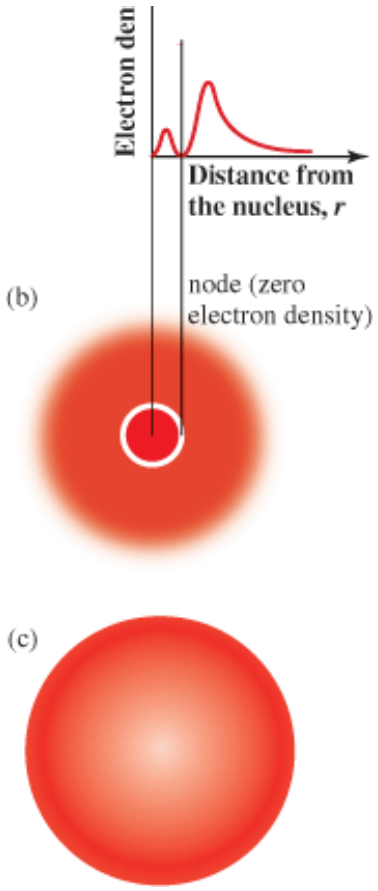


FIGURE 4.27 Different depictions of the 2*s* orbital:
(a) An electron density plot versus distance from the nucleus,
(b) an electron density picture and
(c) a boundary surface diagram.

Electron density plots are useful because plots for several orbitals can be superimposed to indicate the relative sizes of various orbitals. Electron density plots do not, however, show the three-dimensionality of an orbital.

Electron density pictures can indicate the three-dimensional nature of orbitals. One type of orbital picture is a two-dimensional colour pattern in which the density of colour represents electron density. Figure 4.27b shows such an electron density picture of the 2*s* orbital. This two-dimensional pattern of colour density shows a cross-sectional slice through the middle of the orbital. Figures 4.27a, 4.27b show that the 2*s* orbital has one spherical node, as we discussed on the previous page.

A boundary surface diagram provides a simplified orbital picture. In this representation, we draw a solid surface that encloses most (usually 90%) of the electron density. Thus, the electron density is high inside the boundary surface but very low outside. Figure 4.27c shows a boundary surface diagram of the 2*s* orbital. One drawback of boundary surface diagrams is that they do not show details of electron density below the surface, including spherical nodes. They do, however, show all planar nodes, and from those it is possible to deduce the number of hidden spherical nodes.

A useful analogy for understanding the value of boundary surfaces is a swarm of bees around a hive. At any one time, some bees will be off foraging for nectar, so a boundary surface drawn around all the bees might cover several hectares. This would not be a very useful map of bee density. A boundary surface containing 90% of the bees, on the other hand, would be only slightly bigger than the hive itself. This would be a very useful map of bee density, because anyone inside that boundary surface would surely interact with bees.

Another drawback of boundary surface diagrams is that all details of electron density inside the surface are

lost. Thus, if we want to convey the maximum information about orbitals, we must use combinations of the various depictions.

The advantages and disadvantages of the three types of plots can be seen by how they show one characteristic feature of orbitals. Figure 4.27a shows clearly that there is a value for *r* where the electron density falls to zero. A place where electron density is zero is called a **node**. Figure 4.27b shows the node for the 2*s* orbital as a white ring. In three dimensions, this node is a spherical surface. Figure 4.27c does not show the node, because the spherical nodal surface is hidden inside the 90% boundary surface. The two-dimensional graph shows the location of the node most clearly, the electron density picture gives the best sense of the shape of the node, while the boundary surface diagram fails to show it at all.

Orbital Size

Experiments that determine atomic radii provide information about the sizes of orbitals. In addition, theoretical models of the atom can predict how the electron density of a particular orbital changes with distance from the nucleus.

In any particular atom, orbitals get larger as the value of *n* increases. The *n* = 2 orbitals are larger than the *n* = 1 orbital, the *n* = 3 orbitals are larger than the *n* = 2 orbitals, and so on. The electron density plots in figure 4.28 show this trend for the first three *s* orbitals of the hydrogen atom. This plot also shows that the number of nodes increases as *n* increases.

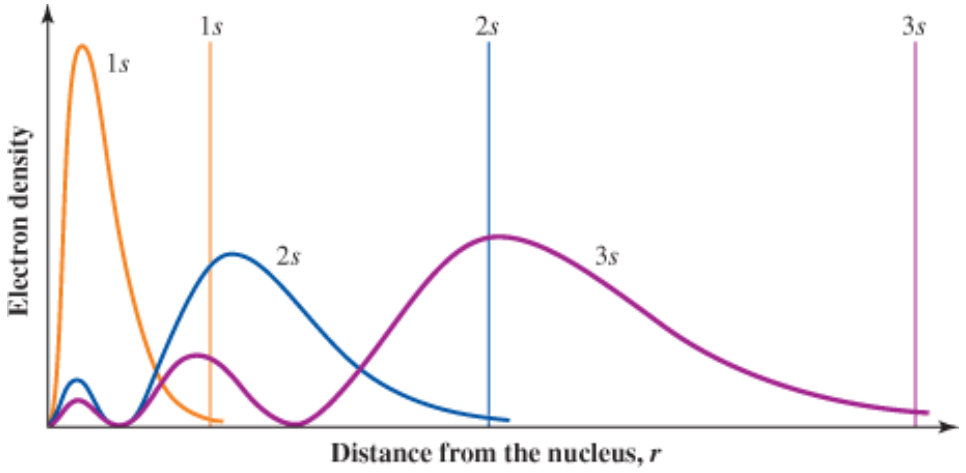


FIGURE 4.28 Electron density plots for the 1*s*, 2*s* and 3*s* atomic orbitals of the hydrogen atom. The vertical lines indicate the values of *r* where the 90% boundary surface would be located.

In any particular atom, all orbitals with the same principal quantum number are similar in size. As an example, figure 4.29 shows that the *n* = 3 orbitals of the copper atom have their maximum electron densities at similar distances from the nucleus. The same regularity holds for all other atoms. The quantum numbers other than *n* affect orbital size only slightly. We describe these small effects in the context of orbital energies later in this section.

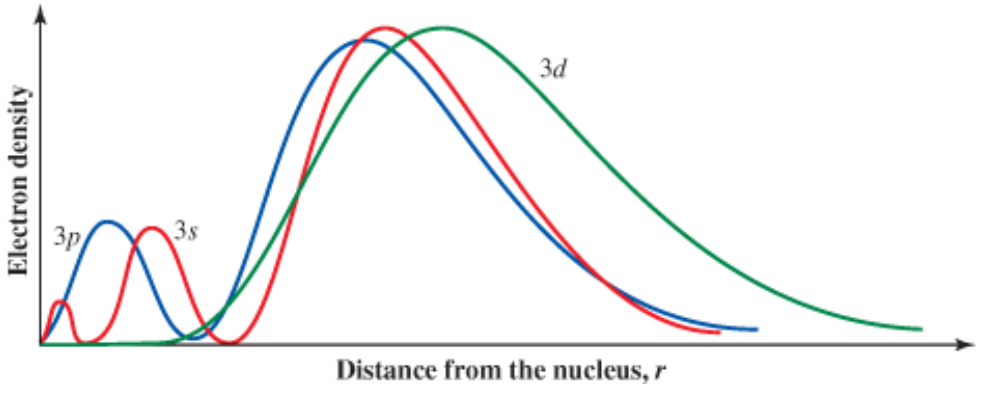


FIGURE 4.29 Electron density plots for the 3*s* (red line), 3*p* (blue line), and 3*d* (green line) orbitals for the copper atom. All three orbitals are nearly the same size.

A specific orbital becomes smaller as the atomic nuclear charge increases. As the positive charge of the nucleus increases, the electrostatic force exerted by the nucleus on the negatively charged electrons increases and electrons become more tightly bound. This reduces the radius of the orbital. As a result, each orbital shrinks in size as atomic number increases. For example, figure 4.30 shows that the 2*s* orbital steadily decreases in size across the second row of the periodic table from Li ($Z = 3$) to Ne ($Z = 10$). The atomic number, Z, is equal to the number of protons in the nucleus, so increasing Z means increasing nuclear charge.

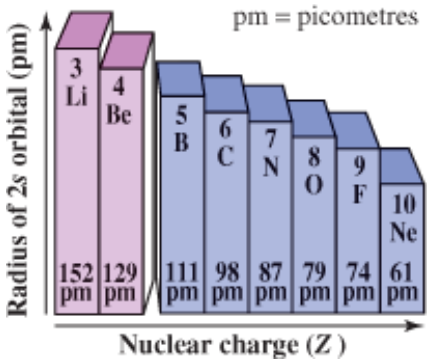


FIGURE 4.30 The radius of the 2*s* orbital decreases as Z increases. The number at the bottom of each column is the radius of the 2*s* orbital in pm (picometres).

Details of Orbital Electron Distributions

The electron distributions of orbitals strongly influence chemical interactions. Hence, we need to have detailed pictures of these electron distributions to understand the chemistry of the elements.

The quantum number $l = 0$ corresponds to an *s* orbital. According to the restrictions on quantum numbers, there is only one *s* orbital for each value of the principal quantum number. The electron distribution of *s* orbitals is spherical, with radii and number of nodes that increase as n increases. Figure 4.31 shows a boundary surface diagram of the 1*s* orbital.



FIGURE 4.31 Boundary surface diagram of the 1*s* orbital.

We introduced the concept of the phase of a wave in section 4.2, and this concept also applies to orbitals. An *s* orbital has a single phase, which we refer to as either positive (+) or negative (-). We generally depict different phases using + and–signs superimposed on the orbital electron distribution, or by using different colours corresponding to + and–phases.

The quantum number $l = 1$ corresponds to a *p* orbital. An electron in a *p* orbital can have any of three values for m_l, so for each value of *n* there are three different *p* orbitals. The nonspherical electron distribution of *p* orbitals can be shown in various ways. The most convenient representation shows the three orbitals with identical electron distributions but pointing in three different directions. Figure 4.32 shows boundary surface diagrams of the 2*p* orbitals. Each *p* orbital has high electron density in one particular direction, perpendicular to the other two orbitals, with the nucleus at the centre of the system. The three different orbitals can be represented so that each has its electron density concentrated on both sides of the nucleus along a preferred axis. We can write subscripts on the orbitals to distinguish the three distinct orientations: p_x, p_y and p_z. Each *p* orbital also has a nodal plane that passes through the nucleus. The nodal plane for the p_x orbital is the *yz* plane, for the p_y orbital the nodal plane is the *xz* plane and for the p_z orbital it is the *xy* plane. The two lobes of a single *p* orbital have opposite phases; this is shown in figure 4.32 by using a different colour for each lobe.

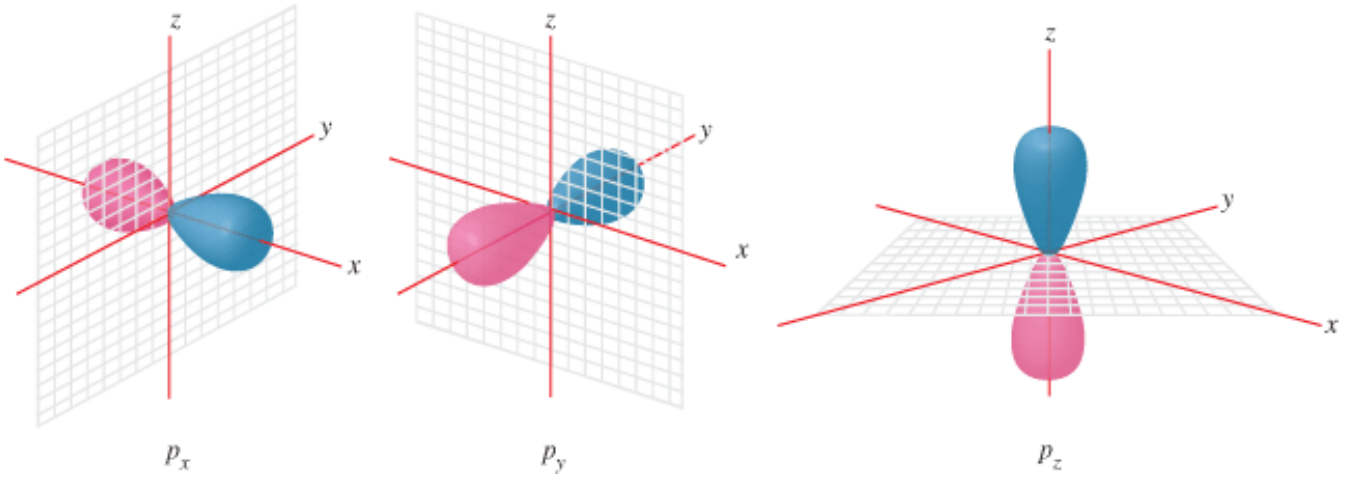


FIGURE 4.32 Boundary surface diagrams of the three 2*p* orbitals. The three orbitals have the same overall electron distribution, but each is oriented perpendicular to the other two. The nodal plane in each case is illustrated by the grey hatched surface.

As *n* increases, the number of nodes within each *p* orbital increases, just as for *s* orbitals. Nevertheless, the directionality of the electron distribution does not change. Each *p* orbital is perpendicular to the other two in its set and has its lobes along its preferred axis, where electron density is high. To an approaching atom, therefore, an electron in a 3*p* orbital presents the same characteristics as one in a 2*p* orbital, except that the 3*p* orbital is bigger. Consequently, the electron distributions and relative orientations of the 2*p* orbitals in figure 4.32 represent the prominent spatial features of all *p* orbitals.

The quantum number $l = 2$ corresponds to a *d* orbital. An electron in a *d* orbital can have any of five values for m_l (-2, -1, 0, +1 and +2), so there are five different orbitals in each set. Each *d* orbital has two nodal planes. Consequently, the electron distributions of the *d* orbitals are more complicated than their *s* and *p* counterparts. The boundary surface diagrams in figure 4.33 show these orbitals in the most convenient way. In these drawings, three orbitals have electron distributions that look like three-dimensional 'cloverleaves' lying in a plane with the lobes pointed between the axes. A subscript identifies the plane in which each lies: d_{xy}, d_{xz} and d_{yz}. A fourth orbital has an electron distribution that is a cloverleaf in the *xy* plane, but its lobes point along the *x*- and *y*-axes. This orbital is designated $d_{x^2-y^2}$. In each of these 'cloverleaf' orbitals, the lobes situated opposite each other have the same phases, as shown in figure 4.33. The electron distribution in the fifth orbital is quite different. Its major lobes point along the *z*-axis, but there is also a 'doughnut' of electron density in the *xy* plane. This orbital is designated d_{z^2}. The two lobes have the same phase, while the 'doughnut' is of opposite phase.

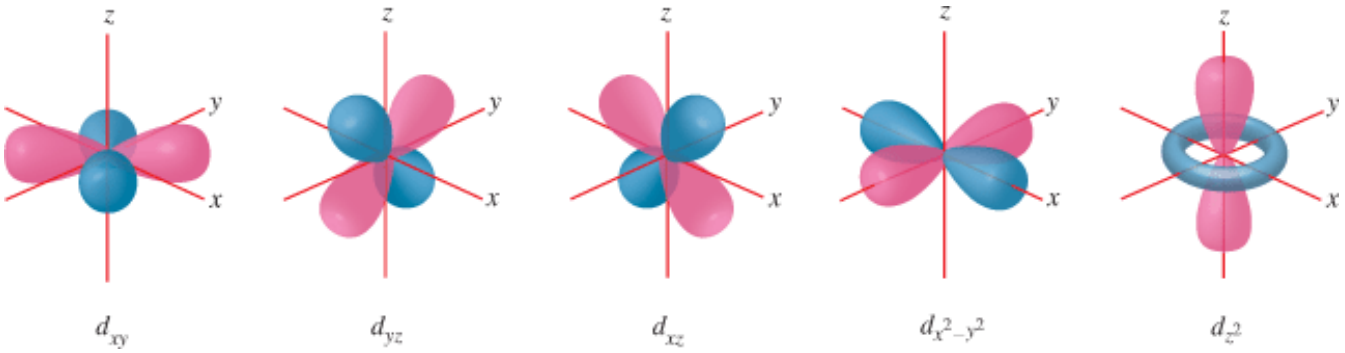


FIGURE 4.33 Boundary surface diagrams of the *d* orbitals. Four of the five have the same cloverleaf shape with two nodal planes at right angles to each other. The d_{z^2} orbital has the *z*-axis as its preferred axis. It has two nodes that are shaped like cones, one above and one below the *xy* plane.

The quantum number $l = 3$ corresponds to an *f* orbital. The possible values of m_l (-3, –2, -1, 0, +1, +2 and +3) mean that there are seven *f* orbitals, but as they become important only for the lanthanoid elements and beyond, we will not detail their properties here.

Orbital Energies

A hydrogen atom can absorb a photon and change from its most stable, lowest energy state (ground state) to a less stable, higher energy state (excited state), as described in section 4.2. We can explain this process using atomic orbitals. When a hydrogen atom absorbs a photon, its electron can undergo a transition to an orbital that has a larger principal quantum number, i.e. a higher energy. Figure 4.34 illustrates this process for the $1s \rightarrow 2p$ transition in the hydrogen atom.

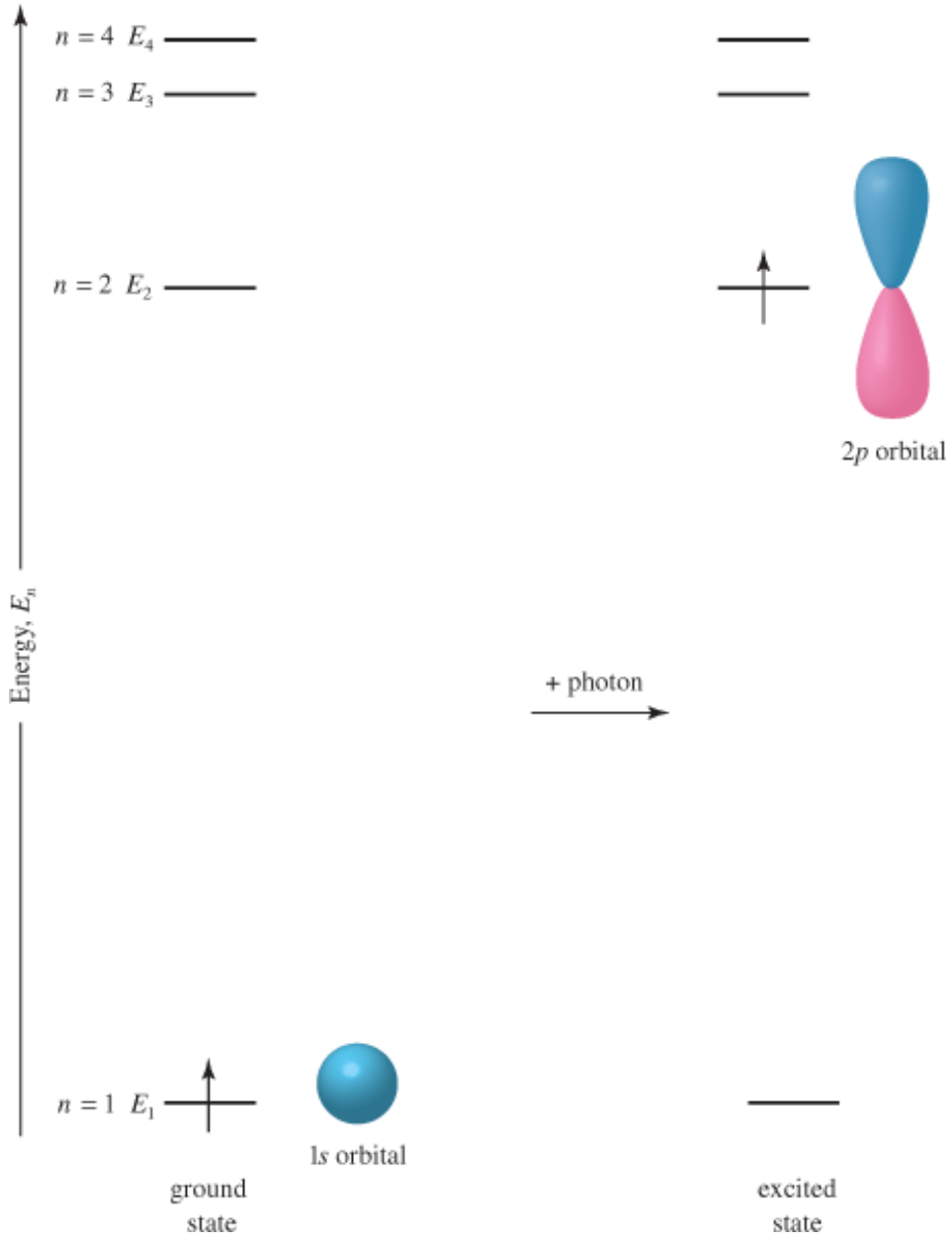


FIGURE 4.34 When a hydrogen atom in its ground state absorbs light of wavelength 121.6 nm, it is converted to an excited state, in which the electron occupies a 2*p* orbital.

Electronic transitions cannot necessarily occur between any set of orbitals; in the hydrogen atom, and other one-electron systems, they are governed by the following selection rules:

1. Δn = anything. There is no restriction on the values of the initial and final principal quantum numbers.
2. $\Delta l = \pm 1$. The azimuthal quantum number must increase or decrease by 1. This means that we cannot have a transition from an *s* orbital to another *s* orbital, or from a *p* orbital to another *p* orbital.
3. $\Delta m_l = 0, \pm 1$. The magnetic quantum number may stay the same, or it can increase or decrease by 1.

The atomic orbital model explains the spectra and energy levels of the hydrogen atom perfectly. For a one-electron system like the hydrogen atom, the energy levels for all orbitals depend only on the principal quantum number, *n*. All orbitals having the same value of *n* have the same energy and are said to be **degenerate**. For multi-electron systems, experiments show that the underlying principles are the same, although the details for each kind of atom are different. Variations in nuclear charge and the number of electrons change the magnitudes of the electrical forces that hold electrons in their orbitals. Differences in forces cause changes in orbital energies that can be understood qualitatively using forces of electrical attraction and repulsion, as we describe later in this chapter. As a consequence, the degeneracy of orbitals for each level of *n* is partially removed.

The Effect of Nuclear Charge

A helium +1 cation, like a hydrogen atom, has one electron. Absorption and emission spectra show that He^+ has energy levels that depend on *n* only, just like the hydrogen atom. Nevertheless, figure 4.35 shows that the emission spectra of He^+ and H differ, which means that these two species must have different energy levels. We conclude that something besides *n* influences orbital energy.

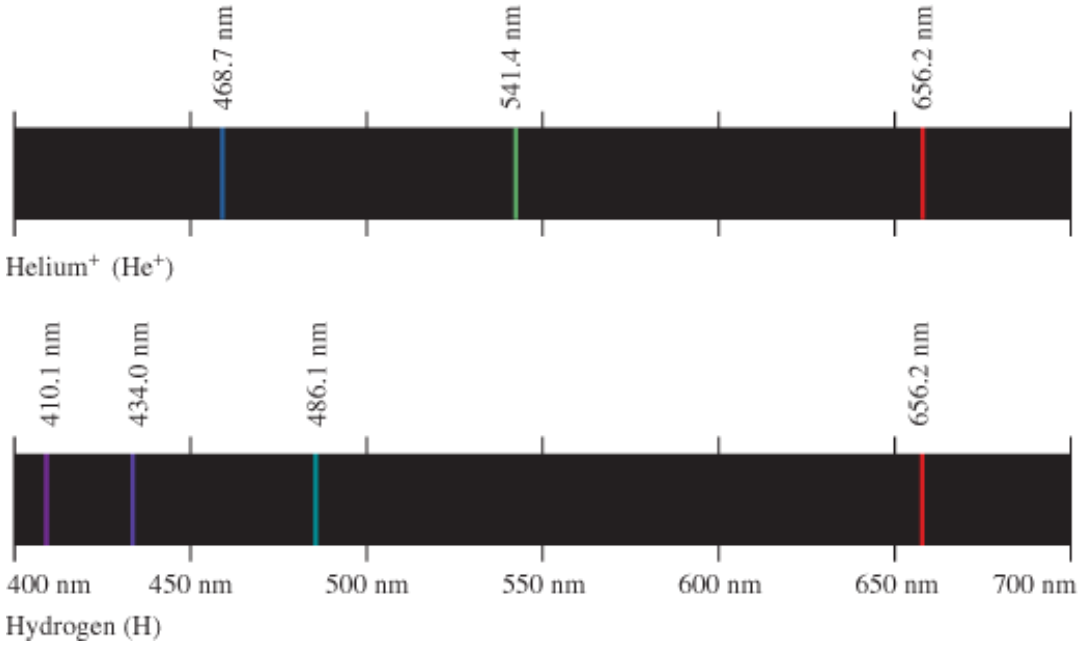


FIGURE 4.35 The emission spectra of He^+ and H reveal transitions at characteristic energies. Most of the emitted photons have different energies because He^+ has quantised energy levels that are different from those of H.

The difference between He^+ and H is in their nuclei. A hydrogen nucleus is a single proton with a +1 charge, whereas a helium nucleus contains two protons (and two neutrons) and has a charge of +2. The larger nuclear charge of He^+ attracts its single electron more strongly than the smaller charge of H. As a result, He^+ binds the electron with a stronger force. Thus, any given energy level in the helium ion is lower in energy than the corresponding level in the hydrogen atom.

The energy of an orbital can be determined by measuring the amount of energy required to remove an electron completely from that orbital. This is the **ionisation energy (E_i)**.

$$H \longrightarrow H^+ + e^- \qquad E_{i_H} = 2.18 \times 10^{-18}\ J$$

$$He^+ \longrightarrow He^{2+} + e^- \qquad E_{i_{He^+}} = 8.72 \times 10^{-18}\ J$$

The ionisation energy of He^+ is four times that of H. Thus, the ground state orbital for He^+ must be four times lower in energy than the ground state orbital for H. Spectral analysis shows that each orbital of a helium cation is four times lower in energy than its counterpart orbital in a hydrogen atom, showing that orbital energy depends on Z^2 in a one-electron system. While the energy levels in H and He^+ are different for corresponding orbitals due to the Z^2 relationship, there are some orbital energies that coincide and hence we can get emission energies that are identical for both species (see figure 4.35). Figure 4.36 shows the relationship between the energy levels of He^+ and H. The diagram is in exact agreement with calculations based on the Schrödinger equation.

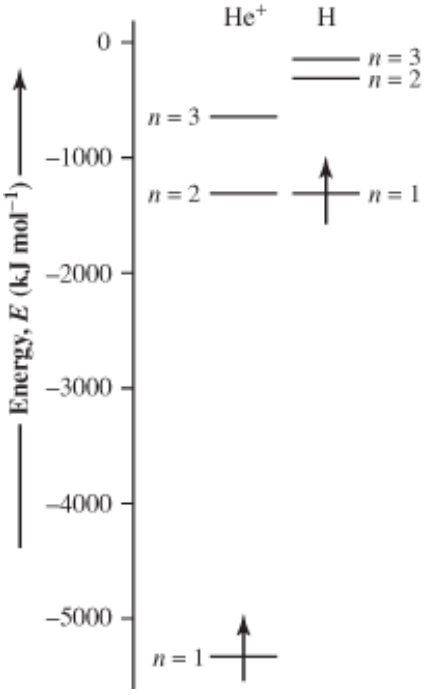


FIGURE 4.36 An energy level diagram for He^+ and H. Each species has one electron, but the different nuclear charges make each He^+ orbital four times lower in energy than the corresponding H orbital.

The Effect of Other Electrons

A hydrogen atom or a helium cation are rare examples of one-electron systems; most other atoms and ions contain collections of electrons. In a multi-electron atom, electrons affect each other's properties. These electron–electron interactions make the orbital energies of every element unique.

A given orbital is of higher energy in a multi-electron atom than it is in the single-electron ion with the same nuclear charge. For instance, figure 4.37 shows that it takes more than twice as much energy to remove the electron from He^+ (one electron) as it does to remove one of the electrons from a neutral He atom (two electrons). This demonstrates that the 1*s* orbital in He^+ is more than two times lower in energy than the 1*s* orbital in neutral He. The nuclear charge of both species is +2, so the smaller ionisation energy for He must result from the presence of the second electron. A negatively charged electron in a multi-electron atom is attracted to the positively charged nucleus, but it is repelled by the other negatively charged electrons. This electron–electron repulsion contributes to the lower ionisation energy of the helium atom.

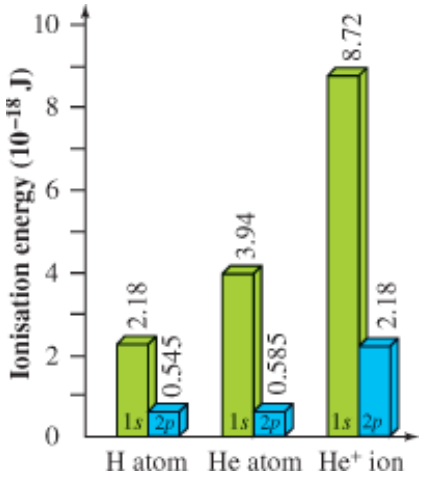


FIGURE 4.37 Ionisation energies.

Shielding

Figure 4.38 shows a free electron approaching a He^+ cation. The +2 charge of the nucleus attracts the incoming electron, but the negative charge of the He^+ 1*s* electron repels it. As electrons have a like charge, electron–electron repulsion cancels a portion of the attraction between the nucleus and the incoming electron. Chemists call this partial cancellation **shielding**.

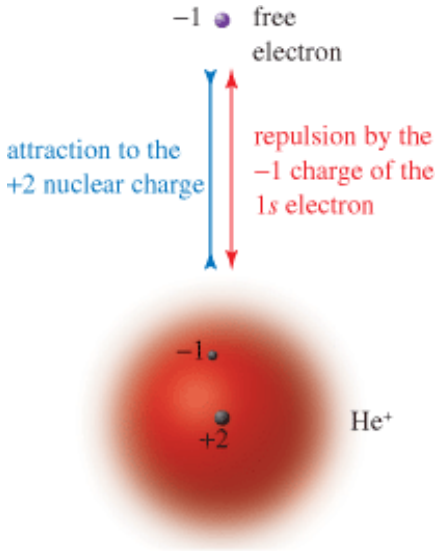


FIGURE 4.38 As a free electron approaches a He^+ cation, it is attracted to the +2 charge on the nucleus but repelled by the -1 charge on the 1*s* electron. When it is far from the cation, the free electron experiences a net charge of +1.

With its -1 charge, a bound electron could reduce the total charge by a maximum of 1 charge unit. Indeed, when an approaching electron is far enough away from a He^+ ion, it feels an attraction due to the net charge on the ion, +1. However, the 1*s* orbital is spread out all around the nucleus. This means that, as an approaching electron gets close enough, the 1*s* electron shields only part of the total nuclear charge. Consequently, an approaching electron is subject to a net attraction resulting from some **effective nuclear charge (Z_{eff})** less than +2 but greater than +1.

Incomplete shielding can be seen in the ionisation energies of hydrogen atoms, helium atoms and helium ions (figure 4.37). Without shielding, the ionisation energy of a helium atom would be the same as that of a helium ion; both would be $8.72 \times 10^{-1}8$ J. With *complete* shielding, one helium electron would compensate for one of the protons in the nucleus, making $Z_{eff} = +1$. The energy required to remove an electron from a helium atom would then be the same as the energy required to remove an electron from a hydrogen atom, 2.18×10^{-18} J. The actual ionisation energy of a helium atom is 3.94×10^{-18} J, about twice the fully shielded value and about half the totally unshielded value (figure 4.39). Shielding is incomplete because both electrons in helium occupy an extended region of space, so neither is completely effective at shielding the other from the +2 charge of the nucleus.

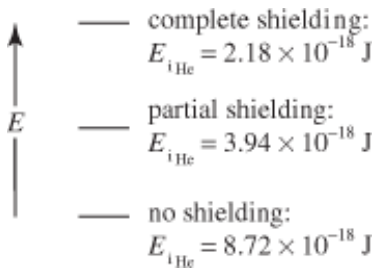


FIGURE 4.39 Ionisation energies of a helium atom with different amounts of shielding.

Electrons in compact orbitals pack around the nucleus more tightly than electrons in large, diffuse orbitals. As a result, the effectiveness in shielding nuclear charge decreases as orbital size increases. Because the size of an orbital increases with *n*, an electron's ability to shield decreases as *n* increases. In a multi-electron atom, lower *n* electrons are concentrated between the nucleus and higher *n* electrons. The negative charges of these inner electrons counteract most of the positive charge of the nucleus.

The efficient shielding by electrons with small values of *n* can be appreciated by comparing the ionisation energies of electrons in the 2*p* orbitals in figure 4.37. Consider an excited-state helium atom that has one of its electrons in the 1*s* orbital and its other electron in a 2*p* orbital. It takes 0.585×10^{-18} J to remove the 2*p* electron from this excited-state helium atom. This value is close to that of an excited hydrogen atom with its lone electron in a 2*p* orbital, 0.545×10^{-18} J. It is much less than the 2*p* orbital ionisation energy of an excited He^+ ion, 2.18×10^{-18} J. These data show that Z_{eff} is quite close to +1 for the 2*p* orbital of an excited atom. In the excited He atom, the electron in the 1*s* orbital is very effective at shielding the electron in the 2*p* orbital from the full +2 charge of the nucleus.

In multi-electron atoms, electrons with a given value of *n* generally provide effective shielding for orbitals with a larger value of *n*. That is, $n = 1$ electrons shield the $n = 2$, $n = 3$ and larger orbitals, whereas $n = 2$ electrons provide effective shielding for the $n = 3$, $n = 4$ and larger orbitals but provide little shielding for the $n = 1$ orbital. The amount of shielding also depends on the electron distribution of the shielded orbital and decreases with increasing azimuthal quantum number, *l*. The shaded area of the electron density plot in figure 4.40 emphasises that the 2*s* orbital has a region of significant electron density near the nucleus. A 2*p* orbital lacks this inner layer, so virtually all of its electron density lies outside the region occupied by the 1*s* orbital. Consequently, a 1*s* orbital shields the 2*p* orbital more effectively than the 2*s* orbital, even though both $n = 2$ orbitals are about the same size. Thus, a 2*s* electron is subject to a larger effective nuclear charge than a 2*p* electron. This results in stronger electrostatic attraction to the nucleus, which makes the 2*s* orbital lower in energy than the 2*p* orbitals. The 2*p* orbitals of any multi-electron atom are always slightly higher in energy than the 2*s* orbital.

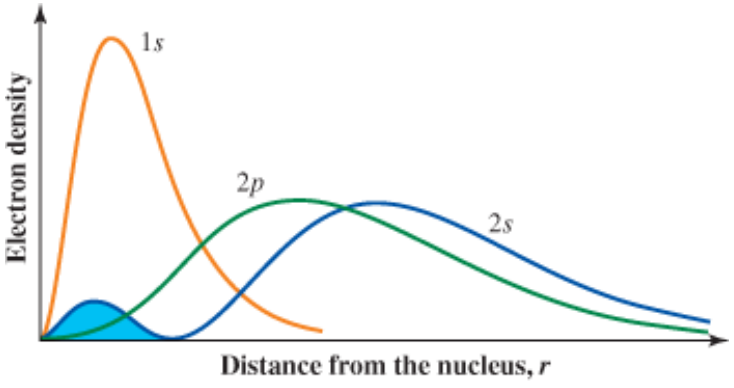


FIGURE 4.40 Electron density plots for the 1*s*, 2*s* and 2*p* orbitals. Unlike the 2*p* orbital, the 2*s* orbital has significant electron density very near the nucleus (shaded region).

The shielding differences experienced by the 2*s* and 2*p* orbitals also extend to larger values of *n*. The 3*s* orbital is of lower energy than the 3*p*, the 4*s* orbital is of lower energy than the 4*p*, and so on. Orbitals with higher *l* values show similar effects. The 3*d* orbitals are always higher in energy than the 3*p* orbitals, and the 4*d* orbitals are higher in energy than the 4*p* orbitals. These effects can be summarised in a single general statement: *The higher the value of the l quantum number, the more that orbital is shielded by electrons in smaller, lower energy orbitals.*

In a one-electron system (H, He^+, Li^{2+} and so on) the energy of the orbitals depends only on *Z* and *n*. In multi-electron systems, orbital energy depends primarily on *Z* and *n*, but it also depends significantly on *l*. In a sense, *l* finetunes orbital energies and as a consequence there are fewer degenerate orbitals.

The relative orbital energies for a multi-electron atom are shown in figure 4.41. It can be seen that, whereas in a one-electron system the *ns*, *np* and *nd* orbitals are degenerate, this is not the case in a multi-electron atom.

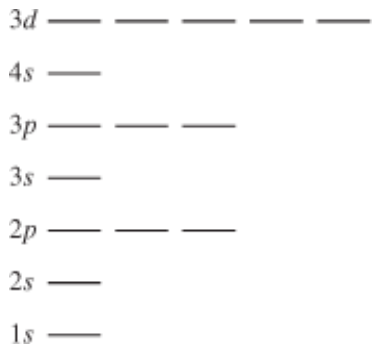


FIGURE 4.41 An energy level diagram (not to scale) for a multielec tron atom. The orbital energies now depend on *l* in addition to both *Z* and *n*, and so, in contrast to one-electron systems (figure 4.36), orbitals having the same principal quantum number *n* are no longer degenerate.

Electrons with the same *l* value but different values of m_l do not shield one another effectively. For example, when electrons occupy different *p* orbitals, the amount of mutual shielding is slight. This is because shielding is effective only when much of the electron density of one orbital lies between the nucleus and the electron density of another. Recall from figure 4.32 (p. 133) that the *p* orbitals are perpendicular to one another, with high electron densities in different regions of space. The electron density of the $2p_x$ orbital does not lie between the $2p_y$ orbital and the nucleus, so there is little shielding. The *d* orbitals also occupy different regions of space from one another, so mutual shielding among electrons in these orbitals is small as well.

WORKED EXAMPLE 4.9

Shielding

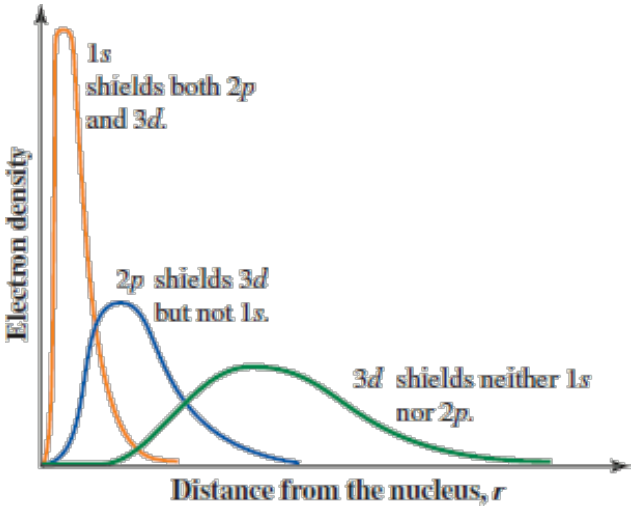
Draw a qualitative electron density plot showing the 1*s*, 2*p* and 3*d* orbitals to scale. Label the plot in a way that summarises the shielding properties of these orbitals.

Analysis

This is a qualitative problem that asks us to combine information about three different orbitals on a single plot. We need to find electron density information and draw a single graph to scale.

Solution

Figures 4.28, 4.29 and 4.40 show electron density plots of the $n = 1$, $n = 2$ and $n = 3$ orbitals. We extract the electron distributions of the 1*s*, 2*p* and 3*d* orbitals from these graphs. Then we add labels that summarise the shielding properties of these orbitals. Shielding is provided by small orbitals whose electron density is concentrated closer to the nucleus than that of larger orbitals. In this case, 1*s* shields both 2*p* and 3*d*; 2*p* shields 3*d*, but not 1*s*; and 3*d* shields neither 1*s* nor 2*p*. The shielding patterns can be labelled as shown.



Is our answer reasonable?

We know that the most important factor for orbital size is the value of *n* and that small orbitals shield better than large ones, so the shielding sequence makes sense.

PRACTICE EXERCISE 4.9

Construct and label a graph illustrating that the 2*s* orbital shields the 3*s* orbital more effectively than the 3*s* shields the 2*s*.

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4.6 Structure of the Periodic Table

As we have seen in chapter 1, the periodic table lists the elements in order of increasing atomic number. Because the number of electrons in a neutral atom is the same as its atomic number, this list is also in order of increasing number of atomic electrons. The periodic table organises atoms in rows (periods) and groups such that atoms with the same valence electron configuration, leading to similar chemical properties, are located in the same group. We have since learned that the electrons are mainly responsible for an atom's chemical properties, and equipped with the knowledge of orbital electron distributions and energies we can now start to understand the reasons for the placement of atoms in the periodic table.

The Aufbau Principle and Order of Orbital Filling

The ground state of an atom is, by definition, the most stable arrangement of its electrons. *Most stable* means that the electrons occupy the lowest energy orbitals available. We construct the **ground-state configuration** of an atom by placing electrons in the orbitals starting with the lowest in energy and moving progressively upward. We have seen earlier that shielding causes the orbitals with the same principal quantum number to increase in energy as l increases. Consequently, the 2*s* orbital, being of lower energy than the 2*p* orbital, fills first. Similarly, 3*s* fills before 3*p*. The energy differences between orbitals become less pronounced the further away the orbitals are from the nucleus. The consequence of this is that, for orbitals with principal quantum numbers larger than $n = 2$, the order of orbital energies is not necessarily as expected. For example, the 4*s* orbital fills before the 3*d* orbitals. Therefore, the order of orbital filling is as given in figure 4.42a. At higher levels, there are a number of exceptions to this filling sequence. These will be discussed on pp. 145–6. In accordance with the Pauli exclusion principle, each successive electron is placed in the lowest energy orbital whose quantum numbers are not already assigned to another electron. This is called the **Aufbau principle** (*Aufbau* is a German word literally meaning 'build-up').

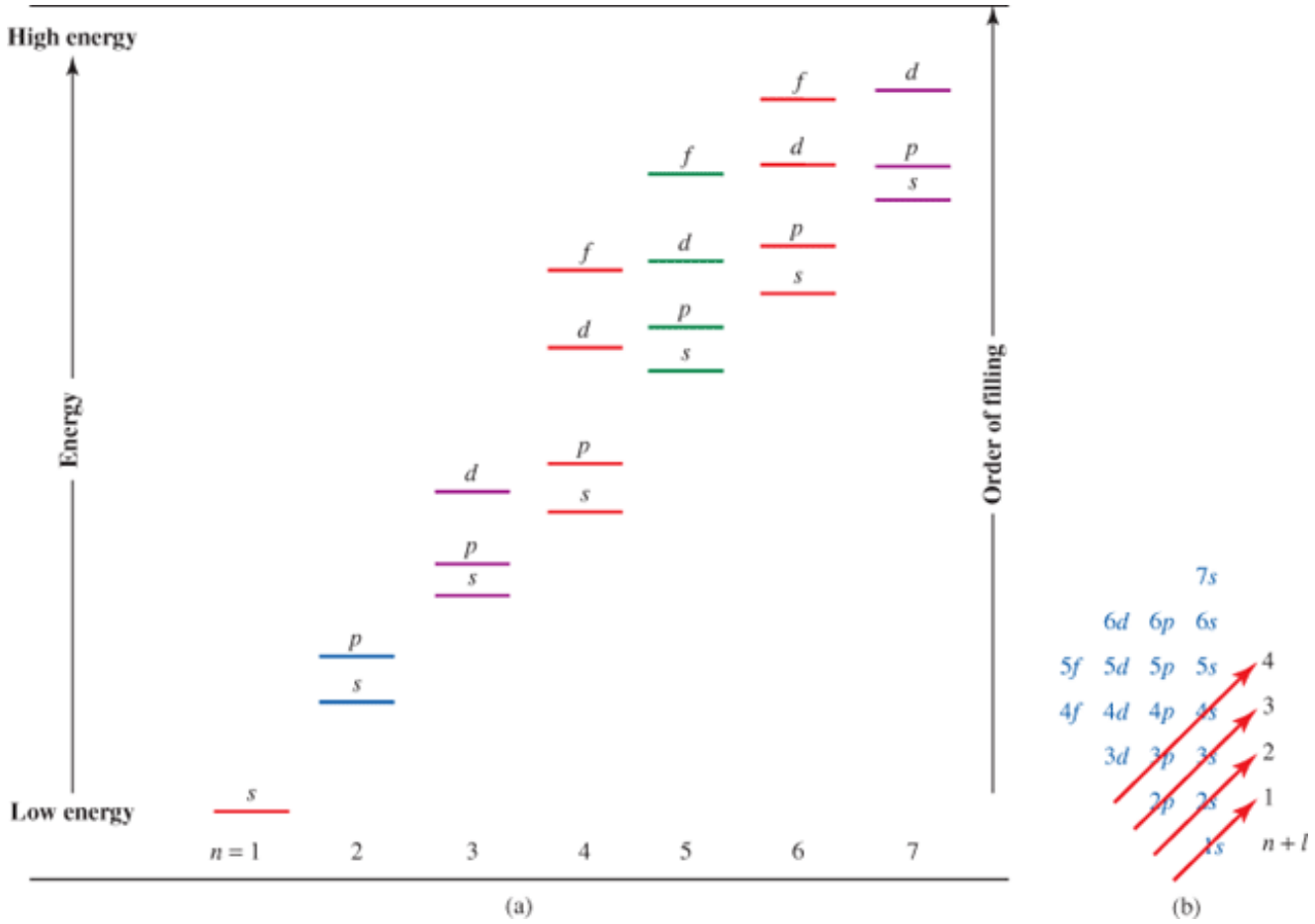


FIGURE 4.42

(a) The order of filling orbitals with electrons

(b) An easy way to remember the general order of electron filling. Orbitals fill in order of increasing ($n + l$). Where orbitals have the same value of ($n + l$), the one with the lowest n will fill first, followed by the others in increasing order of n. Note, however, for higher values of n, there are a number of exceptions to this general order (see the electron configurations given in figure 4.44).

In applying the Aufbau principle, remember that a full description of an electron requires four quantum numbers: n, l, m_l and m_s. Each combination of n and l describes one quantised energy level. Moreover, each level with $l > 1$ includes multiple orbitals, each with a different value of m_l. For any combination of n and l, all orbitals with the same value of l are degenerate, i.e. in an atom they have the same energy. For example, the 2p energy level ($n = 2$, $l = 1$) consists of three distinct p orbitals ($m_l = -1$, 0 and +1), all with the same energy. In addition, the spin quantum number, m_s, describes the two possible different spin orientations of an electron.

In other words, the 2p energy level consists of 3 orbitals with different m_l values that can hold as many as 6 electrons without violating the Pauli exclusion principle. The same is true of every set of p orbitals (3p, 4p etc.). Each set can be described by 6 different sets of quantum numbers and can therefore hold 6 electrons. A similar analysis for other values of l shows that each s energy level contains a single orbital and can hold up to 2 electrons, each d energy level consists of 5 different orbitals that can hold up to 10 electrons, and each f energy level consists of 7 different orbitals that can hold up to 14 electrons.

The Pauli exclusion and Aufbau principles dictate the length of the periods in the periodic table. After 2 electrons have been placed in the 1s orbital (He), the next electron must go in a higher energy 2s orbital (Li). After 8 additional electrons have been placed in the 2s and 2p orbitals (Ne), the next electron must go in a higher energy 3s orbital (Na). The periodic table organises atoms in rows (periods) and groups such that atoms with similar chemical properties, as indicated by their valence electron configuration, are located in the same group. Because the periodic table starts with the filling of the 1s orbital, every row has to finish before the next s orbital with higher principal quantum number has to be filled. The start of the next row is an atom with one electron in that s orbital.

Here is a summary of the conditions for atomic ground states:

1. The electrons in the atom occupy the lowest energy orbitals (see figure 4.42a).

2. No two electrons can have identical sets of quantum numbers.
3. Orbital capacities are as follows: *s* has 2 electrons; *p* set has 6 electrons; *d* set has 10 electrons; *f* set has 14 electrons.

Armed with these conditions, we can correlate the rows and columns of the periodic table with values of the quantum numbers *n* and *l*. This is shown in the periodic table in figure 4.43. Remember that the elements are arranged so that *Z* increases one unit at a time from left to right across a row. At the end of each row, we move to the next higher value of *Z* one row down on the left side of the periodic table.

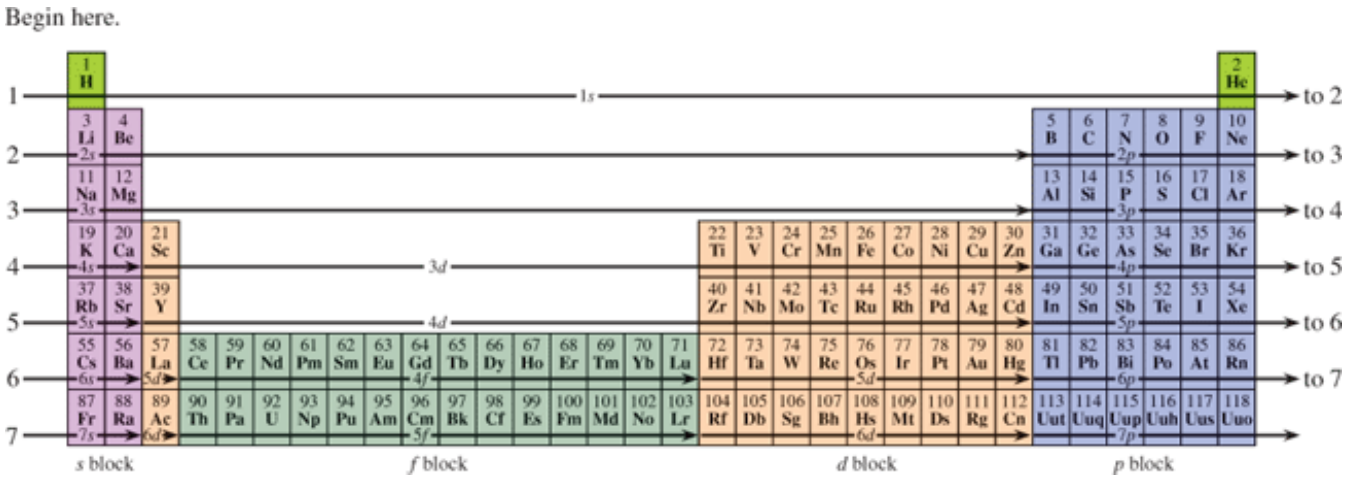


FIGURE 4.43 The periodic table in block form, showing the filling sequence of the atomic orbitals. Filling proceeds from left to right across each row and from the right end of each row to the left end of the succeeding row.

The number of elements per row increases as we increase *n*. The first period contains only hydrogen and helium. Then there are two 8-element periods, followed by two 18-element periods, and finally two 32-element periods.

In figure 4.44, each row is labelled with the highest principal quantum number of any of its occupied orbitals. For example, elements of the third row (Na to Ar) have electrons in orbitals with $n = 3$ (in addition to electrons with $n = 1$ and 2). Each column is labelled with its group number, starting with group 1 on the left and proceeding to group 18 on the right (the *f* block does not have group numbers). In general, elements in the same group of the periodic table have the same arrangement of electrons in their highest energy occupied orbitals, giving rise to their similar chemical properties.

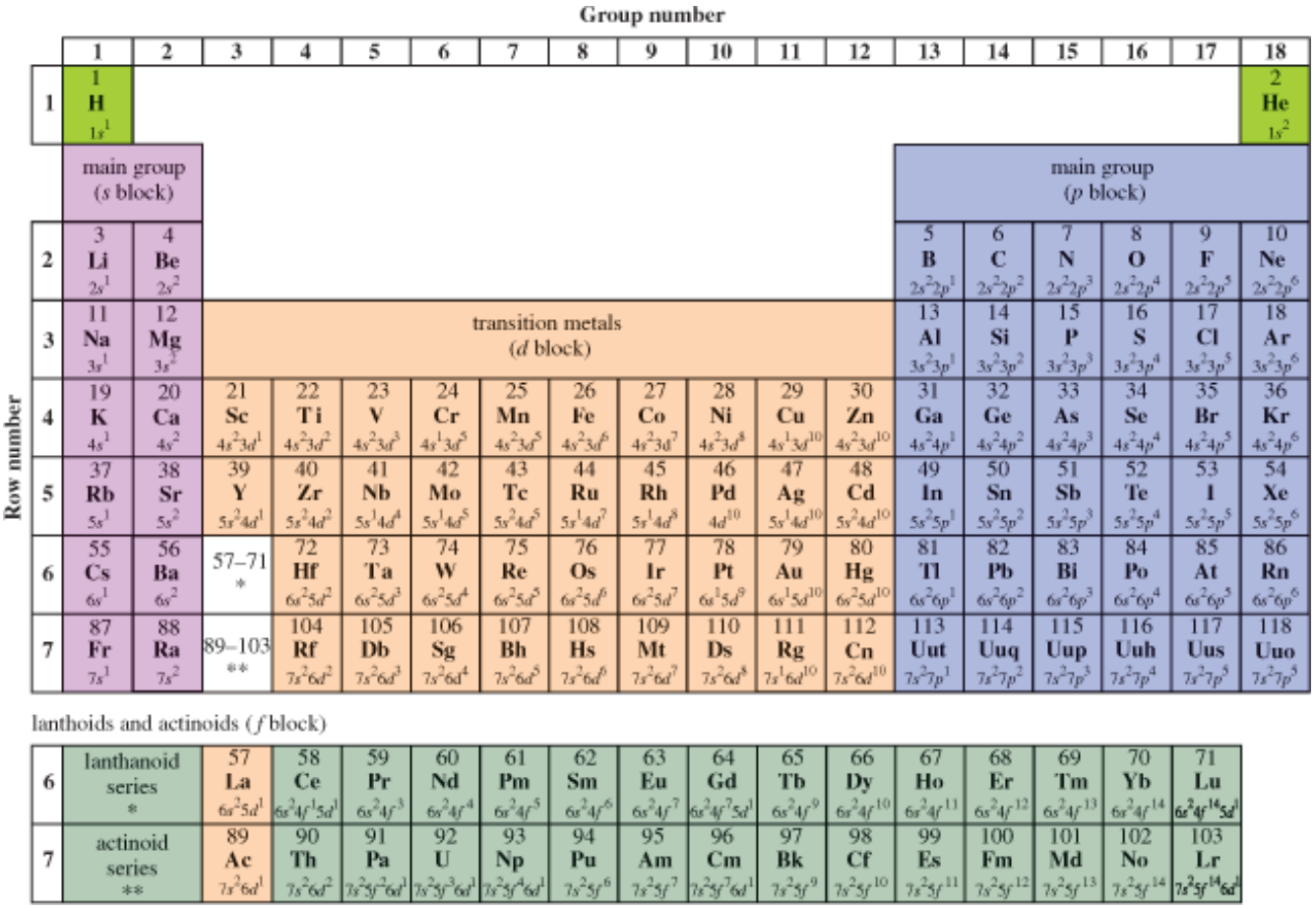


FIGURE 4.44 The periodic table with its rows and blocks labelled to show the relationship between sectors of the table and ground-state configurations. Rows are labelled with the highest principal quantum number of the occupied orbitals, and each block is labelled with the letter (*s*, *p*, *d*, *f*) indicating the orbital set that is filling. Electron configurations for elements 103–118 are tentative, and are based on the electron configurations of other elements in the same group.

Every period ends at the end of the *p* block. This indicates that, when the *np* orbitals are full, the next orbital to accept electrons is the $(n + 1)s$ orbital. For example, after filling the 3*p* orbitals from Al ($Z = 13$) to Ar ($Z = 18$), the next element, potassium, has its final electron in the 4*s* orbital rather than in one of the 3*d* orbitals. This confirms (see figure 4.42a) that the 4*s* orbital of the potassium atom is of lower energy than the 3*d* orbital. According to the Aufbau principle, the 3*d* orbitals fill after the 4*s* orbital is full, starting with scandium ($Z = 21$).

A similar situation exists at the end of the next row. When the 4*p* orbital is full (Kr, $Z = 36$), the next element (Rb, $Z = 37$) has an electron in the 5*s* orbital rather than either a 4*d* or 4*f* orbital. In fact, electrons are not added to the 4*f* orbitals until element 58, after the 5*s*, 5*p* and 6*s* orbitals have filled.

The seven *f* orbitals can hold 14 electrons, and therefore there should be 14 *f*-block elements. However, the periodic table shown in figure 4.44 shows 15 elements in both the lanthanoid and actinoid series. This reflects the debate over whether the first element in each row (La and Ac, respectively) is part of the *d* block or *f* block. Older versions of the periodic table place La and Ac directly beneath Sc and Y, giving 14 lanthanoid and actinoid elements. However, it is clear that the chemistry of both La and Ac resembles that of the lanthanoids and actinoids respectively, more than main-group or transition elements, despite their f^0 electron configurations (indeed, the terms lanthanoids and actinoids derive from lanthanum and actinum, respectively).

WORKED EXAMPLE 4.10

Orbital Filling Sequence

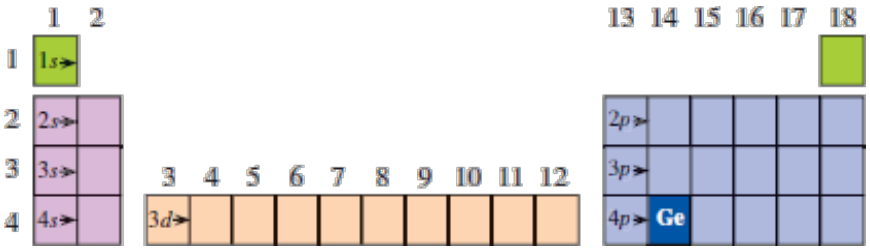
Which orbitals are filled, and which set of orbitals is partially filled, in a germanium atom?

Analysis

For this qualitative problem, use the periodic table to determine the order of orbital filling. Locate the element in a block and identify its row and column, then use figure 4.43 to establish the sequence of filled orbitals.

Solution

Germanium is element 32. Consult figure 4.43 to determine that Ge is in group 14, row 4 of the *p* block.



Starting from the top left of the periodic table and working left to right across the rows until we reach Ge, we identify the filled orbitals: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s* and 3*d*. Germanium is in row 4 of the *p* block, so the 4*p* set of orbitals is partially filled.

Is our answer reasonable?

Ge has $Z = 32$, meaning its neutral atoms contain 32 electrons. We can count how many electrons each orbital can hold: 2 for each *s* orbital, 6 for each *p* orbital set and 10 for each *d* orbital set. $2(1s) + 2(2s) + 6(2p) + 2(3s) + 6(3p) + 2(4s) + 10(3d) = 30$ electrons, leaving 2 in the partially filled 4*p* orbital set.

PRACTICE EXERCISE 4.10

Determine which orbitals are filled and which set is partially filled for the element Zr.

Valence Electrons

The chemical behaviour of an atom is determined by its size and the electrons that are accessible to an approaching chemical reagent. Accessibility has a spatial component and an energetic component. An electron is accessible *spatially* when it occupies one of the largest orbitals of the atom. Electrons on the perimeter of the atom, farthest from the nucleus, are the first ones encountered by an incoming chemical reagent. An electron is accessible *energetically* when it occupies one of the highest energy occupied orbitals of the atom. Electrons in high-energy orbitals are more chemically active than electrons in lower energy orbitals.

Similar electron accessibility generates similar chemical behaviour. For example, iodine has many more

electrons than chlorine, but these two elements display similar chemical behaviour, as reflected by their placement in the same group of the periodic table. This is because the chemistry of chlorine and iodine is determined by the number of electrons in their largest and highest energy occupied orbitals: 3*s* and 3*p* for chlorine, and 5*s* and 5*p* for iodine. Each of these elements has seven accessible electrons, and this accounts for their chemical similarities.

Accessible electrons are called **valence electrons**, and inaccessible electrons are called **core electrons**. Valence electrons may participate in chemical reactions, while core electrons do not. In general, valence electrons are those that have been added in the period of the periodic table (see figure 4.44) that the atom is located in. For example, carbon with $Z = 6$ is located in period 2, so its valence electrons are those in the 2*s* and 2*p* orbitals (totalling 4). The situation is similar for phosphorus in period 3, which has 3*s* and 3*p* valence electrons (totalling 5). Manganese in period 4 has valence electrons in the 4*s* and 3*d* orbitals (totalling 7).

The nearly equal energies of *ns* and $(n - 1)d$ orbitals create some ambiguity about valence and core electrons for elements in the *d* and *f* blocks. For example, titanium forms a chloride and an oxide with chemical formulae consistent with four valence electrons: $TiCl_4$ and TiO_2. This shows that the two 3*d* electrons of titanium participate in chemical reactions. On the other hand, zinc forms compounds, such as $ZnCl_2$ and ZnO, with only two electrons involved in its chemistry. This chemical behaviour indicates that zinc's ten 3*d* electrons, which completely fill the 3*d* orbitals, are inaccessible for chemical reactions. When the *d* orbitals are partially filled, the *d* electrons participate in chemical reactions, but, when the *d* orbitals are completely filled, the *d* electrons do not generally participate in reactions (see below for a few exceptions). The predominant oxidation state of 3+ throughout the *f*-block elements also suggests that generally only one *d* or *f* electron (see ground state configurations in figure 4.44) is accessible for chemical reactions. The definitions of core and valence electrons do not depend on whether the electrons are used in chemical reactions, but rather whether they are in an accessible energy level or not.

We find that the number of valence electrons can be determined easily from group numbers in the periodic table. For groups 1–10, the number of valence electrons equals the group number. As examples, potassium and rubidium, members of group 1, have just one valence electron each. Tungsten, in group 6, has six valence electrons: two 6*s* electrons and four 5*d* electrons. For groups 12–18, the number of valence electrons equals the group number minus 10 (the number of electrons it takes to fill the *d* orbitals). Thus, antimony and nitrogen, in group 15, have 15 - 10 = 5 valence electrons each (two *s* and three *p*). For group 11, the number of valence electrons is expected to be 1 (the one *s* electron). However, often compounds of these elements involve their *d* electrons.

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4.7 Electron Configurations

A complete specification of how an atom's electrons are distributed in its orbitals is called an **electron configuration**. There are three common ways to represent electron configurations. One is a complete specification of quantum numbers. The second is a shorthand notation from which the quantum numbers can be inferred. The third is a diagrammatic representation of orbital energy levels and their occupancies.

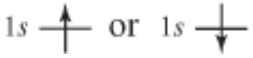
A list of the values of all quantum numbers is easy for the single electron in a hydrogen atom:

- $n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$
- $n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$

Either designation is equally valid, because under normal conditions these two states are equal in energy. In a large collection of hydrogen atoms, half the atoms have one designation and the other half have the other designation.

As the number of electrons in an atom increases, a listing of all quantum numbers quickly becomes tedious. For example, iron, with 26 electrons, would require the specification of at least 26 sets of four quantum numbers. To save time and space, chemists have devised a shorthand notation to write electron configurations. The orbital symbols (1*s*, 2*p*, 4*d* etc.) are followed by superscripts designating how many electrons are in each set of orbitals. The compact configuration for a hydrogen atom is $1s^1$, indicating 1 electron in the 1*s* orbital. For an iron atom the compact configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$.

The third way to represent an electron configuration uses an energy level diagram to designate orbitals. Each orbital is indicated by a horizontal line arranged vertically in order of increasing energy. Each electron is represented by an arrow and is placed on the appropriate horizontal line (orbital). The direction of the arrow indicates the value of m_s. By convention, we fill orbitals starting from the left-hand side, and the arrow points upward for $m_s = +\frac{1}{2}$ and downward for $m_s = -\frac{1}{2}$. The configuration of hydrogen can be represented by a single arrow in a 1*s* orbital.



A neutral helium atom has two electrons. To write the ground-state electron configuration of He, we apply the Aufbau principle. One unique set of quantum numbers is assigned to each electron, moving from the lowest energy orbital upward until all electrons have been assigned. The lowest energy orbital is always 1*s* (n = 1, l = 0, m_l = 0). Both helium electrons can occupy the 1*s* orbital, provided one of them has $m_s = +\frac{1}{2}$ and the other has $m_s = -\frac{1}{2}$. Below are the three representations of helium's ground-state electron configuration.

$n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$
$n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$

$1s^2$



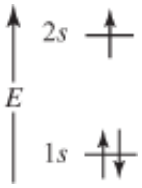
The two electrons in this configuration are said to be paired electrons, meaning that they are in the same orbital, with opposing spins. Opposing spins cancel, so paired electrons have zero net spin.

A lithium atom has three electrons. The first two electrons fill lithium's lowest possible energy level, the 1*s* orbital, and the third electron occupies the 2*s* orbital. The three representations for the ground-state

electron configuration of a lithium atom are shown below.

$n = 2,\ l = 0,\ m_l = 0,\ m_s = +\frac{1}{2}$
$n = 1,\ l = 0,\ m_l = 0,\ m_s = +\frac{1}{2}$
$n = 1,\ l = 0,\ m_l = 0,\ m_s = -\frac{1}{2}$

$1s^2 2s^1$



The set $n = 2$, $l = 0$, $m_l = 0$, $m_s = -\frac{1}{2}$ is equally valid for the third electron.

The next atoms of the periodic table are beryllium and boron. You should be able to write the three different representations (the set of quantum numbers, the shorthand notation and the energy level diagram) for the ground-state configurations of these elements. The filling principles are the same as we move to higher atomic numbers.

WORKED EXAMPLE 4.11

An Electron Configuration

Construct an energy level diagram and the shorthand notation of the ground-state configuration of aluminium. Provide one set of valid quantum numbers for the highest-energy electron.

Analysis

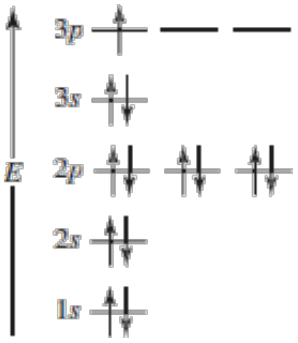
First consult the periodic table to locate aluminium and determine how many electrons are present in a neutral atom. Then construct the electron configuration using the patterns of the periodic table.

Solution

Aluminium has $Z = 13$, so a neutral atom of Al has 13 electrons. Place the 13 electrons sequentially, using arrows, into the lowest energy orbitals available. The $n = 1$ orbital is filled by two electrons, eight electrons fill the $n = 2$ orbitals, two electrons fill the 3*s* orbital, and one electron goes in a 3*p* orbital.

The last electron could be placed in any of the 3*p* orbitals, because these three orbitals are equal in energy. The final electron could also be given either spin orientation. By convention, we place electrons in unfilled orbitals starting with the left-hand side, with spins pointed up.

The shorthand notation is $1s^2 2s^2 2p^6 3s^2 3p^1$.



The highest energy electron is in a 3*p* orbital, meaning $n = 3$ and $l = 1$. The value of m_l can be any of three values: +1, -1 or 0. The spin quantum number, m_s, can be $+\frac{1}{2}$ or $-\frac{1}{2}$. One valid set of quantum numbers is:

$$n = 3, l = 1, m_l = 1, m_s = +\frac{1}{2}$$

You should be able to write the other five possible sets.

Is our answer reasonable?

Aluminium, in group 13, has three valence electrons. The configurations show three electrons with $n = 3$, so the configuration is consistent with the valence electron count.

PRACTICE EXERCISE 4.11

Determine the energy level diagram and shorthand notation for the electron configuration of the fluorine atom.

Electron configurations become longer as the number of electrons increases. To make the writing of a configuration even more compact, chemists make use of the regular pattern for the electrons with lower principal quantum numbers. Compare the configurations of neon and aluminium shown below.

Ne (10 electrons) $1s^2 2s^2 2p^6$

Al (13 electrons) $1s^2 2s^2 2p^6 3s^2 3p^1$

The description of the first 10 electrons in the configuration of aluminium is identical to that of neon. We can take advantage of this pattern and represent that portion as [Ne]. With this notation, the configuration of Al becomes [Ne]$3s^2 3p^1$. The element at the end of each row of the periodic table has a **noble gas configuration**. These configurations can be written in the following shorthand notation.

Notation	Configuration	Element
[He]	$1s^2$	He (2 electrons)
[Ne]	[He]$2s^2 2p^6$	Ne (10 electrons)
[Ar]	[Ne]$3s^2 3p^6$	Ar (18 electrons)
[Kr]	[Ar]$4s^2 3d^{10} 4p^6$	Kr (36 electrons)
[Xe]	[Kr]$5s^2 4d^{10} 5p^6$	Xe (54 electrons)
[Rn]	[Xe]$6s^2 5d^{10} 4f^{14} 6p^6$	Rn (86 electrons)

To write the configuration of any other element, we first consult the periodic table to find its location relative to the noble gases. Then we specify the configuration of the preceding noble gas and build the remaining portion of the configuration according to the Aufbau principle.

A Shorthand Electron Configuration

Determine the electron configuration of indium, first in shorthand form and then in full form.

Analysis

Locate the element in the periodic table, and find the nearest noble gas with a smaller atomic number. Start with the electron configuration of that noble gas, and add enough additional electrons to the next-filling orbitals to give the neutral atom.

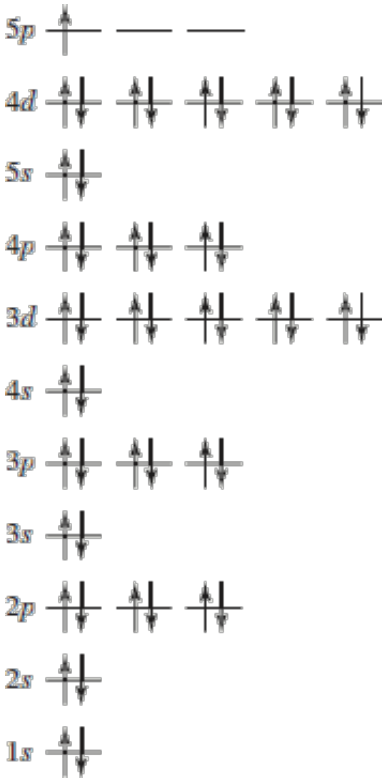
Solution Indium, In, ($Z = 49$) is in row 5, group 13. The nearest noble gas of smaller Z is Kr ($Z = 36$). Thus, the configuration of In has 36 electrons in the Kr configuration and 13 additional electrons. The last orbital to fill in Kr is 4*p*, and the periodic table shows that the next orbitals to fill are the 5*s*, 4*d* and 5*p* orbitals.

Configuration of indium: $[Kr]5s^2 4d^{10} 5p^1$

To write the full configuration, expand the krypton configuration.

$[Kr] = [Ar]4s^2 3d^{10} 4p^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

Full configuration of In (49 electrons): $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^1$



Note that it is usual to indicate empty orbitals in an energy level diagram when they are part of a set of degenerate orbitals. For example, in the energy level diagram above, we show the two empty *p* orbitals of the 5*p* set because one of the set contains a single electron.

Is our answer reasonable?

Indium, in group 13, has three valence electrons. The configurations show three electrons with $n = 5$, so the configuration is consistent with the valence electron count.

PRACTICE EXERCISE 4.12

Determine the compact notation for the electron configuration of the cadmium atom.

Electron–electron Repulsion

The Aufbau principle allows us to assign quantum numbers to aluminium's 13 electrons without ambiguity. The first 12 electrons fill the 1*s*, 2*s*, 2*p* and 3*s* energy levels, and the last electron can occupy any 3*p* orbital with either spin orientation. But what happens when more than one electron must be placed in a *p* energy level? Carbon atoms, for example, have six electrons, two of which occupy 2*p* orbitals. How should these two electrons be arranged in the 2*p* orbitals? As figure 4.45 shows, three different arrangements (of the 15 possible) of these electrons obey the Pauli exclusion principle:

1. The electrons could be paired in the same 2*p* orbital (same m_l value but different m_s values).
2. The electrons could occupy different 2*p* orbitals with opposite spin orientations (different m_l values and different m_s values).
3. The electrons could occupy different 2*p* orbitals with the same spin orientation (different m_l values but the same m_s value).

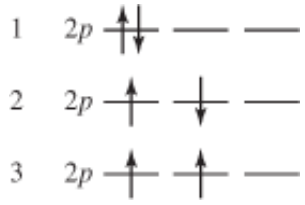


FIGURE 4.45 Three different arrangements of two 2*p* electrons that obey the Pauli exclusion principle.

These three arrangements have different energies because electrons that are close together repel each other more than electrons that are far apart. As a result, for two or more degenerate orbitals, the lowest energy situation results when electrons occupy the orbitals that keep them furthest apart. Placing two electrons in different *p* orbitals keeps them relatively far apart, so an atom is of lower energy with the two electrons in different *p* orbitals. Thus, arrangements 2 and 3 are of lower energy than arrangement 1.

Arrangements 2 and 3 look spatially equivalent, but experiments show that a configuration that gives unpaired electrons the same spin orientation is always of lower energy than one that gives them opposite orientations. **Hund's rule** summarises the way in which electrons occupy orbitals of equal energies. *The lowest energy configuration involving orbitals of equal energies is the one with the maximum number of electrons with the same spin orientation.*

According to Hund's rule, arrangement 3 of figure 4.45 is consistent with the ground-state configuration for carbon atoms.

Applying Hund's Rule

Write the shorthand electron configuration and draw the ground-state orbital energy level diagram for the valence electrons in a sulfur atom.

Analysis

From the periodic table, we see that sulfur has 16 electrons and is in the *p* block, group 16. To build the ground-state configuration, apply the Aufbau and the Pauli exclusion principles and then apply Hund's rule if needed.

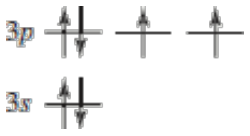
Solution

The first 12 electrons fill the four lowest energy orbitals.

$$1s^2 2s^2 2p^6 3s^2$$

Sulfur's remaining four electrons occupy the three 3*p* orbitals. The complete configuration is $1s^2 2s^2 2p^6 3s^2 3p^4$ or $[\text{Ne}]3s^2 3p^4$.

To minimise electron–electron repulsion, put three of the 3*p* electrons in different orbitals, all with the same spin, and then place the fourth electron, with opposite spin, in the first orbital. In accord with Hund's rule, this gives the same value of m_s to all electrons that are not paired. Below is the energy level diagram for sulfur's valence electrons.



Is our answer reasonable?

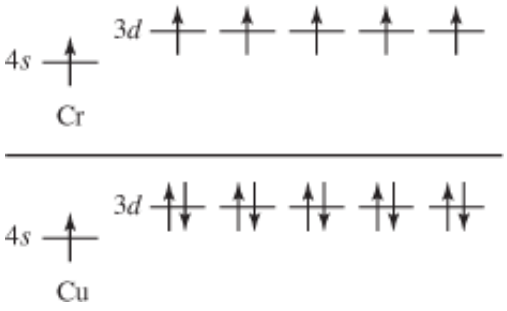
Sulfur, in row 3 and group 16, has six valence electrons. The configurations show six electrons with $n = 3$, so the configuration is consistent with the valence electron count. The electrons are spread among the three 3*p* orbitals, which minimises electron–electron repulsion.

PRACTICE EXERCISE 4.13

Determine the compact electron configuration for the nitrogen atom and write one valid set of quantum numbers for its valence electrons.

Orbitals with Nearly Equal Energies

The filling order embodied in the periodic table predicts a regular progression of ground-state configurations. Experiments show, however, that some elements have ground-state configurations different from the predictions of the regular progression. Among the first 40 elements, there are only two exceptions: copper and chromium. Chromium ($Z = 24$) is in group 6, four elements into the *d* block. We would predict that the ground-state valence configuration of chromium should be $4s^2 3d^4$. Instead, experiments show that the ground-state configuration of this element is $4s^1 3d^5$. Likewise, the configuration of copper ($Z = 29$) is $4s^1 3d^{10}$ rather than the predicted $4s^2 3d^9$.



Look again at figure 4.42a, which shows that these two sets of orbitals are nearly the same in energy. Each $(n - 1)d$ orbital has nearly the same energy as its *ns* counterpart. In addition, each $(n - 2)f$ orbital has nearly the same energy as its $(n - 1)d$ counterpart. Table 4.3 lists these orbitals and the atomic numbers for which the filling sequence differs from the expected pattern. These configurations are also indicated in figure 4.44.

TABLE 4.3 Atomic orbitals with nearly equal energies

Orbitals	Atomic numbers affected	Example
4*s*, 3*d*	24, 29	Cr: [Ar]$4s^1 3d^5$
5*s*, 4*d*	41, 42, 44, 45, 46, 47	Ru: [Kr]$5s^1 4d^7$
6*s*, 5*d*, 4*f*	57, 58, 64, 78, 79	Au: [Xe]$6s^1 4f^{14} 5d^{10}$
6*d*, 5*f*	89, 91–93, 96	U: [Rn]$7s^2 5f^3 f 6d^1$

Often, an *s* orbital contains only one electron rather than two. Five of the exceptional ground-state configurations have a common pattern and are easy to remember: Cr and Mo are $s^1 d^5$, and Cu, Ag and Au are $s^1 d^{10}$. The other exceptional cases follow no recognisable patterns, because they are generated by subtle interactions between all the electrons. Among elements with valence electrons filling orbitals with nearly equal energies, several factors help to determine the ground-state configuration. The details are beyond the scope of this book, except that you should recognise that even a subtle change can cause variations in the filling pattern predicted by the periodic table.

Configurations of Ions

The electron configurations of atomic ions are written using the same procedure as for neutral atoms, taking into account the proper number of electrons. An anion has one additional electron for each unit of negative charge. A cation has one fewer electron for each unit of positive charge.

For most atomic ions, the electron configuration can be deduced easily from that of the corresponding neutral atom. For example, Na^+, Ne and F^- all contain 10 electrons, and each has the configuration $1s^2 2s^2 2p^6$. Atoms and ions that have the same number of electrons are said to be **isoelectronic**.

In general, you would expect that the last electron to be added would be the first electron to be lost on ionisation. The nearly equal energies of *ns* and (*n* - 1)*d* orbitals causes the configurations of some cations to differ from the configurations predicted by the filling pattern of the periodic table. Remember that the energy ranking of orbitals such as 4*s* and 3*d* depends on a balance of several factors, and that even a small variation in that balance can change the order of the orbitals. This feature is particularly important for the transition metals, for which the *d* orbitals are occupied. Experiments show that in transition metal cations the (*n* - 1)*d* orbitals are *always* of lower energy than the *ns* orbitals; therefore, the first electrons are lost from the *s* orbital before those in *d* orbitals. For example, an Fe^{3+} cation contains 23 electrons. The first 18 electrons fill the 1*s*, 2*s*, 2*p*, 3*s* and 3*p* orbitals, as predicted by the periodic table. However, the five remaining electrons populate the 3*d* set, leaving the 4*s* orbital empty. Thus the configuration of the Fe^{3+} cation is $[Ar]3d^5$.

Vanadium, V, atoms ($[Ar]4s^2 3d^3$) and Fe^{3+} cations ($[Ar]3d^5$) have different configurations, even though each has 23 electrons as shown in figure 4.46.

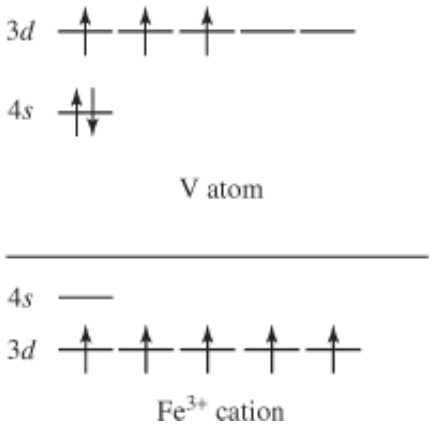


FIGURE 4.46 Transition metal atoms and cations have different valence-electron configurations, even when the species contain the same number of electrons.

WORKED EXAMPLE 4.14

Configuration of a Cation

What is the ground-state electron configuration of a Cr^{3+} cation?

Analysis

Use the Aufbau principle, remembering that because Cr is a transition metal, its 4*s* orbital will be emptied before the 3*d* orbital.

Solution A neutral chromium atom has 24 electrons, so the corresponding Cr^{3+} cation has 21 electrons. The first 18 electrons follow the usual filling order to give the argon core configuration: $1s^2 2s^2 2p^6 3s^2 3p^6$, or [Ar]. Place the remaining three electrons in the 3*d* set of orbitals, following Hund's rule: $[Ar]3d^3$.



Is our answer reasonable?

For any transition metal cation, the empty 4*s* orbital is slightly higher in energy than the partially filled 3*d* orbital. Thus, the isoelectronic V^{2+} and Cr^{3+} cations both have the [Ar]$3d^3$ configuration. On the other hand, the isoelectronic neutral atom scandium has the configuration [Ar]$4s^2 3d^1$.

PRACTICE EXERCISE 4.14

Determine the ground-state electron configuration (compact form) of a Ru^{3+} cation.

We can summarise the discussion in this section into guidelines for building atomic or ionic electron configurations:

1. Count the total number of electrons.
    a. Add electrons for anions.
    b. Subtract electrons for cations.
2. Fill orbitals to match the nearest noble gas of smaller atomic number.
3. Add remaining electrons to the next orbitals to be filled according to the Pauli exclusion and Aufbau principles, as well as Hund's rule.
    a. For neutral atoms and anions, place electrons in *ns* before $(n - 1)d$ and $(n - 2)f$).
    b. For cations, determine the electron configuration for the neutral atom and remove the required number of electrons with the highest energy.
4. Look for exceptions and correct the configuration if necessary.

Magnetic Properties of Atoms

How do we know that an Fe^{3+} ion in its ground state has the configuration [Ar]$3d^5$ rather than the [Ar]$4s^2 3d^3$ configuration predicted by the orbital filling sequence? Remember that electron spin gives rise to magnetic properties. Consequently, any atom or ion with unpaired electrons has non-zero net spin and is attracted by a strong magnet. We can divide the electrons of an atom or ion into two categories with different spin characteristics. In filled orbitals, all the electrons are paired. Each electron with spin orientation $+\frac{1}{2}$ has a partner with spin orientation $-\frac{1}{2}$. The spins of these electrons cancel each other, giving a net spin of zero. An atom or ion with all electrons paired is not attracted by strong magnets and is termed **diamagnetic**. In contrast, spins do not cancel when unpaired electrons are present (in the ground state of an atom with spins aligned in the same direction). An atom or ion with unpaired electrons is attracted to strong magnets and is called **paramagnetic**. Moreover, the spins of all the unpaired electrons are additive, so the amount of paramagnetism shown by an atom or ion is

proportional to the number of unpaired spins.

In Fe^{3+}, Hund's rule dictates that the five *d* electrons all have the same spin orientation. For these five electrons, the spins all act together, giving a net spin of $5 \times \frac{1}{2} = \frac{5}{2}$. The alternative configuration for Fe^{3+}, $[Ar]4s^2 3d^3$, is paramagnetic, too, but its net spin is $3 \times \frac{1}{2} = \frac{3}{2}$ as it has only three unpaired electrons. Experiments show that Fe^{3+} has a net spin of $\frac{5}{2}$. In fact, magnetic measurements on a wide range of transition metal cations are all consistent with the $(n - 1)d$ orbitals being occupied rather than the *ns* orbital.

WORKED EXAMPLE 4.15

Unpaired Electrons

Which of these species is paramagnetic: F^-, Zn^{2+} or Ti?

Analysis

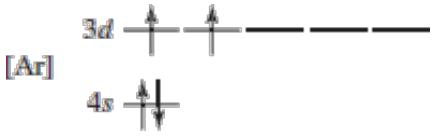
Paramagnetism results from unpaired spins, which exist only in partially filled sets of orbitals. We need to build the configurations and then look for any orbitals that are partially filled.

Solution

F^-: A fluorine atom has 9 electrons, so F^- has 10 electrons. The configuration is $1s^2 2s^2 2p^6$. There are no partially filled orbitals, so the fluoride ion is diamagnetic.

Zn^{2+}: The parent zinc atom has 30 electrons, and the cation has 28, so the configuration for Zn^{2+} is $[Ar]3d^{10}$. Again, there are no partially filled orbitals, so this ion is also diamagnetic.

Ti: A neutral titanium atom has 22 electrons. The ground-state configuration is $[Ar]4s^2 3d^2$. The spins of the 4*s* electrons cancel, but the two electrons in 3*d* orbitals have the same spin orientation, so their effect is additive. This ion is paramagnetic, with a net spin of $\frac{1}{2} + \frac{1}{2} = 1$.



Is our answer reasonable?

Filled orbitals always have all electrons paired, and two of these three species have no partially filled orbitals. Only Ti has a partially filled orbital set.

PRACTICE EXERCISE 4.15

Most transition metal cations are paramagnetic. Which cations in the first transition metal series have net charges less than +4 and are exceptions to this generalisation?

The ground-state configurations of most neutral atoms and many ions contain unpaired electrons, so we might expect most materials to be paramagnetic. On the contrary, most substances are diamagnetic. This is because stable substances seldom contain free atoms. Instead, in molecular substances, atoms are bonded together through pairing of electrons to give molecules (see chapter 5), and such bonding results in the cancellation of overall spin. As a result, paramagnetism is observed primarily among compounds of the transition and lanthanoid metals, whose cations have partially filled *d* and *f* orbitals. We will examine the magnetic properties of transition metal complexes in detail in chapter 13.

Excited States

The ground-state configuration is the lowest energy arrangement of electrons, so an atom or ion will usually have this configuration. When an atom absorbs energy, however, it can reach an excited state with a new electron configuration. For example, sodium atoms normally have the ground-state configuration [Ne]$3s^1$, but when sodium atoms are in the gas phase, an electrical discharge can induce transfer of the 3*s* electron to a higher-energy orbital, such as 4*p*. Excited atoms are unstable and spontaneously return to the ground-state configuration, giving up their excess energy in the process.

Excited-state configurations are perfectly valid as long as they meet the restrictions given in table 4.2. In the electrical discharge of a sodium-vapour lamp, for instance, we find some sodium atoms in excited states with configurations such as $1s^2 2s^2 2p^6 3p^1$ or $1s^2 2s^2 2p^5 3s^2$. These configurations use valid orbitals and are in accord with the Pauli exclusion principle, but they describe atoms that are of higher energy than those in the ground state. It should be noted that both the Aufbau principle and Hund's rule can be violated when writing excited-state electronic configurations, but the Pauli exclusion principle must *always* be obeyed.

Excited states play important roles in chemistry. Properties of atoms can be studied by observing excited states. In fact, chemists and physicists use the characteristics of excited states extensively to probe the structure and reactivity of atoms, ions and molecules. Excited states also have practical applications. For example, sodium-vapour lamps, which are used for street lighting, use the emissions from excited sodium atoms returning to their ground states, and the dazzling colours of a fireworks display come from photons emitted by various metal ions in excited states.

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4.8 Periodicity of Atomic Properties

The periodicity of physical and chemical properties, which is summarised in the periodic table of the elements, is one of the most useful organising principles in chemistry. The regular periodic trends can be explained using electron configurations and nuclear charges. The most important of those trends is the atomic radius, which we will discuss first, since it influences all other periodic trends.

Atomic Radii

The size of an atom is determined by its electron cloud and therefore by the sizes of its orbitals. As we have seen earlier, these sizes are determined by a number of factors, including effective nuclear charge (Z_{eff}), orbital energy and electron distribution.

Assume you are moving from left to right across period 2 of the periodic table ($n = 2$). While Z increases, the electrons that are added do not shield the increasing nuclear charge effectively, so Z_{eff} increases. A larger Z_{eff} exerts a stronger electrostatic attraction on the electron cloud, and this results in smaller orbitals. Moving from *left to right* across that period, orbitals become *smaller and of lower energy*.

Now assume you proceed down group 1 of the periodic table. As n increases, we would expect orbitals to increase in energy and become larger. However, as Z increases, we would expect orbitals to become smaller and decrease in energy. Which trend dominates here? Recall that the number of core electrons increases as we move down any group. For example, sodium ($Z = 11$) has 10 core electrons and 1 valence electron. In the next period, potassium ($Z = 19$) has 18 core electrons and 1 valence electron. The shielding provided by potassium's additional 8 core electrons largely cancels the effect of the additional 8 protons in its nucleus. Consequently, increased shielding largely offsets the increase in Z value from one period to the next and, therefore, valence orbitals become larger and increase in energy from top to bottom of a group.

In summary we can say that *atomic size decreases from left to right and increases from top to bottom of the periodic table* (figure 4.47).

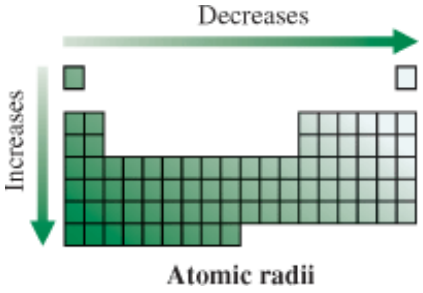


FIGURE 4.47 Representation of the periodic table showing that atomic radius decreases from left to right within a row and increases from top to bottom within a group.

A convenient measure of atomic size is the radius of the atom. Figure 4.48 shows the trends in **atomic radii**. For example, the atomic radius decreases smoothly across the third period, from 186 pm for sodium to 97 pm for argon (blue arrow). The atomic radius increases smoothly down group 1, from 152 pm for lithium to 265 pm for caesium (red arrow). Notice, however, that the atomic radius changes very little across the *d* and *f* blocks. This is due to shielding. For these elements, the largest orbital is the filled *ns* orbital. Moving from left to right across a row, Z increases, but electrons add to the smaller $(n - 1)d$ or $(n - 2)f$ orbitals. An increase in Z by 1 unit is matched by the addition of 1 shielding electron. From the perspective of the outlying *s* orbital, the increases in Z are balanced by increased shielding from the added *d* or *f* electrons. Thus, the electron in the outermost occupied orbital, *ns*, is subject to an effective nuclear charge that changes very little across these blocks. As a consequence, the relative changes in atomic size across the *d* and *f* blocks are much smaller than those found in the *s* and *p* blocks.

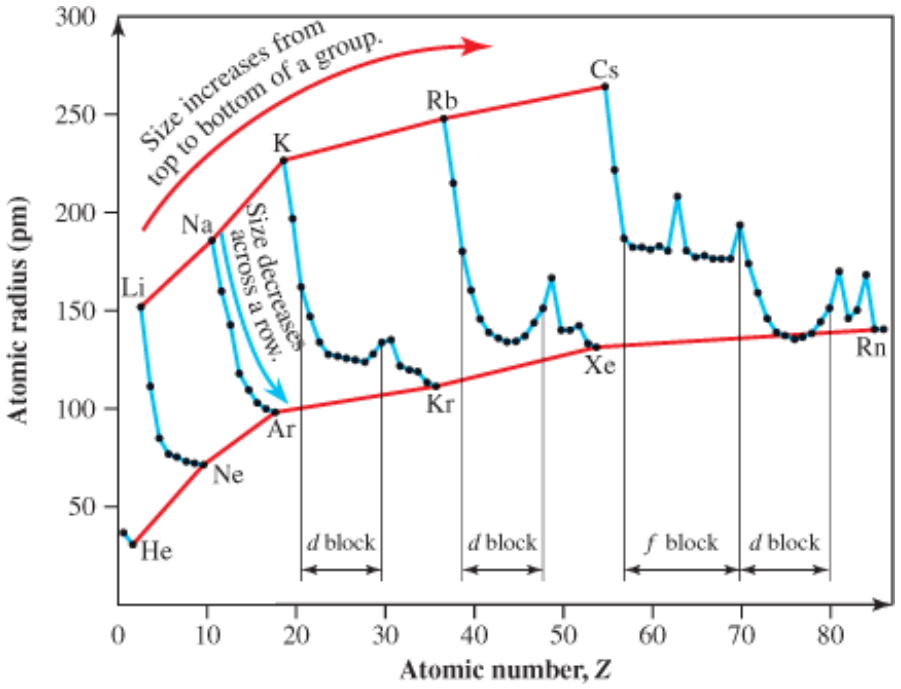


FIGURE 4.48 The radii of atoms vary in periodic fashion (data are for atoms in the gas phase). Atomic radius decreases from left to right within any row (blue lines) and increases from top to bottom within any group (red lines).

A knowledge of periodic trends in physical and chemical properties and an understanding of the principles that give rise to these trends are important since they enable you, for example, to predict certain chemical behaviours, even if you are not familiar with a particular element.

WORKED EXAMPLE 4.16

Trends in Atomic Radii

For each of the following pairs, predict which atom is larger and explain why:

(a) Si or Cl,

(b) S or Se and

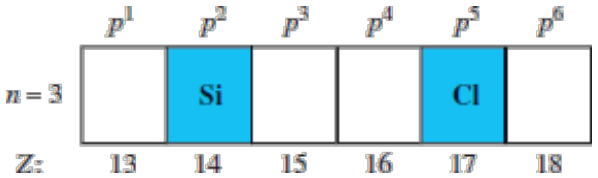
(c) Mo or Ag.

Analysis

Qualitative predictions about atomic size can be made on the basis of an atom's position in the periodic table.

Solution

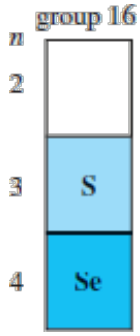
(a) Silicon and chlorine are in the third row of the periodic table.



Chlorine's nuclear charge (+17) is larger than silicon's (+14), so chlorine's nucleus exerts a

stronger pull on its electron cloud. Chlorine also has three more electrons than silicon, which increases the possibility that shielding effects could counter the extra nuclear charge. Remember, however, that electrons in the same type of orbital do a poor job of shielding one another from the nuclear charge. For Si and Cl, shielding comes mainly from the core electrons, not from the electrons in the 3*p* orbitals. Because shielding effects are similar for these elements, the effective nuclear charge increases from Si to Cl. Therefore, we conclude that chlorine, with its greater nuclear attraction for the electron cloud, is the smaller atom.

(b) Sulfur and selenium are in group 16 of the periodic table. Although they both have the s^2p^2 valence configurations, selenium's least stable electrons are in orbitals with a larger *n* value. Orbital size increases with *n*. Selenium also has a greater nuclear charge than sulfur, which raises the possibility that nuclear attraction could offset increased *n*.



Remember, however, that much of this extra nuclear charge is offset by the shielding influence of the core electrons. Selenium has 18 core electrons and sulfur has 10. Thus, we conclude that selenium, with its larger *n* value, is larger than sulfur.

(c) Molybdenum and silver are in the same row of the *d* block.



They have the following configurations.

$$\text{Mo} = [\text{Kr}]5s^14d^5 \quad \text{Ag} = [\text{Kr}]5s^14d^{10}$$

In each case, 5*s* is the largest occupied orbital (see p. 132 for an explanation.) The 4*d* orbitals are smaller, with their electron density located mostly inside the 5*s* orbital. Consequently, 4*d* is effective at shielding 5*s*. The nuclear charge of silver is five units larger than that of molybdenum, but silver also has five extra shielding electrons in *d* orbitals. These offset the extra nuclear charge, making Mo and Ag nearly the same size.

Is our answer reasonable?

The trends in figure 4.48 confirm the results. Chlorine lies to the right of silicon in the same row of the periodic table. Size decreases from left to right in any row; thus, chlorine is smaller than silicon. Selenium is immediately below sulfur in the same column of the periodic table. Size increases down a column; thus, selenium is larger than sulfur. Molybdenum and silver occupy the same row of the *d* block of the periodic table, across which size changes relatively little; thus, molybdenum and silver are nearly the same size.

PRACTICE EXERCISE 4.16

Use periodic trends to determine which of the

following are smaller than As and which are larger: P, Ge, Se and Sb.

Ionisation Energy

When an atom absorbs a photon, the gain in energy promotes an electron to a higher energy orbital in which the electron is, on average, further from the nucleus and therefore experiences less electrical attraction to the nucleus. If the absorbed photon has enough energy, an electron can be ejected from the atom.

The minimum amount of energy needed to remove an electron from a neutral atom is the first ionisation energy (E_{i1}). Ionisation energies are measured for gaseous elements to ensure that the atoms are isolated from one another.

Variations in ionisation energy mirror variations in orbital energy, because an electron in a higher energy orbital is easier to remove than one in a lower energy orbital.

Figures 4.49 and 4.50 show how the first ionisation energies of gaseous atoms vary with atomic number. Notice the general trends in ionisation energy. Ionisation energy increases from left to right across each period (third period: 496 kJ mol^{-1} for Na to 1520 kJ mol^{-1} for Ar) and decreases from top to bottom of each group (group 18: 2372 kJ mol^{-1} for He to 1037 kJ mol^{-1} for Rn). As with atomic radius, ionisation energy changes less for elements in the *d* and *f* blocks, because increased shielding from the *d* and *f* orbitals offsets increases in *Z*. As a rule of thumb, the trend in the ionisation energies is inverse to that of the atomic radii, i.e. smaller atoms have higher ionisation energies. Therefore, the trend in the ionisation energies can be rationalised in similar fashion.

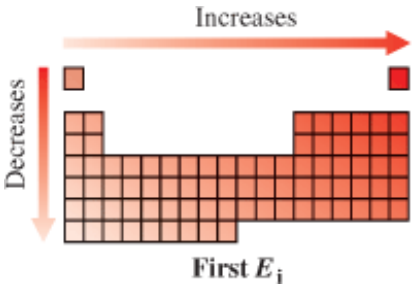


FIGURE 4.49 Representation of the periodic table showing that first ionisation energy increases from left to right within a row and decreases from top to bottom within a group.

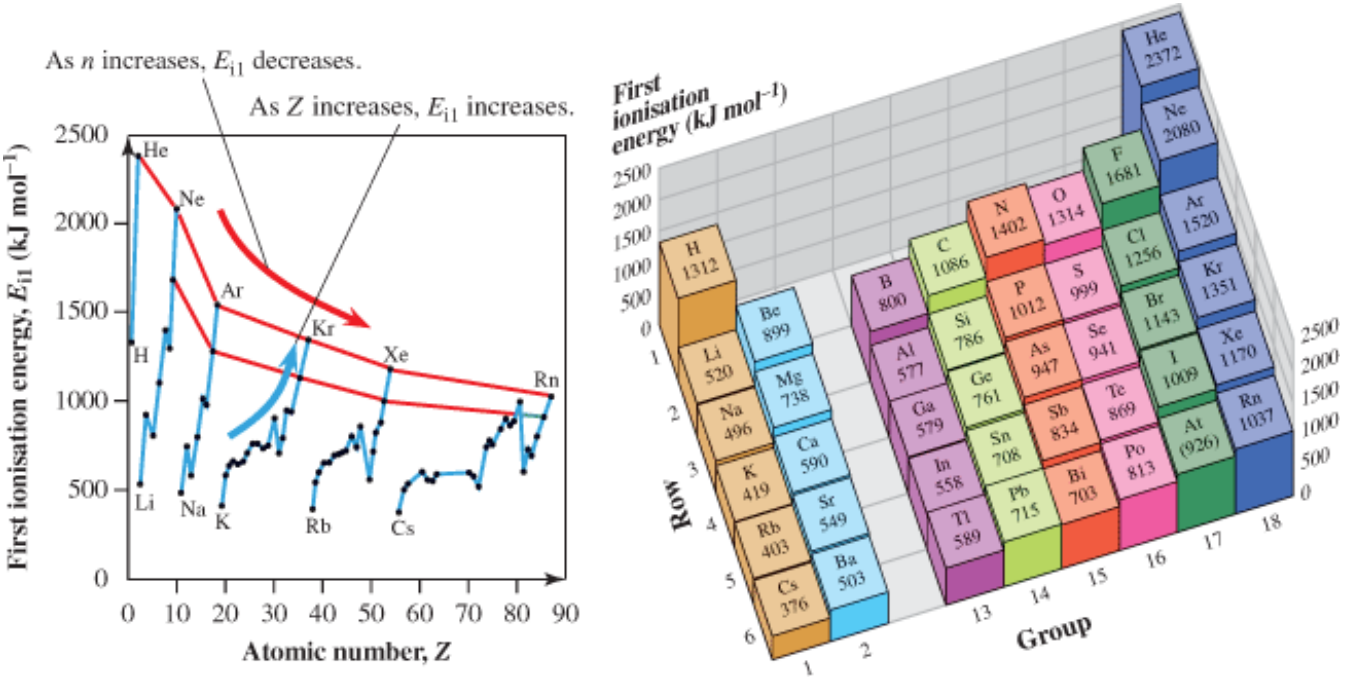


FIGURE 4.50 The first ionisation energy generally increases from left to right across a period (blue arrow) and decreases from top to bottom down a group (red arrow) of the periodic table.

Higher Ionisations

A multi-electron atom can lose more than one electron, but ionisation becomes more difficult as cationic charge increases. The first three ionisation energies for a magnesium atom in the gas phase provide an illustration.

Process			Configurations			E_i
$Mg(g)$	$\rightarrow$	$Mg^+(g) + e^-$	$[Ne]3s^2$	$\rightarrow$	$[Ne]3s^1$	738 kJ mol^{-1}
$Mg^+(g)$	$\rightarrow$	$Mg^{2+}(g) + e^-$	$[Ne]3s^1$	$\rightarrow$	$[Ne]$	1450 kJ mol^{-1}
$Mg^{2+}(g)$	$\rightarrow$	$Mg^{3+}(g) + e^-$	$[Ne]$	$\rightarrow$	$[He]2s^22p^5$	7730 kJ mol^{-1}

Notice that the second ionisation energy of magnesium is almost twice as large as the first, even though each electron is removed from a 3*s* orbital. This is because Z_{eff} increases as the number of electrons decreases. That is, the positive charge on the magnesium nucleus remains the same throughout the ionisation process, but the net charge of the electron cloud decreases with each successive ionisation. As the number of electrons decreases, each electron feels a greater electrostatic attraction to the nucleus (due to minimised electron–electron repulsion), resulting in a larger ionisation energy.

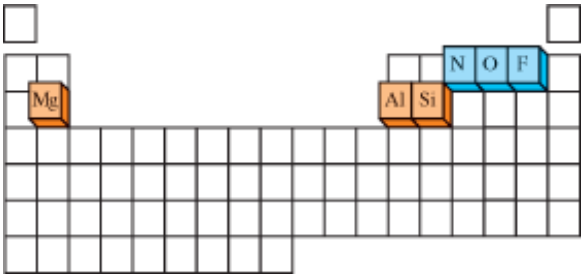
The third ionisation energy of magnesium is more than 10 times the first ionisation energy. This large increase occurs because the third ionisation removes a core electron (2*p*) rather than a valence electron (3*s*). Removing core electrons from any atom requires much more energy than removing valence electrons. The second ionisation energy of any group 1 metal is substantially larger than the first ionisation energy; the third ionisation energy of any group 2 metal is substantially larger than the first or second ionisation energy, and so on. Appendix G gives the first three ionisation energies for the first 36 elements.

Irregularities in Ionisation Energies

Ionisation energies deviate somewhat from smooth periodic behaviour. These deviations can be attributed to shielding effects and electron–electron repulsion. Aluminium, for example, has a smaller first ionisation energy than either of its neighbours in row 3 (see figure 4.48).

Element	Z	Atom configuration	E_{i1}	Cation configuration
Mg	12	$[Ne]3s^2$	738 kJ mol^{-1}	$[Ne]3s^1$
Al	13	$[Ne]3s^23p^1$	577 kJ mol^{-1}	$[Ne]3s^2$
Si	14	$[Ne]3s^23p^2$	786 kJ mol^{-1}	$[Ne]3s^23p^1$

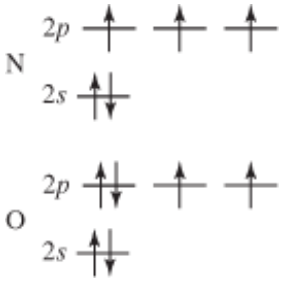
The configurations of these elements show that a 3*s* electron must be removed to ionise magnesium, whereas a 3*p* electron must be removed to ionise aluminium or silicon. Shielding makes the 3*p* orbitals of significantly higher energy than a 3*s* orbital, and this difference in energy more than offsets the increase in nuclear charge in going from magnesium to aluminium. A second electron in a different 3*p* orbital does not contribute to the shielding of the other 3*p* electron and thus the increased Z_{eff} means that it is harder to remove an electron from Si than from Al.



As another example, oxygen has a smaller ionisation energy than either of its neighbours in row 2.

Element	Z	Atom configuration	E_{i1}	Cation configuration
N	7	$1s^22s^22p^3$	1402 kJ mol^{-1}	$1s^22s^22p^2$
O	8	$1s^22s^22p^4$	1314 kJ mol^{-1}	$1s^22s^22p^3$
F	9	$1s^22s^22p^5$	1681 kJ mol^{-1}	$1s^22s^22p^4$

Remember that electron–electron repulsion has a destabilising effect. The ionisation energy of oxygen is less than that of nitrogen, despite the increased nuclear charge, because the p^4 configuration in the O atom has significantly greater electron–electron repulsion than the p^3 configuration in the N atom.



Electron Affinity

A neutral atom can add an electron to form an anion. The energy change when an electron is added to an

atom in the gas phase is called the **electron affinity (E_{ea})**. Both ionisation energy (E_i) and electron affinity measure the stability of a bound electron, but for different species. Below, for example, are the values for fluorine.

$$\begin{aligned} F(g) &\rightarrow F^+(g) + e^- \quad E_{il} = 1681\,kJ\,mol^{-1} \\ F(g) + e^- &\rightarrow F^-(g) \quad E_{ea} = -322\,kJ\,mol^{-1} \end{aligned}$$

Energy is released when an electron is added to a fluorine atom to form a fluoride anion. This means that a fluoride anion is of lower energy than a fluorine atom plus a free electron. Another way of saying this is that fluorine atoms have an affinity for electrons.

The energy associated with removing an electron to convert an anion to a neutral atom (that is, the reverse of electron attachment) has the same magnitude as the electron affinity, but the opposite sign. Removing an electron from F^-, for example, requires energy, giving a positive energy change.

$$F^-(g) \rightarrow F(g) + e^- \quad \Delta E = 322\,kJ\,mol^{-1}$$

The Aufbau principle must be obeyed when an electron is added to a neutral atom, so the electron goes into the lowest energy orbital available. Hence, we expect trends in electron affinity to parallel trends in orbital energy. However, electron–electron repulsion and shielding are more important for negative ions than for neutral atoms, so there is no clear trend in electron affinities as *n* increases. Thus, there is only one general pattern: *Electron affinity tends to become more negative from left to right across a period of the periodic table.*

The plot in figure 4.51 shows how electron affinity changes with atomic number. The blue lines reveal the trend: Electron affinity increases in magnitude across each period of the periodic table. This trend is due to increasing effective nuclear charge, which binds the added electron more tightly to the nucleus. Notice that, in contrast to the pattern for ionisation energies (figure 4.50), values for electron affinities remain nearly constant among elements occupying the same group of the periodic table.

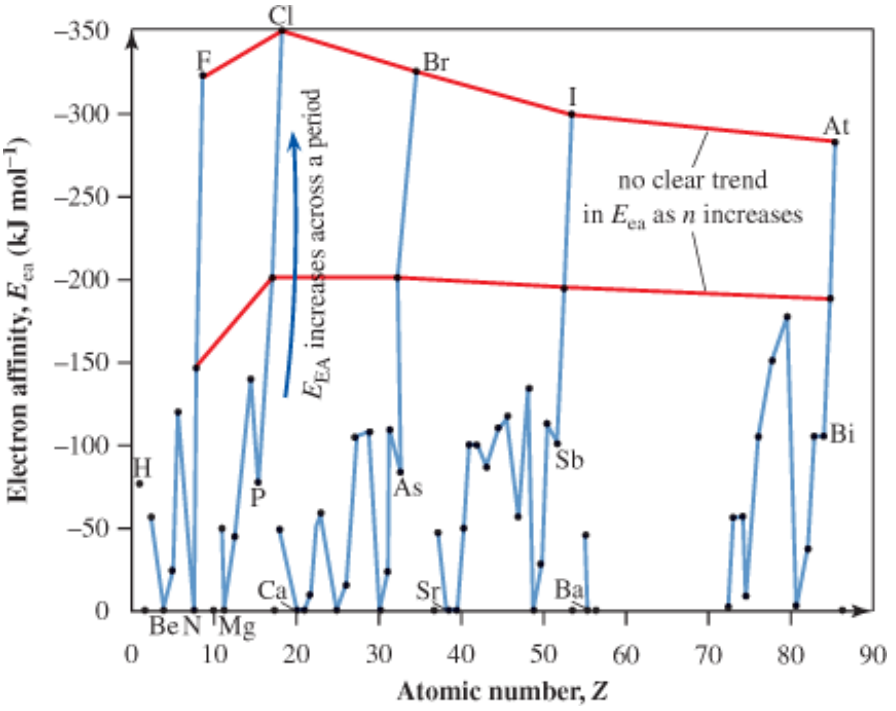


FIGURE 4.51 The electron affinity of atoms varies with atomic number. In moving across any period (blue lines), the electron affinity becomes more negative, but this is the only clear trend.

The electron affinity values for many of the elements shown in figure 4.51 appear to lie on the *x*-axis. Actually, these elements have positive electron affinities, meaning the resulting anion is of higher energy

than the neutral atom. Moreover, the second electron affinity of every element is large and positive. Positive electron affinities cannot be measured directly. Instead, these values are estimated using other methods.

Although electron affinity values show only one clear trend, there is another recognisable pattern in the values that are positive. When the electron that is added must occupy a new orbital, the resulting anion is unstable. Thus, all the elements of group 2 have positive electron affinities because their valence *ns* orbitals are filled. Similarly, all the noble gases have positive electron affinities because their valence *np* orbitals are filled. Elements with half-filled orbitals also have less negative electron affinities than their neighbours. As examples, N (half-filled 2*p* orbital set) has a positive electron affinity, and so does Mn (half-filled 3*d* orbital set).

Sizes of Ions

An atomic cation is always smaller than the corresponding neutral atom. Conversely, an atomic anion is always larger than the neutral atom. Figure 4.52 illustrates these trends, and electron–electron repulsion explains them. A cation has fewer electrons than its parent neutral atom. This reduction in the number of electrons means that the cation's remaining electrons experience less electron–electron repulsion. An anion has more electrons than its parent neutral atom. This increase means that there is more electron–electron repulsion in the anion than in the parent neutral atom.

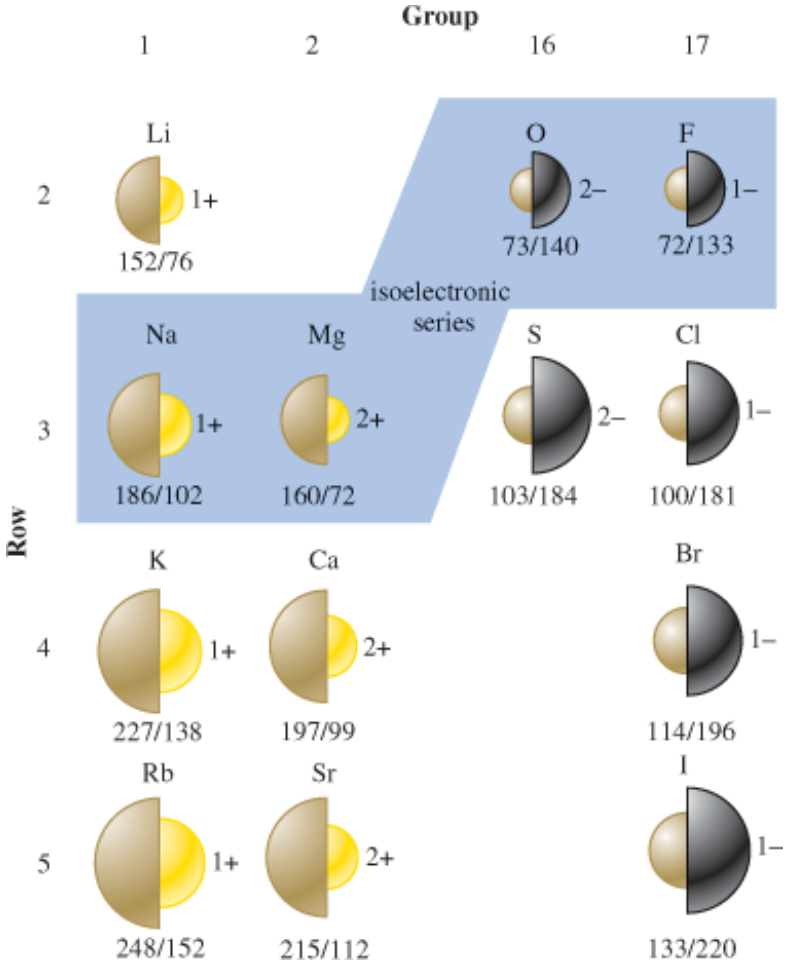


FIGURE 4.52 Comparison of the sizes (radius, *r*, in pm) of neutral atoms (brown) and their ions (cations yellow; anions black) for some elements. The blue highlight indicates isoelectronic ions.

Figure 4.52 also highlights the relationships between isoelectronic species, i.e. those that possess equal numbers of electrons. As noted earlier, the F^- anion and the Na^+ cation are isoelectronic, each having 10 electrons and the configuration [He]$2s^2 2p^6$. For isoelectronic species, properties change regularly with *Z*. For example, table 4.4 shows two properties of the 10-electron isoelectronic sequence. A progressive increase in nuclear charge results in a corresponding decrease in ionic radius, a result of stronger electrical force between the nucleus and the electron cloud. For the same reason, as *Z* increases, it becomes progressively more difficult to remove an electron.

TABLE 4.4 Trends in an isoelectronic sequence

	Species			
Property	O^{2-}	F^-	Na^+	Mg^{2+}
Z	8	9	11	12
radius (pm)	140	133	102	72
ionisation energy (kJ mol^{-1})	$< 0 (-E_{ea_2})$	322 ($-E_{ea}$)	4560 (E_{i2})	7730 (E_{i3})

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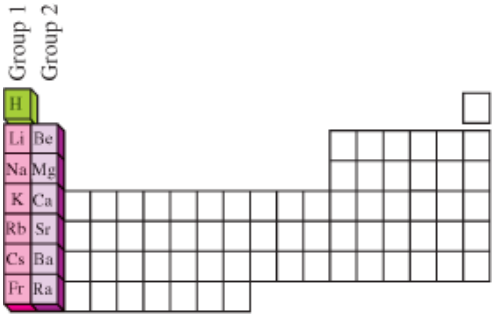
4.9 Ions and Chemical Periodicity

The elements that form ionic compounds are found in specific places in the periodic table. Atomic anions are restricted to elements on the right side of the table: the halogens, oxygen and sulfur. All the elements in the *s*, *d* and *f* blocks form compounds containing atomic cations.

Cation Stability

Knowing that the energy cost of removing core electrons is always very large, we can predict that the ionisation process will stop when all valence electrons have been removed. Thus, a knowledge of ground-state configurations is all that we need to make qualitative predictions about cation stability.

Each element in group 1 of the periodic table has one valence electron. These elements form ionic compounds containing M^+ cations. Examples are KCl and Na_2CO_3. Each element in group 2 of the periodic table has two valence electrons and forms ionic compounds containing M^{2+} cations. Examples are $CaCO_3$ and $MgCl_2$.



Beyond these two groups, the removal of all valence electrons is usually not energetically possible. For example, iron has eight valence electrons but forms only two stable cations, Fe^{2+} and Fe^{3+}. Compounds of iron containing these ions are abundant in the Earth's crust. Pyrite, FeS_2, and iron(II) carbonate, $FeCO_3$, or siderite, are examples of Fe^{2+} salts. Iron(III) oxide, Fe_2O_3, or haematite, can be described as an arrangement of Fe^{3+} cations and O^{2-} anions. One of the most abundant iron ores, magnetite, has the chemical formula Fe_3O_4 and contains a 2 : 1 ratio of Fe^{3+} and Fe^{2+} cations. The formula of magnetite can also be written as $FeO{\cdot}Fe_2O_3$ to emphasise the presence of two different cations.

Other metallic elements form ionic compounds with cation charges ranging from +1 to +3. Aluminium nitrate nonahydrate, $Al(NO_3)_3{\cdot}9H_2O$, (the word 'nonahydrate' means nine water molecules are associated with the compound) is composed of Al^{3+} cations, NO_3^- anions, and water molecules. Silver nitrate, $AgNO_3$, which contains Ag^+ cations, is a water-soluble silver salt that is used in silver plating.

Anion Stability

Halogens, the elements in group 17 of the periodic table, have the largest electron affinities of all the elements. So halogen atoms (ns^2np^5) readily accept electrons to produce halide anions (ns^2np^6). This allows halogens to react with many metals to form binary compounds, called halides, which contain metal cations and halide anions. Examples include NaCl (chloride anion), CaF_2 (fluoride anion), AgBr (bromide anion) and KI (iodide anion).

Isolated atomic anions with charges more negative than -1 are always unstable, but oxide (O^{2-}, $1s^22s^22p^6$) and sulfide (S^{2-}, $[Ne]3s^23p^6$) are found in many ionic solids, such as CaO and Na_2S. The lattice energies (see pp. 170–1) of these solids are large enough to make the overall reaction energy releasing despite the large positive second electron affinity of the anions. In addition, three-dimensional arrays of surrounding cations stabilise the –2 anions in these solids.

Metals, Nonmetals and Metalloids

Ion formation is only one pattern of chemical behaviour. Many other chemical trends can be traced to valence electron

configurations, but we need the description of chemical bonding from chapter 5 to explain such periodic properties. Nevertheless, we can relate important patterns in chemical behaviour to the ability of some elements to form ions. One example is the subdivision of the periodic table into metals, nonmetals and metalloids, first introduced in chapter 1.

The elements that can form cations relatively easily are metals. All metals have similar properties, in part because their outermost *s* electrons are relatively easy to remove. All elements in the *s* block have ns^1 or ns^2 valence configurations. The *d*-block elements have one or two *ns* electrons and various numbers of $(n - 1)d$ electrons. Examples are titanium ($4s^23d^2$) and silver ($5s^14d^{10}$). Elements in the *f* block have two *ns* electrons and a number of $(n - 2)f$ electrons. Samarium, for example, has the valence configuration $6s^24f^6$. The metallic behaviour of these elements occurs partly because the *s* electrons are shared readily among all atoms. Metals form ionic salts because *s* electrons (and some *p*, *d* and *d f* electrons) can be readily removed from the metal atoms to form cations.

Whereas the other blocks contain only metals, elemental properties vary widely within the *p* block. We have already noted that aluminium ($3s^23p^1$) can lose its three valence electrons to form Al^{3+} cations. The six elements within the triangle in figure 4.53 also lose *p* electrons easily and therefore have metallic properties. Examples are tin ($5s^25p^2$) and bismuth ($6s^26p^3$).

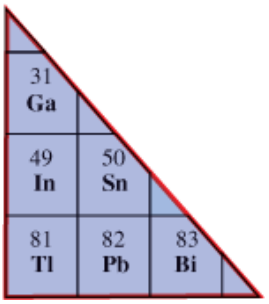


FIGURE 4.53 These six elements lose *p* electrons easily and so have metallic properties.

In contrast, the halogens and noble gases on the right of the *p* block are distinctly nonmetallic. The noble gases, group 18 of the periodic table, are monatomic gases that resist chemical attack because their electron configurations involve completely filled *s* and *p* orbitals.

Elements in any intermediate column of the *p* block display a range of chemical properties even though they have the same valence configurations. Carbon, silicon, germanium and tin all have ns^2np^2 valence configurations; yet carbon is a nonmetal, silicon and germanium are metalloids, and tin is a metal.

Qualitatively, we can understand this variation by recalling that, as the principal quantum number increases, the valence orbitals increase in energy. In tin, the four $n = 5$ valence electrons are bound relatively loosely to the atom, resulting in the metallic properties associated with electrons that are easily removed. In carbon, the four $n = 2$ valence electrons are bound relatively tightly to the atom, resulting in nonmetallic behaviour. Silicon ($n = 3$) and germanium ($n = 4$) fall in between these two extremes.

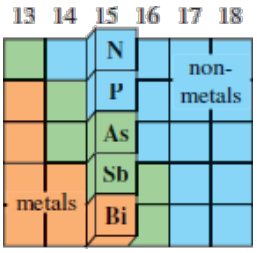
WORKED EXAMPLE 4.17

Classifying Elements

Nitrogen is a colourless diatomic gas. Phosphorus has several elemental forms, one being a red solid that is used in match tips. Arsenic and antimony are grey solids, and bismuth is a silvery solid. Classify these elements of group 15 as metals, nonmetals or metalloids.

Analysis

All elements except those in the *p* block are metals. Group 15, however, is part of the *p* block, within which elements display all forms of elemental behaviour. To decide the classifications of these elements, we must examine this group relative to the diagonal arrangement of the metalloids.



Solution

We see that group 15 passes through all three classes of elements. The elements with the lowest *Z* values, nitrogen and phosphorus, are nonmetals. The element with highest *Z* value, bismuth, is a metal, and the two elements with intermediate *Z* values, arsenic and antimony, are metalloids.

Is our answer reasonable?

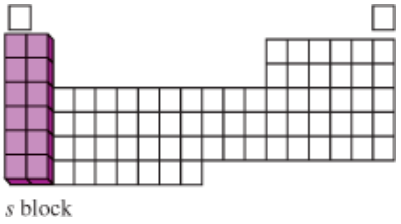
As the principal quantum number increases, valence electrons become progressively easier to remove, and metals are those elements with valence electrons that are easily removed.

PRACTICE EXERCISE 4.17

Classify the 4*p* set of elements, from Ga to Kr as metals, nonmetals or metalloids.

s-block Elements

The electron configuration of any element in groups 1 and 2 of the periodic table contains a core of tightly bound electrons and one or two *s* electrons that are loosely bound. The group 1 metals (ns^1 configuration) and the group 2 metals (ns^2 configuration) form stable ionic salts because their valence electrons are easily removed. Nearly all salts of group 1 metals and many salts of group 2 metals dissolve readily in water, so naturally occurring sources of water frequently contain these ions.



The four most abundant *s*-block elements in the Earth's crust are sodium, potassium, magnesium and calcium (table 4.5). These elements are found in nature in salts such as NaCl, KNO_3, $MgCl_2$, $MgCO_3$ and $CaCO_3$. Portions of these solid salts dissolve in rainwater as it percolates through the Earth's crust. The resulting solution of anions and cations eventually finds its way to the oceans. When water evaporates from the oceans, the ions are left behind. Over many aeons the continual influx of river water containing these ions has built up the substantial salt concentrations found in the oceans.

TABLE 4.5 Abundance of *s*-block elements

Element	Abundance in Earth's crust (% by mass)	Abundance in sea water (mol L^{-1})	Abundance in human blood plasma (mol $^{-1}$)
Na	2.27	0.462	0.142
K	1.84	0.097	0.005
Mg	2.76	0.053	0.003
Ca	4.66	0.100	0.005

Table 4.5 shows that each of the four common *s*-block ions is abundant not only in sea water but also in body fluids, where

they play essential biochemical roles. Sodium is the most abundant cation in fluids that are outside of cells, and proper functioning of body cells requires that sodium concentrations be maintained within a narrow range. One of the main functions of the kidneys is to control the excretion of sodium. Whereas sodium cations are abundant in the fluids outside cells, potassium cations are the most abundant ions in the fluids inside cells. The difference in ion concentration across cell membranes is responsible for the generation of nerve impulses that drive muscle contraction. If the difference in potassium ion concentration across cell membranes deteriorates, muscular activity, including the regular muscle contractions of the heart, can be seriously disrupted.

The cations Mg^{2+} and Ca^{2+} are major components of bones. Calcium occurs in hydroxyapatite, $Ca_5(PO_4)_3(OH)$. The structural function of magnesium in bones is not fully understood. In addition to being essential ingredients of bone, these two cations play key roles in various biochemical reactions, including photosynthesis, transmission of nerve impulses, muscle contraction and the formation of blood clots.

Beryllium behaves differently from the other *s*-block elements because its $n = 2$ orbitals are more compact than orbitals with higher principal quantum numbers. The first ionisation energy of beryllium, 899 kJ mol^{-1}, is comparable with those of nonmetals, so beryllium does not form compounds that are clearly ionic.

Some compounds of the *s*-block elements are important industrial and agricultural chemicals (figure 4.54). For example, K_2CO_3 (potassium carbonate or potash) is obtained from mineral deposits and is the most common source of potassium for fertilisers. Potassium is essential for healthy plant growth. However, potassium salts are highly soluble in water, so potassium quickly becomes depleted from the soil. Consequently, agricultural land requires frequent addition of potassium fertilisers.



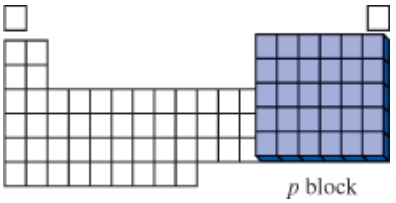
FIGURE 4.54 Potassium, another *s*-block element, is essential for healthy plant growth and is added to agricultural soil in fertilisers.

Three other compounds of *s*-block elements — calcium oxide, CaO or 'lime', sodium hydroxide, NaOH, and sodium carbonate, Na_2CO_3 — are major industrial chemicals. For example, lime is the key ingredient in construction materials such as concrete, cement, mortar and plaster. Two other compounds, calcium chloride, $CaCl_2$, and sodium sulfate, Na_2SO_4, are also of industrial importance.

Many industrial processes make use of anions such as hydroxide, OH^-, carbonate, CO_3^{2-}, and chlorate, ClO_3^-. These anions must be supplied as chemical compounds that include cations. Sodium is most frequently used as this spectator cation because it is abundant, inexpensive and relatively non-toxic. The hydroxide ion is industrially important because it is a strong base (see chapter 11). Sodium hydroxide is used to manufacture other chemicals, textiles, paper, soaps and detergents. Sodium carbonate and sand are the major starting materials in the manufacture of glass. Glass contains sodium and other cations embedded in a matrix of silicate, SiO_3^{2-}, anions. About half the sodium carbonate produced in the world is used in glass making.

p-block Elements

The properties of elements in the *p* block vary across the entire spectrum of chemical possibilities. The elements in group 13, with a single electron in a *p* orbital as well as two valence *s* electrons, display chemical reactivity characteristic of three valence electrons. Except for boron, the elements of this group are metals that form stable +3 cations. Examples are $Al(OH)_3$ and GaF_3. Metallic character diminishes rapidly as additional *p* electrons are added. This change culminates in the elements in group 18. With filled *p* orbitals, these elements are so unreactive that for many years they were thought to be completely inert. Xenon is now known to form compounds with the most reactive nonmetals: oxygen, fluorine and chlorine; krypton also forms a few highly unstable compounds with these elements.



Although the nonmetals do not readily form cations, many of them combine with oxygen to form polyatomic oxoanions. These anions have various stoichiometries, but there are some common patterns. Two second-row elements form oxoanions with three oxygen atoms: carbon (four valence electrons) forms carbonate, CO_3^{2-}, and nitrogen (five valence electrons) forms nitrate, NO_3^-. In the third row, the most stable oxoanions contain four oxygen atoms: SiO_4^{4-}, PO_4^{3-}, SO_4^{2-} and ClO_4^-.

Many of the minerals that form the Earth's crust contain oxoanions. Examples of carbonates are $CaCO_3$ (limestone) and $MgCa(CO_3)_2$ (dolomite). Barite, $BaSO_4$, is a sulfate mineral. An important phosphate is $Ca_5(PO_4)_3F$ (apatite). Two silicates are zircon, $ZrSiO_4$, and olivine, a mixture of $MgSiO_4$ and $FeSiO_4$.

Several leading industrial chemicals contain oxoanions or are acids resulting from addition of H^+ to the anions. Sulfuric acid, H_2SO_4, nitric acid, HNO_3, and phosphoric acid, H_3PO_4, are all industrially important. Heating $CaCO_3$ drives off CO_2 to form CaO, the essential ingredient of building materials mentioned earlier. Other industrially important salts include ammonium sulfate, $(NH_4)_2SO_4$, aluminium sulfate, $Al_2(SO_4)_3$, sodium carbonate, Na_2CO_3, and ammonium nitrate, NH_4NO_3. We will learn more about the *p*-block elements in chapter 14.

Chemistry Research

Counter-terrorism using separation science

Professor Paul Haddad, Director, Australian Centre for Research on Separation Science, University of Tasmania

An important aspect in counter-terrorism measures is the ability to rapidly identify the type of explosive used in a terrorist attack. Improvised explosive devices (IEDs, figure 4.55) are commonly chosen by terrorists in preference to high explosives, such as nitrated organic compounds, because of the relative ease with which the components used in their manufacture can be procured and the low cost of these materials. Typically, IEDs are homemade explosives created from unrestricted materials and consist of an initiation system to supply an electrical charge, a detonator and an explosive charge.



FIGURE 4.55 The ability to identify a type of explosive is important in counter-terrorism.

Inorganic IEDs employ vigorous chemical reactions using strong inorganic oxidisers combined with a suitable fuel. After detonation, these explosives leave residues comprising unconsumed reactants and a range of reaction products, most of which are inorganic anions and cations. Research being conducted in the Australian Centre for Research on Separation Science at the University of Tasmania is investigating whether these residues can be used to identify explosives by means of a 'fingerprint' of the different ions present in the residues. The analytical methodology used for this process must be able to be carried to a blast site and be operated in the field rather than in a laboratory.

One of the analytical techniques under investigation is capillary electrophoresis (CE). In this technique, a mixture of sample ions is introduced into one end of a very fine capillary (75 μm internal diameter) made from fused silica. A large electrical field (e.g. 30 000 V) is applied along the length of the capillary and this induces the sample ions to migrate to the appropriate electrode. Anions migrate to the positively charged anode and cations migrate to the negatively charged cathode. If the rates of migration differ between ions, they will reach the end of the capillary at different times and hence be separated.

After looking at the possible residues from a wide range of IEDs, a target set of 15 anions and 12 cations was chosen. Separation of all these species allows a unique fingerprint to be obtained for each IED. Typical outputs (called 'electropherograms') are shown in figure 4.56 for the type of IED used in the 2002 Bali bombing. The anion and cation 'fingerprints' are displayed. Other IEDs give different 'fingerprints' and can be identified easily. The analyses shown were performed on a portable CE instrument that is about the size of a briefcase and can therefore be transported easily.

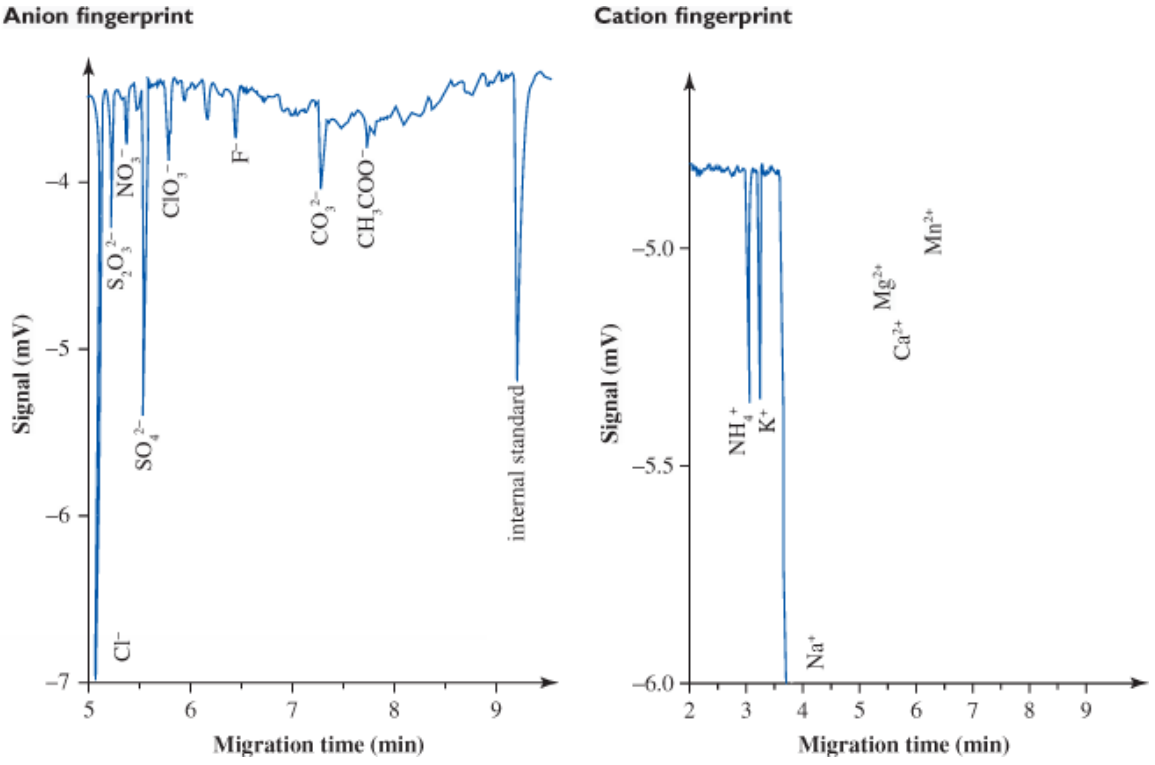


FIGURE 4.56 Typical electropherograms from analysis of residues from improvised explosive devices (IEDs).

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SUMMARY

Characteristics of Atoms

All atoms display certain basic characteristics. They possess mass, occupy volume, attract one another and can combine with one another. Atoms contain positively charged nuclei and negatively charged electrons, and the properties of elements are determined by variations in nuclear charges and numbers of electrons.

Characteristics of Light

Electromagnetic radiation in the form of light may be used to probe the structure of atoms. Light has both wave- and particle-like properties.

The wave properties are characterised by:

- frequency (ν): the number of wave crests passing a given point in 1 second
- wavelength (λ): the distance between successive wave crests
- amplitude: the height of the wave
- phase: the starting position of the wave with respect to one wavelength.

The intensity (or brightness) of light is proportional to the square of the amplitude.

Light waves move at the speed of light, c (approx. 2.998×10^8 m s^{-1}) in a vacuum. The relationship between speed, frequency and wavelength of light is $c = \nu\lambda$. Visible light has wavelengths between 380 and 780 nm. The energy of light is inversely related to its wavelength — the shorter the wavelength, the higher the energy.

The particle properties of light are demonstrated by the photoelectric effect, where light striking the surface of a metal causes electrons to be ejected from the metal. Einstein postulated that this behaviour could be explained by ‘packets’ or ‘bundles’ of light called photons. The energy of a photon is given by the equation $E_{photon} = h\nu_{photon}$, where h is Planck's constant (approximately 6.626×10^{-34} J s). An atom can absorb a photon of a particular energy and form a higher energy excited state. The excited-state atom can then release the excess energy by emitting a photon and returning to its ground state. These photon absorption and emission processes can be observed in atomic spectra. An absorption spectrum gives dark lines in the visible spectrum where light of a particular wavelength has been absorbed, while an emission spectrum gives coloured lines on a dark background which correspond to emission of photons. Atoms can absorb or emit photons of only certain definite energies, meaning that the electrons in atoms have only certain specific energy values — that is, their energies are quantised. We show the quantised energy levels within an atom by means of an energy level diagram.

Properties of Electrons

Like atoms, all electrons display certain basic characteristics. Every electron has a mass of 9.109×10^{-31} kg and a charge of 1.602×10^{-19} C. Electrons have magnetic properties and, like light, electrons also display particle–wave duality. The wavelength associated with an electron is given by the equation $\lambda = \frac{h}{mu}$. The Heisenberg uncertainty principle states that we cannot simultaneously know both the position and the momentum of any particle, and this is particularly important for electrons.

Quantisation and Quantum Numbers

Electrons bound to atoms have quantised energies, while free electrons can have any energy. The quantised energies of bound electrons are linked to their wave properties by the Schrödinger equation

$\hat{H}\psi = E\psi$, which gives both the energies and wavefunctions of a chemical system. This equation can be solved exactly only for systems containing one electron, and a one-electron wave-function is called an orbital.

Quantised properties of an atom can be indexed using quantum numbers. The principal quantum number (n) can have only positive integer values, and indexes both the energy of the electron and orbital size. The size of an orbital increases as n increases. The azimuthal quantum number (l) indexes the angular momentum of an atomic orbital and identifies the shape of the electron distribution of an orbital; it can be zero or any positive integer value smaller than n. Atomic orbitals are labelled according to their l value; s orbitals have $l = 0$, p orbitals have $l = 1$, d orbitals have $l = 2$ and f orbitals have $l = 3$. The magnetic quantum number (m_l) indexes the different possible orientations of the electron distribution of an orbital; it can have any positive or negative integer value from 0 to l. The spin quantum number (m_s) has possible values of $+\frac{1}{2}$ and $-\frac{1}{2}$, corresponding to the two possible spin states of an electron. All electrons within an atom can be described using sets of these four quantum numbers, and the Pauli exclusion principle states that each electron has a unique set.

Atomic Orbital Electron Distributions and Energies

The electron distribution of an orbital can be depicted in a variety of ways. An electron density plot shows the distribution graphically in two dimensions, an electron density picture shows a cross-section of the distribution, while a boundary surface diagram shows the surface which encompasses (usually) 90% of the electron density. Areas of zero electron density within an orbital are called nodes, and the number of these increase as n increases. The electron distribution of an s orbital is spherical, while those of p orbitals and four of the five d orbitals are dumbbell and clover-leaf shaped, respectively. The electron distribution of the d_{z^2} orbital resembles that of a p orbital surrounded by a doughnut. The two lobes of p orbitals have opposite phases, while the phases of the four lobes of a cloverleaf-shaped d orbital alternate. The doughnut of a d_{z^2} orbital is of opposite phase to the rest of the orbital.

The energy of an orbital in a one-electron system is determined by both the atomic number Z and the principal quantum number n. All orbitals in a one-electron system with the same value of n have the same energy — they are degenerate. This degeneracy is destroyed in multi-electron atoms. The energy of an orbital can be determined by measuring the ionisation energy, which is the energy required to remove an electron completely from that (usually valence) orbital. Ionisation energies are dependent on many factors, one of which is the shielding of the valence electrons from the nuclear charge by core electrons. Consequently, a valence electron in a multi-electron atom experiences a charge less than the full nuclear charge; this is called the effective nuclear charge (Z_{eff}). Electrons with a lower n shield electrons of higher n very efficiently, while, within groups of electrons of the same n, those having the lowest value of l shield those of higher l.

Structure of the Periodic Table

The ground-state configuration of an atom is the lowest possible energy arrangement of the electrons. The order of filling atomic orbitals with electrons is dictated by: the Aufbau principle, which states that orbitals are filled in order of increasing energy; the Pauli exclusion principle, which states that no two electrons in an atom can have identical sets of the four quantum numbers; and Hund's rule, which states that electrons occupy sets of degenerate orbitals so as to give the maximum number of unpaired spins. An s orbital can accommodate 2 electrons, a set of p orbitals 6 and a set of d orbitals 10.

The shape of the periodic table of the elements derives from these orbital occupancies and the order in which the orbitals are filled. Elements with the same valence-electron configurations lie in the same group of the periodic table and have similar chemical properties. Valence electrons largely determine the chemistry of an element, while core electrons usually do not participate in chemical reactions.

Electron Configurations

The electron configuration of an atom can be written by recording quantum numbers for all electrons in the atom, using a compact configuration which shows the electron occupancy of each orbital type, or through an energy level diagram which shows the energy and occupancy of each orbital. In the latter, electrons are depicted as arrows pointing either up ($m_s = +\frac{1}{2}$) or down ($m_s = -\frac{1}{2}$). We can also use a shorthand notation that does not explicitly include the core electrons, but abbreviates them using the noble gas configuration of the nearest noble gas with lower *Z*. Some exceptions to the order of orbital filling occur, most notably for Cr and Cu. The order of orbital filling for ions is the same as that for atoms, as shown by the same electron configurations for the isoelectronic series Na^+, Ne and F^-. Atoms or ions having unpaired electrons are paramagnetic and will be attracted to a magnetic field, while species having all electrons paired are diamagnetic and are not attracted to a magnetic field. The electron configurations of excited states can violate Hund's rule and the Aufbau principle but not the Pauli exclusion principle.

Periodicity of Atomic Properties

The size of an atom is determined by factors such as nuclear charge, orbital energy and electron distribution, and shielding. Atomic radii give us a measure of the sizes of atoms. Atomic radii become smaller across a period and larger down a group of the periodic table. The first ionisation energies of the elements generally increase across a period and decrease down a group of the periodic table. Exceptions to these general trends occur when *p* orbitals are occupied by 1 or 4 electrons. Electron affinities become more negative across a period, but there is no clear trend down a group of the periodic table. Atomic cations are always smaller than the neutral atom and atomic anions are always larger than the neutral atom.

Ions and Chemical Periodicity

The nature of cations and anions is determined by the electron configuration of the neutral atom. Group 1 and group 2 elements form 1+ and 2+ cations respectively, while group 17 elements form 1–anions. Isolated atomic anions with charges more negative than 1–are always unstable, and O^{2-} and S^{2-} are found only in combination with cations in ionic solids. Metals generally form cations readily through loss of *s* or *d* electrons. The *p*-block elements may be metals, metalloids or nonmetals. The *s*-block elements are found in the Earth's crust and also in living systems, and *p*-block elements display a wide variety of chemical properties.

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KEY CONCEPTS AND EQUATIONS

Wavelength–frequency relationship *(section 4.2)*

The product of wavelength (λ) and frequency (v) is the speed of light (c).

$$c = v\lambda$$

Energy of a photon *(section 4.2)*

This equation is used to calculate the energy carried by a photon of frequency v. Also, v can be calculated if E is known.

$$E = hv$$

de Broglie equation *(section 4.3)*

This links the wavelength of a particle with its speed and mass.

$$p = \frac{h}{\lambda}$$

$$\lambda_{\text{particle}} = \frac{h}{mu}$$

Quantum numbers for atoms *(section 4.4)*

Each electron in an atom is described by a unique set of four quantum numbers. The allowed values of these quantum numbers are as follows:

Quantum number	**Range**
principal quantum number (n)	1, 2, …, ∞
azimuthal quantum number (l)	0, 1, …, (n - 1)
magnetic quantum number (m_l)	-l, …, -1, 0, +1, …, +l
spin quantum number (m_s)	$-\frac{1}{2}, +\frac{1}{2}$

Periodic table *(section 4.6)*

The periodic table is an aid in writing electron configurations of the elements. An element's location in the table is related to properties such as atomic radius, ionisation energy and electron affinity.

Electron configurations *(section 4.7)*

These guidelines help us to write electron configurations for atoms or ions.

1. Count the total number of electrons.
    a. Add electrons for anions.
    b. Subtract electrons for cations.
2. Fill orbitals to match the nearest noble gas of smaller atomic number.
3. Add remaining electrons to the next orbitals to be filled according to Hund's rule.
    a. For neutral atoms and anions, place electrons in ns before (n - 1)d.
    b. For cations, place electrons in (n - 1)d before ns.
4. Look for exceptions and correct the configuration if necessary.

Periodic trends in atomic and ionic size *(section 4.8)*

Periodic trends are evident in, for example:

- atomic and ionic size
- ionisation energy
- electron affinity.

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REVIEW QUESTIONS

Characteristics of Atoms

4.1 The density of silver is 1.050×10^4 kg m^{-3}, and the density of lead is 1.134×10^4 kg m^{-3}. For each metal:

(a) calculate the volume occupied per atom,

(b) estimate the atomic diameter and

(c) using this estimate, calculate the thickness of a metal foil containing 6.5×10^6 atomic layers of the metal.

4.2 Describe evidence that indicates that atoms have mass.

4.3 Describe evidence that indicates that atoms have volume.

Characteristics of Light

4.4 Calculate the frequencies (Hz) corresponding to the following wavelengths, using power-of-ten notation:

(a) 4.33 nm,

(b) 2.35×10^{-10} m,

(c) 735 mm,

(d) 4.57 μm.

4.5 Calculate the wavelengths corresponding to the following frequencies, expressing the result in the indicated units:

(a) 4.77 GHz (m),

(b) 28.9 kHz (cm),

(c) 60 Hz (mm),

(d) 2.88 MHz (μm).

4.6 Calculate the energy in joules per photon and in kilojoules per mole of the following:

(a) blue-green light with a wavelength of 490.6 nm,

(b) X-rays with a wavelength of 25.5 nm,

(c) microwaves with a frequency of 2.5437×10^{10} Hz.

4.7 What are the wavelength and frequency of photons with the following energies?

(a) 745 kJ mol^{-1}

(b) 3.55×10^{-19} J $photon^{-1}$

4.8 When light of frequency 1.30×10^{15} s^{-1} shines on the surface of caesium metal, electrons are ejected with a maximum kinetic energy of 5.2×10^{-19} J. Calculate:

(a) the wavelength of this light,

(b) the binding energy of electrons to caesium metal and

(c) the longest wavelength of light that will eject electrons.

4.9 A phototube delivers an electrical current when a beam of light strikes a metal surface inside the tube. Phototubes do not respond to infrared photons. Draw an energy level diagram for electrons in the metal of a phototube and use it to explain why phototubes do not respond to infrared light.

4.10 Refer to figure 4.4 to answer the following questions.

(a) What is the wavelength range for radio waves?

(b) What colour is light with a wavelength of 5.8×10^{-7} m?

(c) In what region does radiation with frequency of 4.5×10^{8} Hz lie?

4.11 Determine the wavelengths of radiation that hydrogen atoms absorb to reach the $n = 8$ and $n = 9$ states from the ground state. In what region of the electromagnetic spectrum do these photons lie?

Properties of Electrons

4.12 What is the charge in coulombs of one mole of electrons?

4.13 Determine the wavelengths of electrons with the following kinetic energies:

(a) $1.15 \times 10^{-19}0$ J,

(b) 3.55 kJ mol^{-1},

(c) 7.45×10^{-3} J mol^{-1}.

4.14 Determine the kinetic energies in joules of electrons with the following wavelengths:

(a) 3.75 nm,

(b) 4.66 m,

(c) 8.85 mm.

Quantisation and Quantum Numbers

4.15 List all the valid sets of quantum numbers for a 6*p* 6 electron.

4.16 If you know that an electron has $n = 3$, what are the possible values for its other quantum numbers?

4.17 For the following sets of quantum numbers, determine which describe actual orbitals and which are nonexistent. For each one that is nonexistent, list the restriction that forbids it.

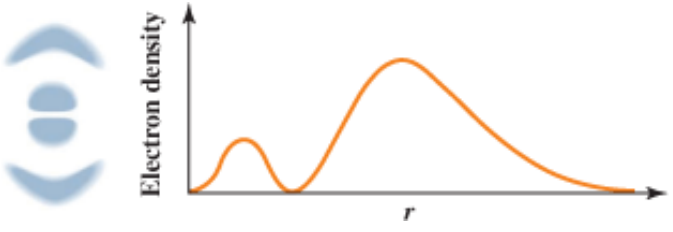
	n	l	m_l	m_s
(a)	3	-1	-1	$\frac{1}{2}$
(b)	3	1	-1	$-\frac{1}{2}$
(c)	3	1	2	$\frac{1}{2}$
(d)	3	2	2	$\frac{1}{2}$

Atomic Orbital Electron Distributions and Energies

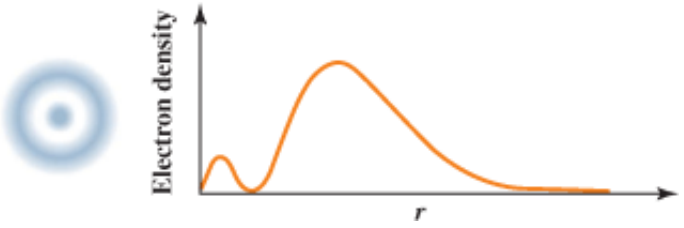
4.18 Refer to figure 4.27. Draw the analogous set of three depictions for an orbital that has $n = 2$, $l = 1$.

4.19 Shown below are electron density pictures and electron density plots for the 1*s*, 2*s*, 2*p* and 3*p* orbitals. Assign the various depictions to their respective orbitals.

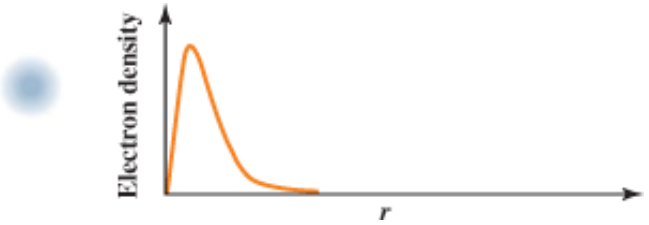
(a)



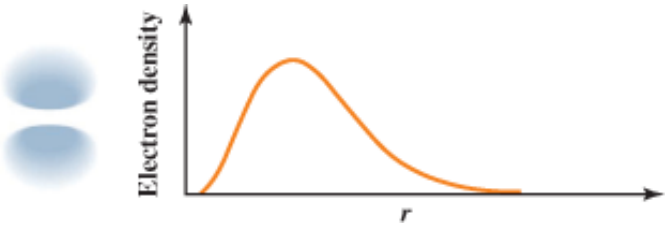
(b)



(c)



(d)



4.20 What are the limitations of plots of electron density versus r?

4.21 The conventional method of showing the three-dimensional electron distribution of an orbital is an electron contour surface. What are the limitations of this representation?

4.22 For each of the following pairs of orbitals, determine which is more stable and explain why.

(a) He 1*s* and He 2*s*

(b) Kr 5*p* and Kr 5*s*

(c) He 2*s* and He^+ 2*s*

4.23 In a hydrogen atom the 3*s*, 3*p* 3 and 3*d* orbitals all have the same energy. In a helium atom, however, the 3*s* orbital is lower in energy than the 3*p* orbital, which in turn is lower in energy than the 3*d* orbital. Explain why the energy rankings of hydrogen and helium are different.

4.24 The energy of the $n = 2$ orbital of the He^+ ion is the same as the energy of the $n = 1$ orbital of the H atom. Explain this fact.

4.25 Refer to figure 4.37 to answer the following questions. In each case, provide a brief explanation of your choice.

(a) Which ionisation energies show that an electron in a 1*s* orbital provides nearly complete shielding of an electron in a 2*p* orbital?

(b) Which ionisation energies show that the stability of $n = 2$ orbitals increases with Z^2?

Structure of the Periodic Table

4.26 Draw the periodic table in block form, and outline and label each of the following sets:

(a) elements that are 1 electron short of filled *p* orbitals,

(b) elements for which $n = 3$ orbitals are filling,

(c) elements with half-filled *d* orbitals,

(d) the first element that contains a 5*s* electron.

4.27 How many valence electrons does each of the following atoms have?

(a) O,

(b) V,

(c) Rb,

(d) Sn,

(e) Cd

Electron Configurations

4.28 Write the complete electron configuration, and list a correct set of quantum numbers for each of the valence electrons in the ground-state configurations of:

(a) Be,

(b) O,

(c) Ne,

(d) P.

4.29 Which of the atoms from question 4.28 are paramagnetic? Draw orbital energy level diagrams to support your answer.

4.30 The following are hypothetical configurations for a beryllium atom. Which use nonexistent orbitals, which are forbidden by the Pauli principle, which are excited states, and which one is the ground-state configuration?

(a) $1s^3 2s^1$

(b) $1s^1 2s^3$

(c) $1s^1 2p^3$

(d) $1s^2 2s^1 2p^1$

(e) $1s^2 2s^2$

(f) $1s^2 1p^2$

(g) $1s^2 2s^1 2d^1$

4.31 Write the correct ground-state electron configurations, in shorthand notation, for C, Cr, Sb and Br.

Periodicity of Atomic Properties

4.32 Arrange the following atoms in order of decreasing first ionisation energy (smallest last): Ar, Cl, Cs and K.

4.33 One element has these ionisation energies and electron affinity (all in kJ mol^{-1}): E_{i1} = 376, E_{i2} = 2420, E_{i3} = 3400, E_{ea} = -45.5. In which column of the periodic table is this element found? Give your reasoning.

4.34 According to appendix G, each of the following elements has a positive electron affinity. For each one, construct its valence orbital energy level diagram and use it to explain why the anion is unstable.

(a) N,

(b) Mg,

(c) Zn

4.35 From the following list, select the elements that form ionic compounds: Ca, C, Cu, Cs, Cl and Cr. Indicate whether each forms a stable cation or a stable anion.

Ions and Chemical Periodicity

4.36 Classify each of the elements from group 16 of the periodic table as a metal, a nonmetal or a metalloid.

4.37 Classify each of the elements listed in question 4.35 as a metal, a nonmetal or a metalloid.

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REVIEW PROBLEMS

4.38 List the properties of electrons and of photons, including the equations used to describe each.

4.39 Write a short description of:

(a) the photoelectric effect,

(b) particle–wave duality,

(c) electron spin and

(d) the uncertainty principle.

4.40 Describe an atomic energy level diagram and the information it incorporates.

4.41 Redraw the first light wave in figure 4.3 to show a wave whose frequency is twice as large as that shown in the figure, but whose amplitude is the same.

4.42 A minimum of 216.4 kJ mol^{-1} is required to remove an electron from a potassium metal surface. What is the longest wavelength of light that can do this?

4.43 In a photoelectric effect experiment, the minimum frequency needed to eject electrons from a metal is 7.5×10^{14} s^{-1}. Suppose that a 366 nm photon from a mercury discharge lamp strikes the metal. Calculate:

(a) the binding energy of the electrons in the metal,

(b) the maximum kinetic energy of the ejected electrons and

(c) the wavelength associated with those electrons.

4.44 Microwave ovens use radiation with a wavelength of 12.5 cm. What is the frequency, and energy in kJ mol^{-1}, of this radiation?

4.45 Barium salts in fireworks generate a yellow-green colour. Ba^{2+} ions emit light with λ = 487, 514, 543, 553 and 578 nm. Convert these wavelengths into frequencies and into energies in kJ mol^{-1}.

4.46 A hydrogen atom emits a photon as its electron changes from $n = 5$ to $n = 1$. What is the wavelength of the photon? In what region of the electromagnetic spectrum is this photon found?

4.47 Write brief explanations of:

(a) shielding,

(b) the Pauli exclusion principle,

(c) the Aufbau principle,

(d) Hund's rule and

(e) valence electrons.

4.48 Construct an orbital energy level diagram for all orbitals with $n < 8$ and $l < 4$. Use the periodic table to help determine the correct order of the energy levels.

4.49 Describe periodic variations in electron configurations; explain how they affect ionisation energy and electron affinity.

4.50 Write the electron configuration for the Mn^{2+} ground state, and give a set of quantum numbers for all electrons in the least stable occupied orbital.

4.51 Arrange the following in order of decreasing size (radius): Cl^-, K^+, Cl and Br^-. Explain your rankings in terms of quantum numbers and electrical interactions.

4.52 Draw energy level diagrams that show the ground-state valence electron configurations for Cu^+, Mn^{2+} and Au^{3+}.

4.53 Write a brief explanation for each of the following.

(a) In a hydrogen atom, the 2*s* and 2*p* 2 orbitals have identical energy.

(b) In a helium atom, the 2*s* and 2*p* orbitals have different energies.

4.54 Refer to figure 4.50 to answer the following questions about first ionisation energies.

(a) Which element shows the greatest decrease from its neighbour of next lower *Z*?

(b) What is the atomic number of the element with the lowest value?

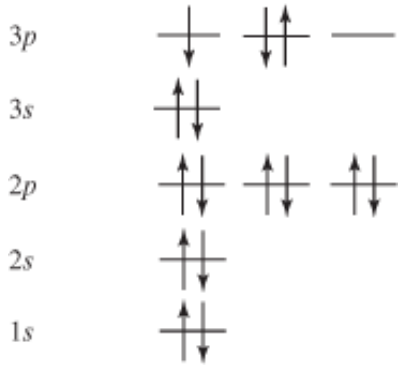
(c) Identify three ranges of *Z* across which the value changes the least.

(d) List the atomic numbers of all elements whose values are between 925 and 1050 kJ mol^{-1}.

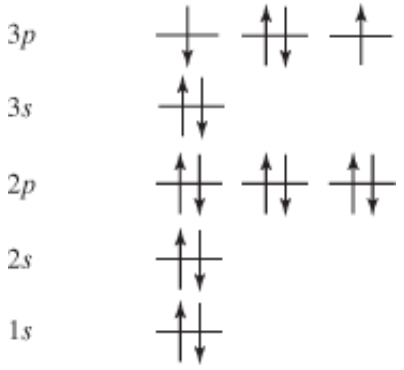
4.55 Which has the most unpaired electrons, S^+, S or S^-? Use electron configurations to support your answer.

4.56 None of the following electron energy diagrams describes the ground state of a sulfur atom. For each, state the reason why it is not correct.

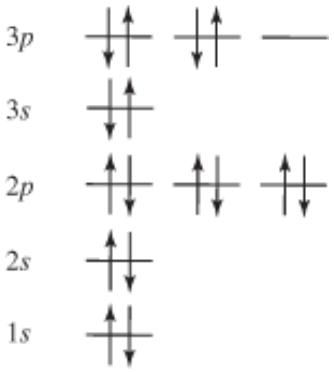
(a)



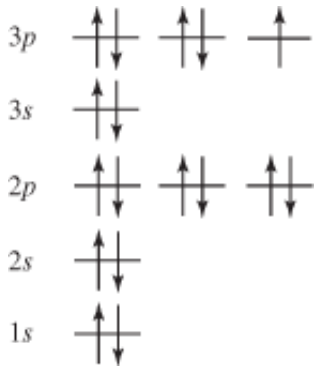
(b)



(c)



(d)



4.57 Identify the ionic compounds that best fit the following descriptions:

(a) the group 2 cation with the second smallest radius combined with a group 16 anion that is isoelectronic with the noble gas from row 3

(b) a +1 ion that is isoelectronic with the noble gas from row 3, combined with the anion formed from the row 2 element with the highest electron affinity

(c) the group 2 metal with the highest second ionisation energy that combines in a 1 : 2 ratio with an element from row 3.

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4.58 The photoelectric effect for magnesium metal has a threshold frequency of $8.95 \times 10^{14}\ s^{-1}$. Can Mg be used in photoelectric devices that sense visible light? Do a calculation to support your answer.

4.59 Energetic free electrons can transfer their energy to bound electrons in atoms. In 1913, James Franck and Gustav Hertz passed electrons through mercury vapour at low pressure to determine the minimum kinetic energy required to produce the excited state that emits ultraviolet light at 253.7 nm. What is that minimum kinetic energy? What wavelength is associated with electrons of this energy?

4.60 The diameter of a typical atom is 10^{-10} m, and the diameter of a typical nucleus is $10^{-1}5$ m. Calculate typical atomic and nuclear volumes and determine what fraction of the volume of a typical atom is occupied by its nucleus.

4.61 Neutrons, like electrons and photons, are particle–waves with diffraction patterns that can be used to determine the structures of molecules. Calculate the kinetic energy of a neutron with a wavelength of 75 pm.

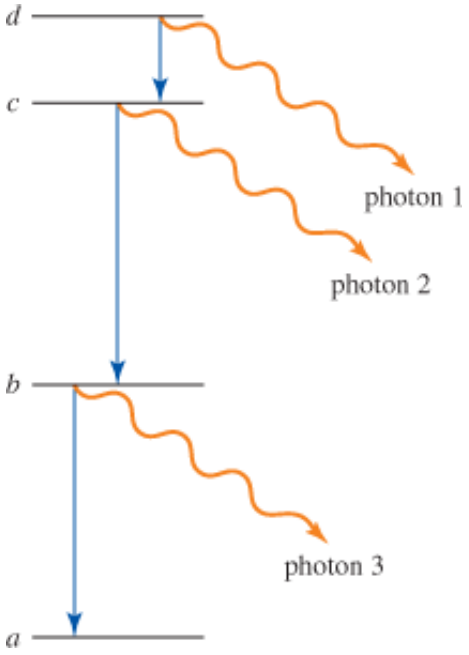
4.62 The human eye can detect as little as 2.35×10^{-18} J of green light with a wavelength of 510 nm. Calculate the minimum number of photons of green light that can be detected by the human eye.

4.63 Gaseous lithium atoms absorb light with a wavelength of 323 nm. The resulting excited lithium atoms lose some energy through collisions with other atoms. The atoms then return to their ground state by emitting two photons with $\lambda = 812.7$ and 670.8 nm. Draw an energy level diagram that shows this process. What fraction of the energy of the absorbed photon is lost in collisions?

4.64 Calculate the wavelengths associated with an electron and a proton, each travelling at 5.000% of the speed of light.

4.65 One hydrogen emission line has a wavelength of 486 nm. Identify the values for n_{final} and $n_{initial}$ for the transition giving rise to this line.

4.66 An atomic energy level diagram, shown to scale, follows.



An excited-state atom emits photons when the electron moves in succession from level *d* to level *c*, from level *c* to level *b*, and from level *b* to the ground state (level *a*). The wavelengths of the emitted photons are 565 nm, 152 nm and 121 nm (not necessarily in the proper sequence). Match

each emission with the appropriate wavelength and calculate the energies of levels *b*, *c* and *d* relative to level *a*.

4.67 Small helium–neon lasers emit 1.0 mJ s^{-1} of light at 634 nm. How many photons does such a laser emit in one minute?

4.68 The argon-ion laser has major emission lines at 488 and 514 nm. Each of these emissions leaves the Ar^+ ion in an energy level that is $2.76 \times 10^{-1}8$ J above the ground state.

(a) Calculate the energies of the two emission wavelengths in joules.

(b) Draw an energy level diagram (in joules per atom) that illustrates these facts.

(c) What frequency and wavelength radiation is emitted when the Ar^+ ion returns to its lowest energy level?

4.69 The series of emission lines that results from excited hydrogen atoms undergoing transitions to the $n = 3$ level is called the Paschen series. Calculate the energies of the first five lines in this series of transitions, and draw an energy level diagram that shows them to scale.

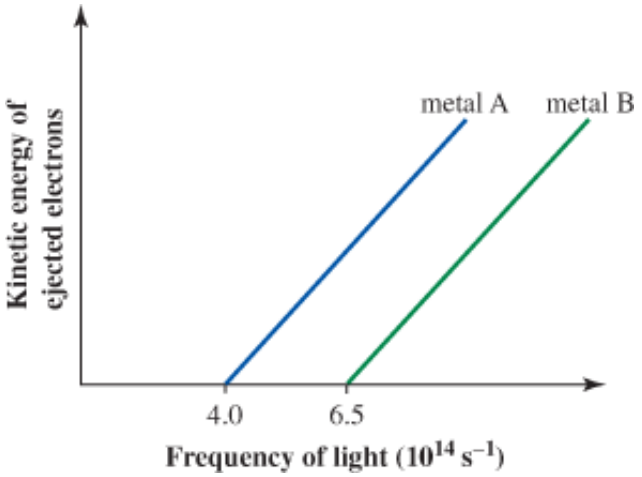
4.70 It takes 486 kJ mol^{-1} to remove electrons completely from sodium atoms. Sodium atoms absorb and emit light of wavelengths 589.6 and 590.0 nm.

(a) Calculate the energies of these two wavelengths in kJ mol^{-1}.

(b) Draw an energy level diagram for sodium atoms that shows the levels involved in these transitions and the ionisation energy.

(c) If a sodium atom has already absorbed a 590.0 nm photon, what is the wavelength of the second photon a sodium atom must absorb in order to remove an electron completely?

4.71 The graph below shows the results of photoelectron experiments on two metals, using light of the same energy.



(a) Calculate the binding energy of each metal. Which has the higher binding energy? Explain.

(b) Calculate the kinetic energies of electrons ejected from each metal by photons with wavelength of 125 nm.

(c) Calculate the wavelength range over which photons can eject electrons from one metal but not from the other.

4.72 Write the electron configuration for the lowest energy excited state of each of the following: Be, O^{2-}, Br^-, Ca^{2+} and Sb^{3+}.

4.73 Write the ground-state configurations for the isoelectronic species Ce^{2+}, La^+ and Ba. Are they the same? What features of orbital energies account for this?

4.74 The ionisation energy of lithium atoms in the gas phase is about half as large as the ionisation energy of beryllium atoms in the gas phase. In contrast, the ionisation energy of Li^+ is about four

times larger than the ionisation energy of Be^+. Explain the difference between the atoms and the ions.

4.75 The figures below show Cl^-, Ar, and K^+ drawn to scale. Decide which figure corresponds to which species and explain your reasoning.

(a)



(b)



(c)



4.76 Make an electron density plot that shows how the 3*s* and 3*p* orbitals are shielded effectively by the 2*p* orbitals. Provide a brief explanation of your plot.

4.77 Use the data in appendix G to explain why the noble gases seldom take part in chemical reactions.

4.78 From its location in the periodic table, predict some of the physical and chemical properties of francium. What element does it most closely resemble?

4.79 What would be the next two orbitals to fill after the 7*p* orbital?

4.80 Which has the more stable 2*s* orbital, a lithium atom or a Li^{2+} cation? Explain your reasoning.

4.81 The first four ionisation energies of aluminium are as follows: E_{i1} = 577 kJ mol^{-1}, E_{i2} = 1817 kJ mol^{-1}, E_{i3} = 2745 kJ mol^{-1} and E_{i4} = 11 578 kJ mol^{-1}.

(a) Explain the trend in ionisation energies.

(b) Rank ions of aluminium in order of ionic radius, from largest to smallest.

(c) Which ion of aluminium has the largest electron affinity?

4.82 The idea of an atomic radius is inherently ambiguous. Explain why this is so.

4.83 Use electron–electron repulsion and orbital energies to explain the following irregularities in first ionisation energies:

(a) Boron has a lower ionisation energy than beryllium.

(b) Sulfur has a lower ionisation energy than phosphorus.

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KEY TERMS

absorption spectrum
amplitude
atomic radius
Aufbau principle
azimuthal quantum number (l)
core electrons
degenerate
diamagnetic
effective nuclear charge (Z_{eff})
electromagnetic radiation
electron affinity (E_{ea})
electron configuration
electron density picture
electron density plot
emission spectrum
energy level diagram
excited state
frequency (v)
ground state
ground-state configuration
Hund's rule
intensity
ionisation energy (E_i)
isoelectronic
light
magnetic quantum number (m_l)
noble gas configuration
node
orbital
paramagnetic
Pauli exclusion principle
phase
photoelectric effect
photons
Planck's constant (h)
principal quantum number (n)
quantised
quantum number
shielding
spin
spin quantum number (m_s)
uncertainty principle
valence electrons
wavelength (λ)

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CHAPTER

5 Chemical Bonding and Molecular Structure

Australia's Samantha Stosur returns a volley. The high-tech fibres in her tennis racquet that are responsible for some of the power are held together by chemical bonds. Producing such high-tech fibres requires a thorough understanding of chemical bonding, because the fibres are constructed of polymers, large molecules that are held together by covalent bonds in which electrons are shared between atoms. The ways in which chemical bonds are formed depend on the nature of the elements involved, and chemical bonds show a variety of forms and strengths.

This chapter describes chemical bonding and its relationship to molecular structure. We discuss the two extremes of chemical bonding: ionic, in which electro static forces hold ionic arrangements together, and covalent, where shared electron pairs dictate the bonding and geometry of individual molecules. We show how simple Lewis theory gives a good approximation of the distribution of electrons within molecules, and how we can use this to predict molecular geometry using valence-shell-electron-pair repulsion theory. We then consider in detail the two predominant theories used to describe covalent bonding: valence bond theory and molecular orbital theory.





KEY TOPICS

5.1 Fundamentals of bonding
5.2 Ionic bonding
5.3 Lewis structures
5.4 Valence-shell-electron-pair repulsion (VSEPR) theory
5.5 Properties of covalent bonds
5.6 Valence bond theory
5.7 Molecular orbital theory: diatomic molecules

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5.1 Fundamentals of Bonding

We learned in chapter 4 that the size, energy levels and electron configuration of an atom determine its chemical properties. In molecular compounds, electrons on atoms interact and are shared between atoms. In ionic compounds, electrons are transferred completely between atoms to form positively and negatively charged ions. Since electrons have both particle- and wave-like properties, bonding interactions can be described from either viewpoint. Keep in mind, though, that these models do not necessarily reflect reality exactly.

The electrostatic energy between two charged species is proportional to the magnitudes of the charges and inversely proportional to the distance between them. Charges of opposite sign attract one another, but like charges repel. The relationship is given by Coulomb's law as:

$$E_{\text{electrostatic}} = K\frac{q_1 q_2}{r}$$

where:

$$\begin{aligned} E_{\text{electrostatic}} &= \text{electrostatic potential energy(J)} \\ q_1 &= \text{charge on species 1 (C)} \\ q_2 &= \text{charge on species 2 (C)} \\ r &= \text{separation distance between the pair of charges (m)} \\ k &= 9.00 \times 10^9\ \text{N m}^2\ \text{C}^{-2}\text{(Coulomb's constant for a vacuum)} \end{aligned}$$

The equation describes the potential energy of one pair of charges. Molecules, however, contain two or more nuclei and two or more electrons. To obtain the total potential energy of a molecule, the equation must be applied to every possible pair of charged species. These pair-wise interactions are of three types (see figure 5.1):

1. Electrons and nuclei attract one another. Attractive interactions are energetically favourable, so an electron attracted to a nucleus is at a lower energy than a free electron.
2. Electrons repel each other, raising the energy and reducing the stability of a molecule.
3. Nuclei repel each other, so these interactions also reduce the stability of a molecule.

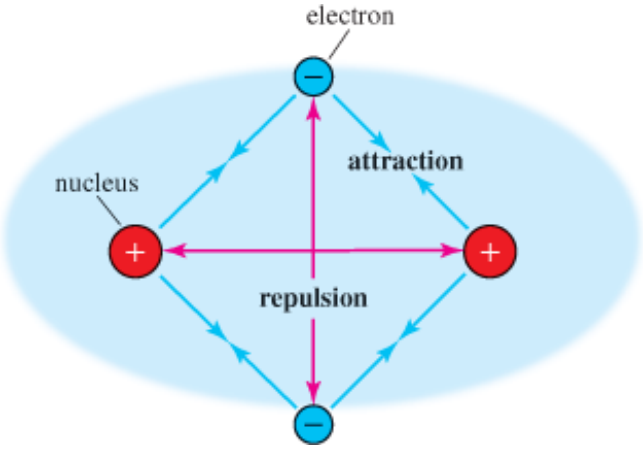


FIGURE 5.1 When electrons are in the region between two hydrogen nuclei, attractive electrostatic forces exceed repulsive electrostatic forces, leading to the stable arrangement of a chemical bond.

In any molecule, these three interactions are balanced to give the molecule its greatest possible stability. This balance is achieved when the electron density is situated between the nuclei of bonded atoms. We view the electrons as being shared between the nuclei and call this shared electron density a **covalent bond**. In any covalent bond, the attractive energy between nuclei and electrons exceeds the repulsive energy arising from nuclear–nuclear and electron–electron interactions.

The Hydrogen Molecule

These concepts are demonstrated below for the simplest stable neutral molecule, molecular hydrogen. A hydrogen molecule contains just two nuclei and two electrons.

Consider what happens when two hydrogen atoms come together and form a covalent bond. As the atoms approach, each nucleus attracts the opposite electron, pulling the two atoms closer together. At the same time, the two nuclei repel each other, as do the two electrons. These repulsive interactions tend to drive the atoms apart.

For H_2 to be a stable molecule, the sum of the attractive energies must exceed the sum of the repulsive energies. Figure 5.1 shows a static arrangement of electrons and nuclei in which the electron–nucleus distances are shorter than the electron–electron and nucleus–nucleus distances. As the charges on the hydrogen nuclei and electrons are 1+ and 1–respectively, the distances between them become crucial in determining the energy of this arrangement. In this case, attractive interactions exceed repulsive interactions, leading to a stable molecule. Notice that the two electrons occupy the region between the two nuclei where they can interact with both nuclei at once; that is, the atoms share the electrons in a covalent bond.

An actual molecule is dynamic, not static, and both the electrons and nuclei move continuously. In a covalent bond, the most probable electron locations are between the nuclei, where, in this model, they can be viewed as being shared between the bonded atoms.

Bond Length and Bond Energy

As two hydrogen atoms come together to form a molecule, attractive forces between nuclei and electrons make the hydrogen molecule more stable than the individual hydrogen atoms. The amount of increased stability depends on the distance between the nuclei, as shown in figure 5.2. At distances greater than 300 pm (300×10^{-12} m), there is almost no interaction between the atoms, so the total energy is the sum of the energies of the two individual atoms. At closer distances, the attraction between the electron of one atom and the nucleus of the other atom increases, and the combined atoms become more stable. Moving the atoms closer together generates greater stability until the nuclei are 74 pm apart. At this distance, we obtain the best possible balance between the attractive and repulsive forces in the molecule. At distances closer than 74 pm, the nucleus–nucleus repulsion begins to dominate and the energy of the system increases rapidly. Thus, at a separation distance of 74 pm, the hydrogen molecule has the maximum energetic advantage (7.22×10^{-19} J) over two separated hydrogen atoms. Experimental studies of molecular motion reveal that nuclei within molecules move continuously, oscillating about their lowest energy separation distance like two spheres attached to opposite ends of a spring.

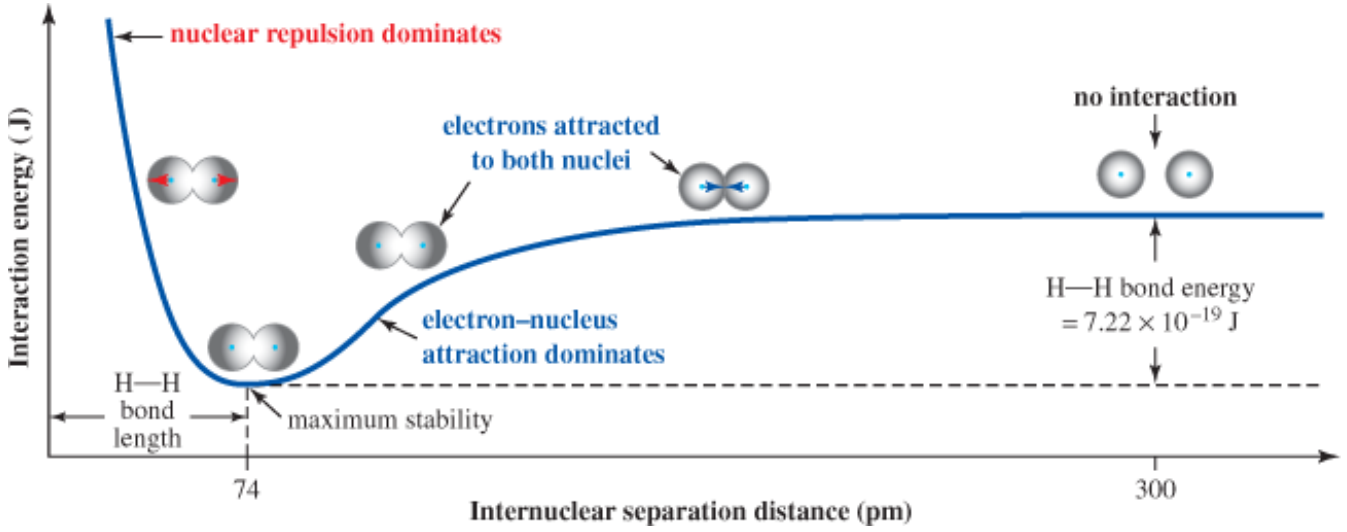


FIGURE 5.2 The interaction energy of two hydrogen atoms depends on the distance between the nuclei.

Figure 5.2 shows two characteristic features of covalent bonds. The separation distance at which the molecule has the maximum energetic advantage over the separated atoms (74 pm for H_2) is known as the **bond length**. The energy difference between the molecule and the separated atoms at this separation distance is called the bond energy. **Bond energy** is defined as the energy required to break the bond and therefore is always positive. Bond lengths and energies are important properties of chemical bonds and, as we will see, they are related. It is usual to quote bond energies in units of kJ mol^{-1}. We can obtain this value for the hydrogen molecule by multiplying the energy of a single H—H bond (7.22×10^{-19} J) by N_A (6.022×10^{23} mol^{-1}). This gives a H—H bond energy of 435 kJ mol^{-1}. Each different chemical bond has a characteristic bond length and bond energy.

The most probable position of the electrons in the hydrogen molecule is between the nuclei. If we rotate the molecule about its internuclear axis (an imaginary line joining the two nuclei) we find that the electron distribution between the nuclei looks exactly the same, regardless of the angle through which it was rotated. In other words, the bond is symmetric with respect to rotation about the internuclear axis. Bonds for which this is true are called **sigma (σ) bonds**.

Other Diatomic Molecules: F_2

Bond formation in H_2 is relatively easy to describe because we need to consider just two electrons. However, even when the atoms within a molecule contain many electrons, we can still consider bond formation as the sharing of only two electrons. We will illustrate this with the fluorine molecule, F_2.

As two fluorine atoms approach each other, the electrons of each atom feel the attraction of the nucleus of the other atom, just as in H_2. In this case, the valence 2*p* electrons are closest to the neighbouring nucleus and experience the strongest attraction. The single electron in one of the 2*p* orbitals approaches the opposite nucleus. Consequently, we can describe the F—F bond as the sharing of two electrons from the fluorine 2*p* orbitals that point directly towards each other (see figure 5.3). Note that the resulting bond is a σ bond.

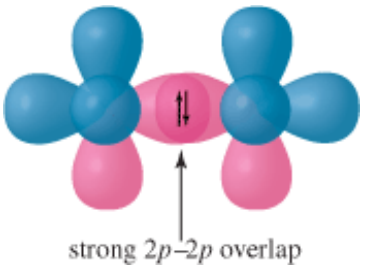


FIGURE 5.3 The chemical bond in F_2 forms from strong electrostatic attraction of the electron in the fluorine 2*p* orbital that points directly at the neighbouring nucleus.

Unequal Electron Sharing

Each nucleus within a hydrogen molecule and each within a fluorine molecule has the same charge. Consequently, both nuclei attract electrons equally. The result is a symmetrical distribution of the electron density around the atoms. In a chemical bond between any two identical atoms, the nuclei share the bonding electrons equally.

In contrast to the symmetrical forces in H_2 and F_2, the bonding electrons in HF experience *unsymmetrical* attractive forces. The effective nuclear charge of a fluorine atom is significantly greater than the effective charge of a hydrogen atom due to the greater number of protons, so the electrons shared between H and F feel a stronger attraction to the F atom. Unequal attractive forces lead to an unsymmetrical distribution of the bonding electrons. The HF molecule is most stable when its bonding electrons are concentrated closer to the fluorine atom and away from the hydrogen atom. This unequal distribution of electron density gives the fluorine end of the molecule a small negative charge and the hydrogen end a small positive charge; however, the molecule as a whole remains electrically neutral. These partial charges are less than one charge unit and are equal in magnitude. To indicate such partial charges, we use the symbols δ+ and δ- (δ is the lower-case Greek letter delta) or an arrow pointing from the negative end towards the positive end of the molecule, or an electron density surface, which shows the spread of charge using colours, with blue being positive and red being negative as shown for HF in figure 5.4. This unequal sharing of electrons results in a **polar covalent bond**. We describe bond polarity and its consequences in section 5.5.

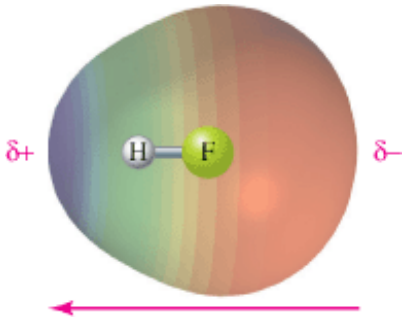


FIGURE 5.4 Unequal sharing of electron density in HF results in a polar covalent bond. The colour gradient represents the variation in electron density shared between the atoms.

Note that, despite being polar, the H—F bond is still a σ bond, because it remains unchanged as we rotate the molecule about the H—F bond axis.

As elements differ in their effective nuclear charges, atoms of each element have a characteristic ability to attract electrons within a covalent bond. This ability is called **electronegativity** and is symbolised by χ (the lower-case Greek letter chi). A bond between two elements of different electronegativities will be polar, and the greater the difference (Δχ), the more polar the bond.

Electronegativity gives a numerical value to how strongly an atom attracts the electrons in a chemical bond. This property of an atom involved in a bond is related to, but distinct from, ionisation energy and electron affinity. (As described in chapter 4, ionisation energy measures how strongly an atom attracts one of its own electrons. Electron affinity specifies how strongly an atom attracts a free electron.)

Electronegativities, which have no units, are estimated by using combinations of atomic and molecular properties. The periodic table shown in figure 5.5 presents commonly used values, developed by the US scientist Linus Pauling (figure 5.6), based on bond energies. These values are often called the Pauling scale.

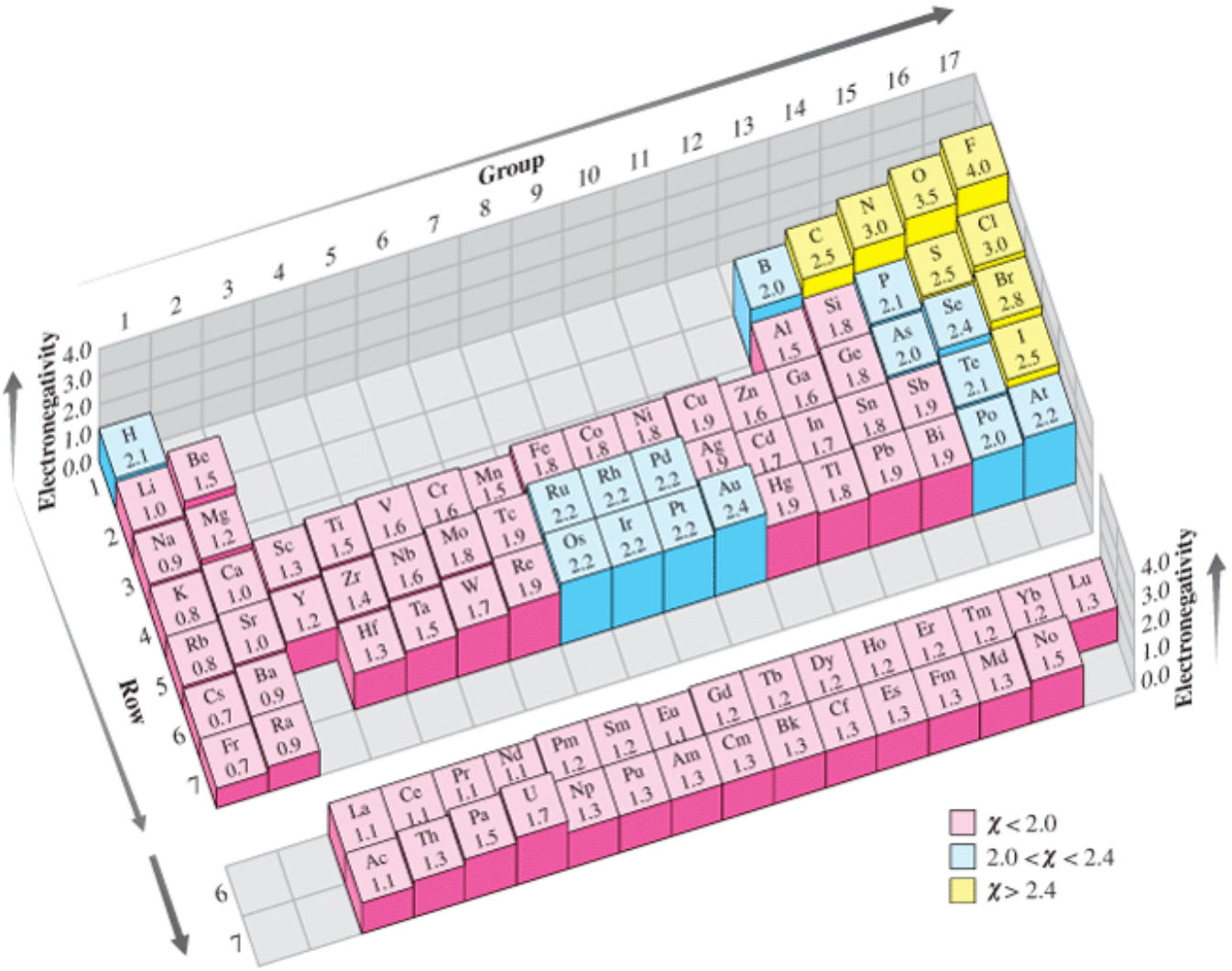


FIGURE 5.5 Electronegativities of the elements vary periodically. While there are some exceptions, the general trend is that electronegativity increases from left to right and decreases from top to bottom of the periodic table. The Pauling scale omits group 18 elements (the noble gases) because they are very unreactive and, with very few exceptions, do not form covalent bonds. Some other electronegativity scales do assign values to these elements.

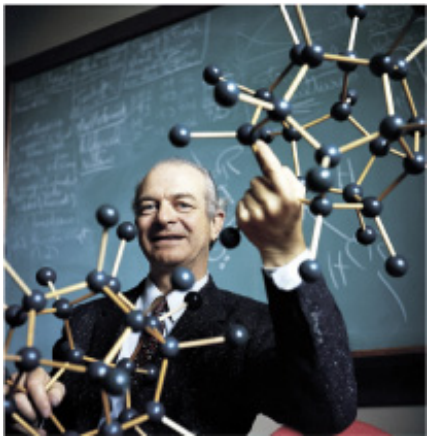


FIGURE 5.6 Linus Pauling (1901–1994) was one of the most influential thinkers of twentieth-century chemistry and was awarded the Nobel Prize in chemistry in 1954 for his research into the nature of the chemical bond. He was also one of the few people to be awarded two Nobel Prizes, receiving the peace prize in 1962 for his stand against nuclear weapons, which led the US government to revoke his passport in 1952.

Figure 5.5 shows that electronegativity is a periodic property. Electronegativities generally increase from the lower left to the upper right of the periodic table. The elements francium and caesium ($\chi = 0.7$) have the lowest value, and fluorine ($\chi = 4.0$) has the highest value. Electronegativities also generally decrease down most groups and increase from left to right across the *s* and *p* blocks. As with ionisation energies and electron affinities, variations in effective nuclear charge and principal quantum number explain electronegativity trends. Metals generally have low electronegativities ($\chi = 0.7$ to 2.4) and nonmetals have high electronegativities ($\chi = 2.1$ to 4.0). As expected from their intermediate character between metals and nonmetals, metalloids have electronegativities that are larger than the values for most metals and smaller than those for most nonmetals.

Electronegativity differences ($\Delta\chi$) between bonded atoms indicate where a particular bond lies on the continuum of bond polarities. Three fluorine-containing substances, F_2, HF and CsF, represent the range of variation. (Note that, as no weighable quantity of francium has ever been isolated, the compound FrF is unknown.) At one end of the continuum, the bonding electrons in F_2 are shared equally between the two fluorine atoms ($\Delta\chi = 4.0 - 4.0 = 0$). At the other limit, CsF ($\Delta\chi = 4.0 - 0.7 = 3.3$) is a compound in which electrons have been fully transferred to give Cs^+ cations and F^- anions. We call such compounds **ionic compounds**, and they will be discussed in more detail in the next section. Most bonds, including the bond in HF ($\Delta\chi = 4.0 - 2.1 = 1.9$), fall between these extremes. These are polar covalent bonds, in which two atoms share electrons unequally.

Chemical Connections

Electromagnetic Radiation and Cancer

The ability of light to provide the energy for chemical reactions enables life to exist on our planet. Green plants absorb sunlight and, with the help of chlorophyll, convert carbon dioxide and water into carbohydrates (e.g. sugars and cellulose), which are essential constituents of the food chain. However, not all effects of sunlight are so beneficial.

As we saw in chapter 4, light has energy that is proportional to its frequency, and, if the photons that are absorbed by a substance have enough energy, they can rupture chemical bonds and initiate chemical reactions. The carbon–carbon and carbon–hydrogen covalent bonds found in organic molecules typically have energies of at least 350 kJ mol^{-1}. Visible light, which ranges from 780 nm to 380 nm in wavelength, has a corresponding energy range of approximately 153 to 315 kJ mol^{-1}, and therefore photons of visible light are not sufficiently energetic to break such bonds. However, ultraviolet radiation, which has shorter wavelengths and hence higher energies, can be dangerous in this respect, particularly light of wavelength less than 340 nm, which has energy greater than 350 kJ mol^{-1}. The sunlight illuminating the Earth contains substantial amounts of UV radiation. Fortunately, a layer of ozone (O_3) in the stratosphere, a region of the atmosphere extending from about 45 to 55 km altitude, absorbs most of the incoming UV, protecting life on the surface. However, some UV radiation does get through, and the part of the spectrum of most concern is called UV-B with wavelengths between 280 and 320 nm.

What makes UV-B so dangerous is its ability to affect the DNA in our cells. (The structure of DNA and its replication is discussed in chapter 25.) Absorption of UV radiation causes constituents of the DNA, called *pyrimidine bases*, to undergo reactions that form bonds between them. This causes transcription errors when the DNA replicates during cell division, giving rise to genetic mutations

that can lead to skin cancers. These skin cancers fall into three classes: basal cell carcinomas, squamous cell carcinomas, and melanomas, the last being the most dangerous. Each year more than 1 million cases of skin cancer are diagnosed worldwide. It is estimated that more than 90% of skin cancers are due to absorption of UV-B radiation (figure 5.7).



FIGURE 5.7 Dawn of a new day brings the risk of skin cancer to those particularly susceptible. Fortunately, understanding the risk allows us to protect ourselves with clothing and sunblock creams.

In recent years, concern has been expressed in some sections of the media over a possible link between the use of mobile phones and brain cancer; it has been proposed by some that radiation from mobile phones (figure 5.8) can cause brain tumours, although a large number of studies have failed to find a causal relationship. This is not surprising, given that mobile phones use microwave radiation, which is of much longer wavelength than ultraviolet light, and hence insufficiently energetic to cause mutation of DNA by breaking covalent bonds.



FIGURE 5.8 A large number of studies have failed to find a causal relationship between microwave radiation and brain tumours. Microwave radiation is not energetic enough to mutate DNA.

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5.2 Ionic Bonding

Compounds formed between elements of very different electronegativities are often predominantly ionic in character. For example, ionic compounds tend to form between cations from groups 1 and 2 and anions from groups 16 and 17. Most ionic compounds are solids with relatively high melting points, particularly if the ionic solids are composed of atomic or small molecular ions. Apart from these high-melting-point ionic solids, there is also a class of compounds called ionic liquids, compounds of large molecular ions. These are, by definition, ionic compounds that have melting point below 100°C. There are some ionic liquids that are liquid even at room temperature, and those have important applications.

The bonding in ionic compounds differs fundamentally from that in covalent compounds; it does not involve the sharing of pairs of electrons. Instead, ionic compounds are held together by the non-directional attractive forces between oppositely charged ions, leading to threedimensional arrangements rather than distinct molecules.

Consider, sodium chloride, NaCl. The structure of this compound has each Na^+ cation surrounded by six Cl^- anions and each Cl^- anion surrounded by six Na^+ cations, as shown in figure 5.9.

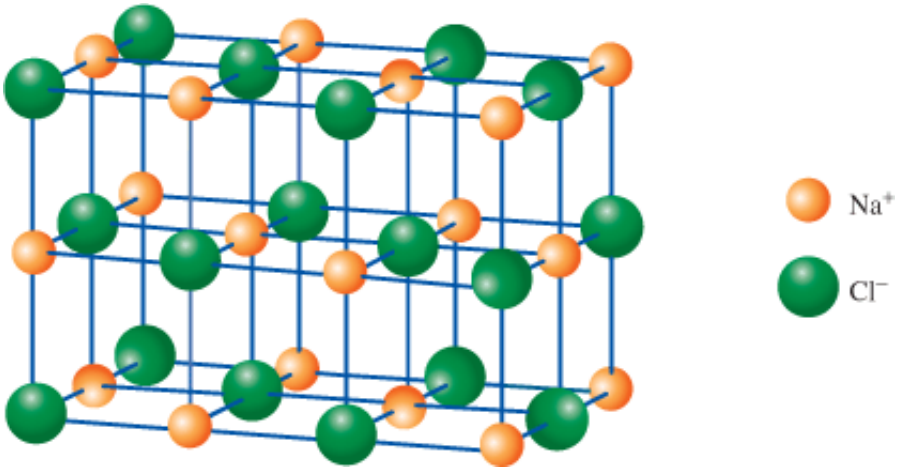


FIGURE 5.9 Representation of part of the structure of sodium chloride, NaCl. Note that each Na^+ cation is surrounded by six Cl^- anions, and each Cl^- anion is surrounded by six Na^+ cations.

This arrangement of Na^+ cations and Cl^- anions was first determined in 1913 by Australian-born Sir William Lawrence Bragg, using X-ray equipment designed by his father, Sir William Henry Bragg (figure 5.10). NaCl was the first compound whose structure was determined by X-ray crystallography (see chapter 7), a field in which the Braggs were pioneers. They were jointly awarded the Nobel Prize in physics in 1915, and William Lawrence Bragg became the youngest ever awardee at the age of 25. Crystal structures determined through analysis of X-ray diffraction data show the precise locations of atoms within a chemical species and give atomic separations accurate to about 1×10^{-12} m. X-ray crystallography is a vital part of modern chemistry and is the source of much of the structural information that you will encounter in later chapters.



FIGURE 5.10 Sir William Lawrence Bragg (left) and his father Sir William Henry Bragg were awarded the Nobel Prize in physics in 1915 for their work on X-ray crystallography.

The distance between the ions in NaCl is determined by a balance of the Coulombic (electrostatic) attractions and repulsions and the short-range repulsive interactions between both the electron densities and nuclei of neighbouring ions. At room temperature, the distance between the centres of neighbouring ions is 2.82×10^{-10} m. Using this number, we can calculate the magnitude of the attractive forces between two neighbouring Na^+ and Cl^- ions using the equation introduced at the start of this chapter.

$$E_{\text{electrostatic}} = K\frac{q_1 q_2}{r}$$

Given that q_1 is $+1.60 \times 10^{-19}$ C, q_2 is -1.60×10^{-19} C (-1.60×10^{-19} C is the fundamental charge of a single electron) and $k = 9.00 \times 10^9$ N m^2 C^{-2}, we obtain a value of -8.17×10^{-19} J, which equates to -492 kJ mol^{-1} when multiplied by the Avogadro constant. This corresponds to the energy released (hence the negative sign) when 1 mole of gaseous Na^+ and gaseous Cl^- ions are brought from an infinite distance to a separation of 2.82×10^{-10} m. However, this value takes into account only the attractive forces to one nearest neighbour, whereas each ion in the crystal has six. If we take all six interactions into account, as well as repulsive interactions between ions of the same charge in the structure, we obtain a value of -769 kJ mol^{-1}. This is a substantial amount of energy, and means that, in order to break 1 mole of the compound into its constituent gaseous ions, we would have to supply 769 kJ of energy. This is called the **lattice energy** of the compound. Among other factors, the lattice energy of a compound is dependent on the charges of the ions; as the charges increase, the lattice energy becomes more positive and the ions become harder to separate from one another. We also expect lattice energy values to decrease as the ions get larger, because *r*, the distance between them, will increase. These trends are illustrated in table 5.1, which gives some lattice energy values for ionic species.

TABLE 5.1 Lattice energies for a number of ionic compounds. All values are in kJ mol^{-1}

	Anion				
Cation	F^-	Cl^-	Br^-	I^-	O^{2-}
Li^+	1030	834	788	730	2799
Na^+	910	769	732	682	2481
K^+	808	701	671	632	2238
Rb^+	774	680	651	617	2163

Mg^{2+}	2913	2326	2097	1944	3795
Ca^{2+}	2609	2223	2132	1905	3414
Sr^{2+}	2476	2127	2008	1937	3217
Ba^{2+}	2341	2033	1950	1831	3029

The effect of ionic size on lattice energy is shown by the fact that the lattice energies of the group 1 chlorides decrease as the size of the cation increases from Li^+ to Rb^+, and the lattice energies of the sodium halides decrease as the size of the anion increases from F^- to I^-. The effect of ionic charge is seen by comparing the lattice energies of the compounds formed from the 2+ ions with halide anions. In all cases, these lattice energies are much larger than those for the 1+/1–combinations. The values for compounds containing 2+ and 2–ions are even larger, with the lattice energy of MgO being almost four times the lattice energy of LiF. However, it is important to note that meaningful comparisons of lattice energy values can be made only between compounds with the same structure type.

While the ionic model describes a number of metal halides, oxides and sulfides well, it does not describe most other chemical substances adequately. Compounds such as CaO, NaCl and MgF_2 behave like simple cations and anions held together by electrostatic attraction, but compounds such as CO, Cl_2 and HF do not. We must describe the bonding in these latter compounds in terms of the sharing of electrons between atoms. There are two predominant theories of bonding which do this. Before we study these, we will look at a simple way of determining the electron distribution in molecules and how we can use this to predict the shape of a particular molecule.

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5.3 Lewis Structures

In this section, we develop a process for making schematic drawings that show how the atoms in a molecule are bonded. In addition, these drawings, known as **Lewis structures**, differentiate between bonding and nonbonding valence electrons in a molecule. From this perspective, writing a Lewis structure is the first step in developing a bonding description of a molecule. Lewis structures are named after their originator, Gilbert Newton Lewis (1875–1946), former Professor of Chemistry at the University of California, Berkeley, USA.

The Conventions

Lewis structures are drawn according to the following conventions:

1. *Each atom is represented by its elemental symbol.* In this respect, a Lewis structure is an extension of the chemical formula.
2. *Only the valence electrons appear in a Lewis structure.* Recall from chapter 4 that only valence electrons are accessible for bonding.
3. *A line joining two elemental symbols represents one pair of electrons that is shared between two atoms.* Two atoms may share up to three pairs of electrons in **single bonds** (2 shared electrons, 1 line), **double bonds** (4 shared electrons, 2 lines) and **triple bonds** (6 shared electrons, 3 lines).
4. *Dots placed next to an elemental symbol represent nonbonding electrons on that atom.* Nonbonding electrons usually occur in pairs with opposing spins (see chapter 4).

The use of these conventions is shown for the HF molecule in figure 5.11.

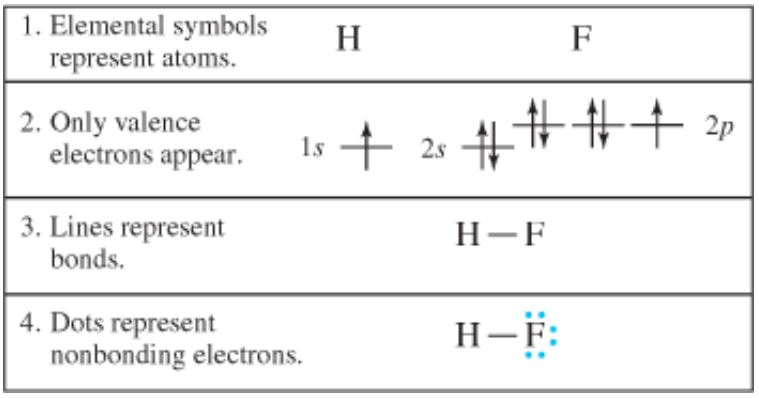


FIGURE 5.11 The Lewis structure conventions for hydrogen fluoride.

These conventions divide electrons in molecules into three groups. Core electrons do not appear in Lewis structures. Bonding valence electrons are shared between atoms and appear as lines. Nonbonding valence electrons are localised on atoms and appear as dots.

We use a five-step procedure to draw Lewis structures:

Step 1: Count the valence electrons.

Step 2: Assemble the bonding framework using single bonds.

Step 3: Place three nonbonding pairs of electrons on each outer atom except H. (*Note:* Outer atoms are those that are bonded to only one other atom, while inner atoms are those bonded to more than one other atom.)

Step 4: Assign the remaining valence electrons to inner atoms.

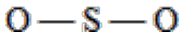
Step 5: Minimise formal charges on all atoms.

Building Lewis Structures

Learning how to draw Lewis structures is best done through examples. We will work through the five steps using the sulfur dioxide molecule, SO_2.

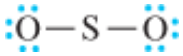
Step 1: Count the valence electrons. If the species is an ion, add or subtract one electron for each negative or positive charge, respectively. Sulfur (group 16) has the valence electron configuration $3s^2 3p^4$, while the configuration of oxygen (also group 16) is $2s^2 2p^4$. Hence, there is a total of (6 + [2 × 6]) = 18 valence electrons from the atoms themselves. The molecule is uncharged, so the total number of valence electrons is 18.

Step 2: Assemble the bonding framework using single bonds. This step is straightforward for organic molecules, which consist predominantly of C and H atoms, as there is no ambiguity as to the possible placement of atoms. However, care must be taken when drawing structures of inorganic molecules. Structures will generally consist of an inner (central) atom connected to two or more other (outer) atoms. The outer atoms will generally be either hydrogen, or the most electronegative of the atoms present, and will be bonded only to the inner atom. In the case of sulfur dioxide, oxygen is the most electronegative element present, so sulfur will be the inner atom. The bonding framework will therefore be as follows.



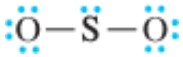
As each single bond in the framework consists of two electrons, we have used four of the original 18 valence electrons so far.

Step 3: Place three nonbonding pairs of electrons on each outer atom except H. With the exception of hydrogen, all outer atoms are associated with eight electrons (four pairs in the valence *s* and *p* orbitals), which may be bonding or nonbonding. Such a set of four pairs of electrons associated with an atom is often called an octet.



The nonbonding pairs are called **lone pairs**. Each O atom is associated with three lone pairs and one bonding pair and therefore has a complete octet. We used (2 × 6) = 12 electrons in this step. Combined with the four used in the previous step, this means 16 of the original 18 electrons have been used.

Step 4: Assign the remaining valence electrons to inner atoms. There are two remaining valence electrons. These are placed on the inner S atom as a lone pair as follows.



We have now accounted for all the valence electrons of SO_2.

Step 5: Minimise formal charges on all atoms. At this point, we need to analyse the structure obtained and check that it makes chemical sense. To do this, calculate the **formal charge** on each atom, and then minimise it by adjusting the electron distribution. Formal charge is defined as the difference between the number of valence electrons in the free atom and the number of electrons assigned to that atom in the Lewis structure.

$$\text{formal charge} = (\text{valence electrons of free atom}) - (\text{lone pair electrons}) - \frac{1}{2}(\text{shared electrons})$$

Assume that lone pair electrons 'belong' to the atom on which they are located, while electrons in bonds are shared equally between the two atoms. A useful feature of formal charges is that the sum of the formal charges on all atoms equals the charge of the species. For a neutral molecule, the sum of the formal charges must be zero. For a cation or anion, the sum of the formal charges equals the charge on the ion.

The formal charges of the atoms in the structure obtained in step 4 are calculated as follows:

S	Valence electrons of free atom	6
	Lone pair electrons	2
	Shared electrons	4
	Formal charge	$6 - 2 - \frac{1}{2}(4) = +2$
O	Valence electrons of free atom	6
	Lone pair electrons	6
	Shared electrons	2
	Formal charge	$6 - 6 - \frac{1}{2}(2) = -1$

We can minimise the formal charges by converting a lone pair of electrons on each O atom to a bonding pair. We can represent this process diagrammatically as follows.



If we analyse the formal charges on the right-hand structure, we find that they are all zero. Therefore, the right-hand structure is the best Lewis structural representation of the SO_2 molecule.

In this structure each oxygen atom is surrounded by eight electrons, and therefore has an octet, while the inner sulfur atom is surrounded by 10 electrons. We generally find octets surrounding atoms from the second period of the periodic table, especially C, N, O and F, as such atoms can accommodate a maximum of eight electrons in the available orbitals. However, the larger atoms from the third and subsequent periods often accommodate more than eight electrons, as observed for the sulfur atom. This is due to the fact that these atoms have more than four orbitals available for valence electrons.

WORKED EXAMPLE 5.1

Lewis Structure of ClF_3

Chlorine trifluoride, ClF_3, is used to recover uranium from nuclear fuel rods in a high-temperature reaction that produces gaseous uranium hexafluoride.

$$2ClF_3(g) + U(s) \rightarrow UF_6(g) + Cl_2(g)$$

Determine the Lewis structure of ClF_3.

Analysis

We follow the five steps outlined previously for drawing a Lewis structure.

Solution

1. All four atoms are halogens (group 17, ns^2np^5), so ClF_3 has 28 valence electrons.
2. Chlorine, with lower electronegativity than fluorine, is the inner atom. Make a single bond to each of the three fluorine atoms.



3. Add three nonbonding pairs to each fluorine atom.



4. Four electrons remain unassigned. Place two electron pairs on the chlorine atom.



5. Determine the formal charges on all the atoms and adjust the electron distribution if necessary. In this case, each atom has a formal charge of zero, and so no redistribution of electrons is required.

Is our answer reasonable?

Step 4 results in 10 electrons around the chlorine atom. However, chlorine is a third-row element and is therefore able to accommodate more than eight electrons. We have followed the rules and obtained the structure with formal charges of zero on every atom, so our answer is reasonable.

PRACTICE EXERCISE 5.1

Determine the Lewis structure of sulfur tetrafluoride, SF_4.

Note that some molecules and all ions will have preferred Lewis structures in which the formal charges are not all zero. In these cases, ensure that negative formal charges are situated on the most electro negative atoms and positive formal charges on the least electronegative atoms (for example, the nitrate ion in figure 5.12, where the more electronegative O atoms, rather than the N atom, have a negative formal charge). It is also important to realise that formal charges are not the same as the partial charges induced as a result of bond polarity. For example, in ClF_3, the chlorine atom would have a $\delta+$ charge, despite the fact that its formal charge is zero.

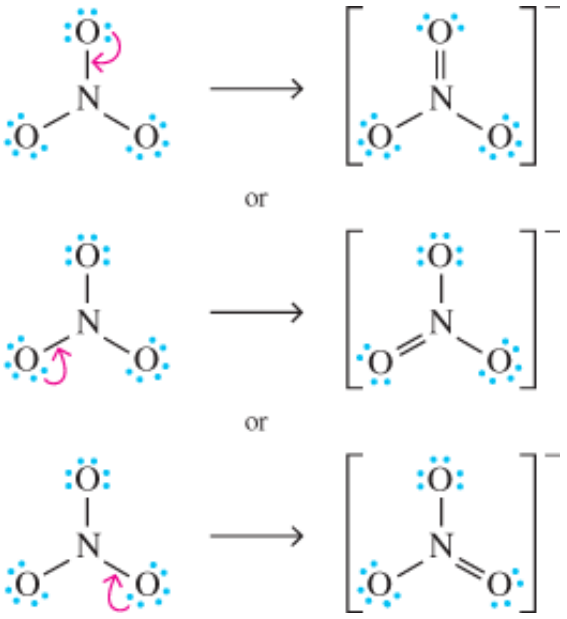


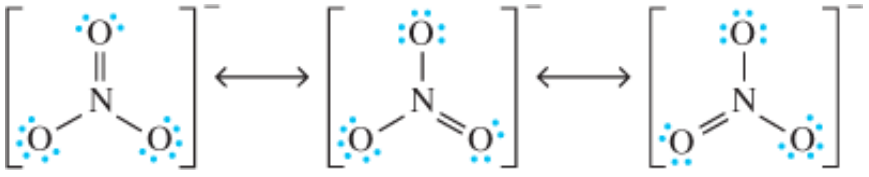
FIGURE 5.12 There are three possible ways to minimise the formal charges in the nitrate ion; any of the three oxygen atoms can supply a pair of electrons.

Resonance Structures

In completing step 5 of the Lewis structure procedure, there might be more than one way to minimise the formal charges on the atoms; that is, more than one Lewis structure is possible for a particular molecule or ion. This is shown below with the nitrate anion, NO_3^-.

The anion has 24 valence electrons, and nitrogen is the inner atom. Three N—O bonds use six electrons, and assigning six electrons to each of the three outer oxygen atoms uses the remaining 18 electrons. This gives a Lewis structure in which the O atoms have formal charges of -1 and the N atom has a formal charge of +2. We can minimise the formal charges by converting the lone pair on one oxygen atom to a bonding pair. However, as figure 5.12 shows, a lone pair from any of the three oxygen atoms can be moved to form this double bond.

Which of these options is the correct Lewis structure? Actually, no single Lewis structure is an accurate representation of NO_3^-. Any single structure of the anion shows nitrate with one N═O double bond and two N—O single bonds. Experiments, however, show that all three N—O bonds are identical (we cannot form two double bonds since nitrogen can accommodate only eight electrons in its orbitals). To show that the nitrate N—O bonds are all alike, we use a composite of the three equivalent Lewis structures. These are then called **resonance structures**. Resonance structures are connected by double-headed arrows to emphasise that a complete depiction requires all of them.



It is essential to realise that electrons in the nitrate anion *do not* 'flip' back and forth among the three bonds, as implied by separate structures. None of these structures actually exist. The true character of the anion is a blend of the three, in which all three nitrogen–oxygen bonds are equivalent. Note also that resonance structures differ *only* in the position of the electrons; you cannot move atoms when drawing resonance structures. The need to show several equivalent structures for species such as the nitrate ion

reflects the fact that Lewis structures are approximate representations of structures with delocalised electrons. While they reveal much about how electrons are distributed in a molecule or ion, they cannot describe the entire story of chemical bonding.

WORKED EXAMPLE 5.2

Resonance Structures of an Oxoanion

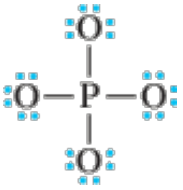
Determine the possible resonance structures of the phosphate anion, PO_4^{3-}.

Analysis

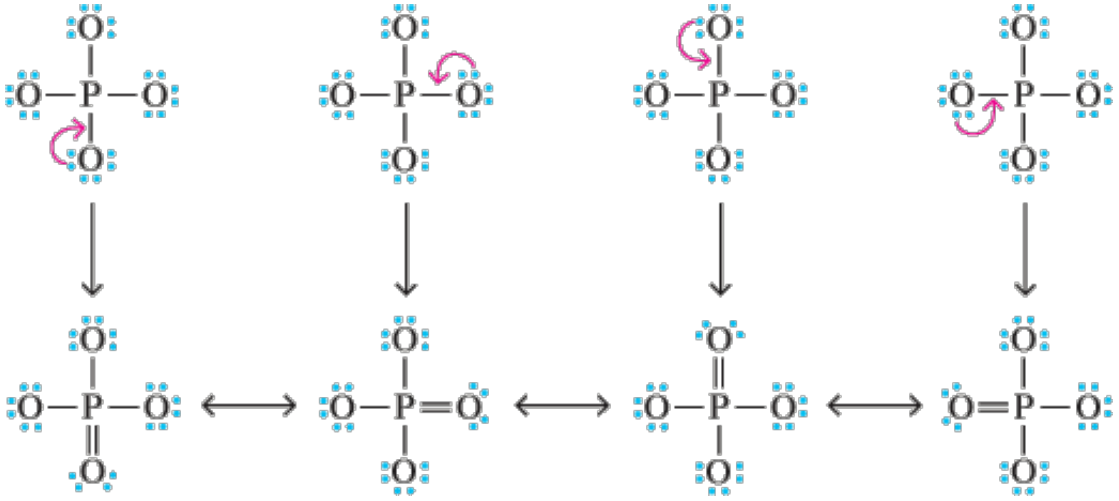
We must first determine the Lewis structure by following the five-step procedure outlined previously. In step 5, we determine the different ways we can minimise the formal charges within the ion, thereby obtaining the resonance structures.

Solution

We have 32 electrons to be used (remember that the ion has a 3–charge). Following the rules outlined previously, we arrive at the following structure, in which all the electrons are used after step 4.



In this structure, the O atoms all have formal charges of -1, while the P atom has a formal charge of +1. Turning one lone pair from an oxygen atom into a bonding pair makes the formal charge on the P atom zero and also makes the formal charge on the O atom involved equal to zero, thereby minimising the formal charges in the ion. We can shift electrons from any of the outer O atoms, so there are four possible resonance structures as shown below. (Note that we have omitted the 3- charge on each structure for clarity.)



Is our answer reasonable?

There are four possible ways to minimise the formal charges, so we must have four resonance structures. The four structures differ only in the position of a double bond, and therefore we can be confident that our answer is correct.

PRACTICE EXERCISE 5.2

Determine the Lewis structure of the acetate anion, CH_3COO^-.

In the examples presented so far, all the resonance structures are equivalent in energy, but resonance structures are not always equivalent. Resonance structures that are not equivalent occur when step 5 requires shifting electrons from atoms of different elements. In such cases, different possible structures may have different formal charge distributions, and the optimal set of resonance structures includes those forms with the lowest possible formal charge on each atom.

WORKED EXAMPLE 5.3

Resonance Structures of N_2O

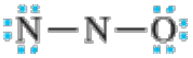
Determine the possible resonance structures of dinitrogen oxide, N_2O, a gas used as an anaesthetic, a foaming agent and a propellant for whipped cream.

Analysis

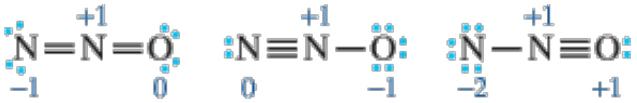
Once again, we first determine the Lewis structure, and then inspect any possible resonance structures.

Solution

We must first choose whether N or O will be the inner atom. As O is more electronegative than N, the structure will have an inner N atom bonded to an O atom and another N atom. The structure we obtain following the first four steps is:



This structure has formal charges of -2 on the outer N atom, +3 on the inner N atom and -1 on the O atom. We can convert lone pairs on the end N atom or the O atom into bonding pairs to reduce the formal charges, but we must ensure that the inner N atom has no more than four electron pairs. This leaves us with the following possibilities, in which the numbers denote the formal charges.



The formal charges of the first two structures are identical, and less than those on the third structure. Thus, the optimal Lewis structure of the N_2O molecule is a composite of the first two structures, which are formally inequivalent, but not the third.



Is our answer reasonable?

We have chosen the two structures in which the formal charges are minimised, and so our answer should be correct. In fact, experimental studies show that the nitrogen–oxygen bond in N_2O is somewhere between an N—O single and an N═O double bond.

PRACTICE EXERCISE 5.3

Determine the Lewis structure of ozone, O_3, in which the three oxygen atoms are linked in a row.

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5.4 Valence-shell-electron-pair Repulsion (VSEPR) Theory

The Lewis structure of a molecule shows how the valence electrons are distributed among the atoms. It does not, however, show the three-dimensional structure, which plays an essential role in determining chemical reactivity. However, we can use the Lewis structure as a starting point to determine the shape of a molecule or ion. The **valence-shell-electron-pair repulsion (VSEPR)** theory considers that molecular shape is determined primarily by the repulsions between pairs of electrons in the molecule or molecular ion, be they bonding pairs or lone pairs. Therefore, to minimise these repulsions, electron pairs around an inner atom within a molecule will be situated as far apart as possible in the preferred three-dimensional structure.

To determine the shape of a molecule using VSEPR theory, we use the following procedure:

1. Determine and draw the Lewis structure of the molecule.
2. Count the number of sets of bonding pairs and lone pairs of electrons around any inner atom, and use table 5.2 to determine the optimum geometry of these sets.
   Note that VSEPR theory makes no distinction between electron pairs in single, double and triple bonds. Each is treated as being one set.

TABLE 5.2 Optimum geometry of sets of electron pairs

Number of sets of electron pairs	Geometry of sets of electron pairs
2	linear
3	trigonal planar
4	tetrahedral
5	trigonal bipyramidal
6	octahedral

3. Modify the geometry, if necessary, to take account of the fact that the magnitudes of repulsions between sets of electron pairs depend on whether the electron pairs involved are bonding pairs (BP) or lone pairs (LP). The repulsions are in the order:

$$\text{LP}-\text{LP} > \text{BP}-\text{LP} > \text{BP}-\text{BP}$$

Therefore, two neighbouring lone pairs on an inner atom will repel each other to a greater extent than will two neighbouring bonding pairs. This is because lone pairs occupy a larger volume than bonding pairs. Note that double bonds occupy a larger volume than single bonds, and some structures may have to be modified for this.

It is important to make the distinction between the geometry of the sets of electron pairs, and the shape of the molecule. The former refers to the way in which sets of electron pairs are arranged around an inner atom of the molecule, while the latter refers to the arrangement of the atoms bonded to that inner atom. As we will see, when lone pairs are present, the two are not the same.

We will now illustrate VSEPR using examples of each different geometry of sets of electron pairs.

Two Sets of Electron Pairs: Linear Geometry

Beryllium Hydride, BeH_2

The Lewis structure of BeH_2 is:

H—Be—H

In this case, we have two sets of electron pairs around the inner atom that we need to situate as far away from each other as possible. This is satisfied by placing the two sets in a **linear** arrangement (table 5.2) and results in a linear shape for this molecule, with a H—Be—H bond angle of 180°. Note that we do not adjust the optimum geometry of the electron pairs, since there are only two single bonding pairs and no lone pairs.

Carbon Dioxide, CO_2

The Lewis structure of CO_2 shows an inner C atom bonded to two outer O atoms.



This is similar to BeH_2 because we have two sets of electron pairs again. Even though each set comprises the two electron pairs of a double bond, the principle is still the same. We place the two sets as far apart as possible, i.e. in a linear arrangement, and this leads to a linear shape. Notice that the lone pairs on the O atoms do not affect the overall shape of the molecule; only sets of electrons that are either bonded to, or lie completely on, an inner atom determine molecular shape.

Three Sets of Electron Pairs: Trigonal Planar Geometry

Boron Trifluoride, BF_3

The Lewis structure of BF_3 shows an inner B atom singly bonded to three F atoms. We have three sets of electron pairs about the inner atom.



The optimal geometry for three sets of electron pairs is **trigonal planar** (table 5.2). In this arrangement, the sets are oriented at 120° to each other and are coplanar. This leads to a trigonal planar shape for the BF_3 molecule, with all atoms coplanar and all F—B—F bond angles of 120°. Note that, again, as all the sets of electron pairs involved are equivalent, we do not have to adjust their optimal geometry.

The Nitrite Ion, NO_2^-

Two possible resonance structures can be drawn for the nitrite ion, which are as follows.



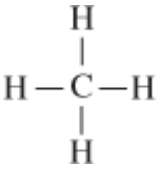
This is the first example we have encountered in which the inner atom bears a lone pair, and this has

important implications when applying VSEPR theory. Note that we can choose either resonance structure and end up with the same result. There are three sets of electron pairs, two sets of bonding pairs and a lone pair. The idealised geometry is trigonal planar. However, in this case, not all the repulsions between the sets of electron pairs are the same; there are BP–BP repulsions and BP–LP repulsions. The BP–LP repulsions are stronger, which means that the two bonding pairs will be pushed slightly closer together than an exact trigonal planar arrangement. The result is that the O—N—O bond angle is about 115°, rather than 120°. This example also illustrates the difference between geometry and shape. The sets of electron pairs have an approximately trigonal planar geometry, but we would describe the shape of the NO_2 ion as bent, because shape refers only to the positions of the atoms and not the electrons.

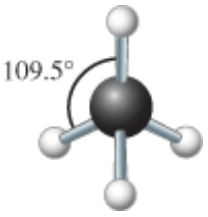
Four Sets of Electron Pairs: Tetrahedral Geometry

Methane, CH_4

The Lewis structure of methane, CH_4, shows that the molecule contains four C—H single covalent bonds, and therefore four sets of equivalent electron pairs.

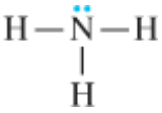


The optimal geometry for four sets of electron pairs is **tetrahedral** (table 5.2). This means that the methane molecule is tetrahedral in shape, with H—C—H bond angles of 109.5°, and the H atoms situated at the four vertices of a tetrahedron.



Ammonia, NH_3

The Lewis structure of ammonia, NH_3, shows a total of four sets of electron pairs, three bonding pairs and a lone pair.



The idealised arrangement of four sets of electron pairs is tetrahedral. But we now have BP–BP and BP–LP repulsions to consider. The single lone pair on the N atom takes up more space than each of the three bonding pairs, and this distorts the idealised arrangement such that the H—N—H angles in ammonia are about 107°. Ammonia adopts a trigonal pyramidal shape, with the N atom lying out of the plane of the three H atoms.

Water, H_2O

Like methane and ammonia, water has four sets of electron pairs, as shown in its Lewis structure, and the idealised arrangement is again tetrahedral.



However, in this case we have two sets of bonding pairs and, significantly, two lone pairs. The LP–LP repulsion dominates, and there are also BP–LP repulsions to consider. The result is that the idealised tetrahedral geometry of the four sets of electron pairs is significantly distorted, such that the H—O—H bond angle in water is about 104.5°. Water adopts a bent shape.

Figure 5.13 shows the different shapes of methane, ammonia and water. The important effect of lone pairs on the shapes of the molecules is evident in these three diagrams.

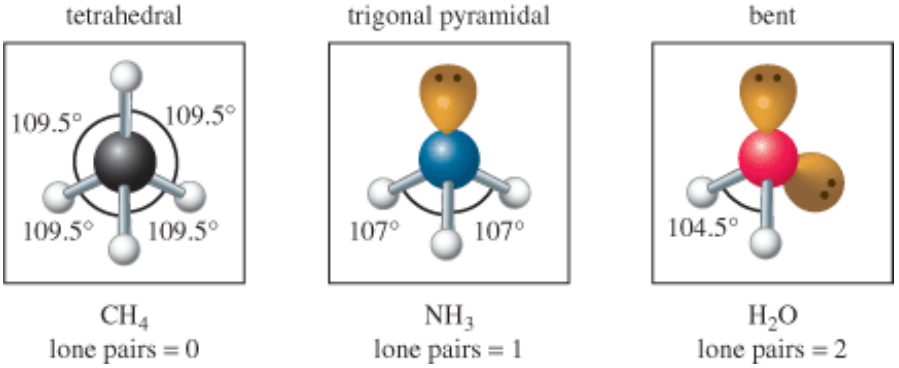


FIGURE 5.13 Representations of the different shapes of methane, ammonia and water molecules, each with four sets of electron pairs.

WORKED EXAMPLE 5.4

Shape of the Hydronium Ion

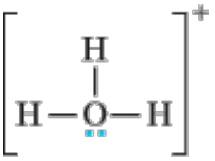
Determine the shape of the hydronium ion, H_3O^+, using VSEPR theory. Make a sketch of the ion that shows the three-dimensional shape, including any lone pairs that may be present.

Analysis

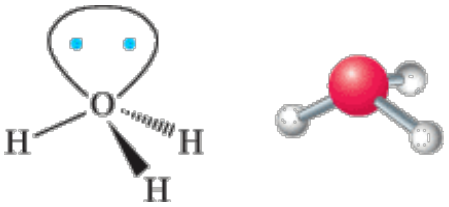
Follow the three-step process described previously. Begin with the Lewis structure, and then use this to determine the number of sets of electron pairs and therefore the geometry of these. Finally, take into account any lone pairs to deduce the molecular shape.

Solution

1. Determine the Lewis structure. A hydronium ion has eight valence electrons. Six are used to make three O—H single bonds, and two are placed as a lone pair on the oxygen atom.



2. There are four sets of electron pairs, three bonding pairs and one lone pair. The idealised geometry is therefore tetrahedral.
3. The presence of a lone pair means that the idealised tetrahedral geometry of the sets of electron pairs will be distorted, owing to LP–BP repulsions. We would therefore expect the H—O—H bond angles to be somewhat less than the 109.5°. The shape of the hydronium ion is trigonal pyramidal, as outlined in the following diagram.



Is our answer reasonable?

The hydronium ion has the same number of electrons and atoms as the ammonia molecule, so it is reasonable for these species to have a similar shape.

PRACTICE EXERCISE 5.4

Determine the shape of chloromethane, CH_3Cl. Make a sketch of the molecule that shows its three-dimensional shape.

Five Sets of Electron Pairs: Trigonal Bipyramidal Geometry

Phosphorus Pentachloride, PCl_5

The Lewis structure of PCl_5 shows five sets of equivalent electron pairs around a phosphorus atom.



The geometry which places these as far apart as possible is **trigonal bipyramidal** (table 5.2). A trigonal bipyramid is so called because it can be viewed as two pyramids that share a triangular base, as shown in figure 5.14a. In contrast to the geometries encountered so far, the five positions in a trigonal bipyramid are not all equivalent. Three positions lie at the corners of an equilateral triangle around the inner atom, separated by 120° bond angles. Atoms in the trigonal plane are in *equatorial positions*. The other two positions lie along an axis above and below the trigonal plane, separated from equatorial positions by 90° bond angles. Atoms in these sites are in *axial positions*. These differences are outlined in figure 5.14b.

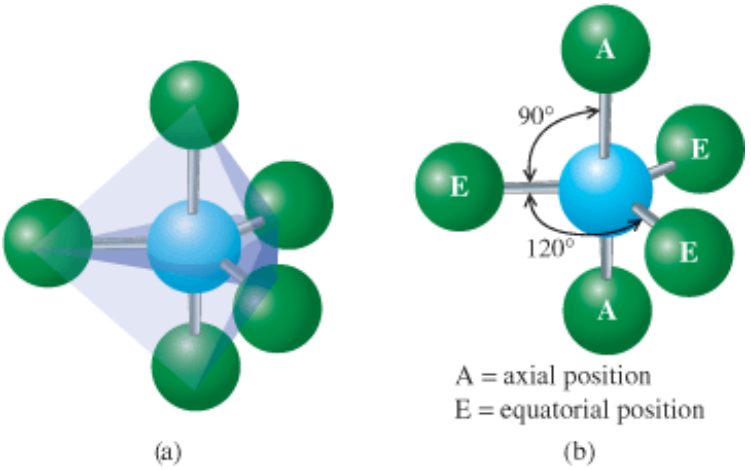


FIGURE 5.14 (a) Model representing the equatorial plane and opposing pyramids that make up a trigonal bipyramid. PCl_5 adopts a regular trigonal bipyramidal shape.

(b) Ball-and-stick model representing a trigonal bipyramid with axial and equatorial sites labelled.

As PCl_5 contains only bonding pairs of electrons, we would expect it to adopt a regular trigonal bipyramidal shape, as shown in figure 5.14.

When lone pairs are present in molecules with five sets of electron pairs, the consequences of the inequivalence of the axial and equatorial sites become more apparent. We will illustrate this with SF_4.

Sulfur Tetrafluoride, SF_4

The Lewis structure of SF_4 (figure 5.15) shows four S—F bonds and one lone pair of electrons on the sulfur atom. We would expect a trigonal bipyramidal geometry for these five sets of electron pairs, but the presence of the lone pair means there will be some slight distortion.

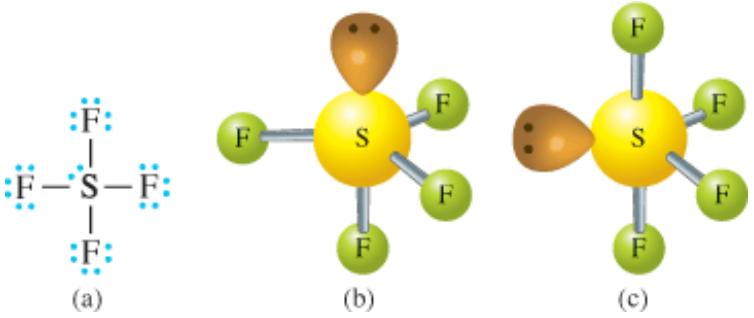


FIGURE 5.15 Views of sulfur tetrafluoride:

(a) Lewis structure

(b) ball-and-stick model of the trigonal pyramid and

(c) ball-and-stick model showing the seesaw form.

In addition, because the equatorial and axial positions of a trigonal bipyramid differ, we can draw two possible structures for SF_4 with the lone pair in either axial or equatorial position. As figure 5.15 shows, placing the lone pair in an axial position gives a trigonal pyramidal shape, whereas placing the lone pair in an equatorial position gives a **seesaw shape**.

Experiments show that SF_4 has the seesaw shape, which means that this is more stable than the trigonal pyramid. This can be explained by noting that the trigonal pyramid structure has three LP–BP repulsions at 90°, while the seesaw has two at 90° and two at 120°. Minimising the number of lowest angle repulsive

interactions involving lone pairs gives the lowest energy structure and consequently the seesaw shape is preferred. Note that, because of the LP–BP repulsions between the lone pair and the axial bond pairs, the axial F—S—F bond angle is slightly less than 180°.

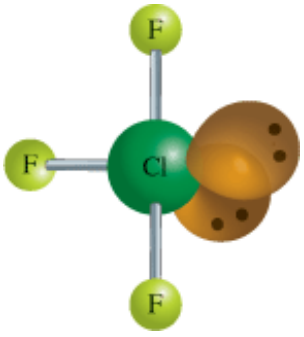
Chlorine trifluoride, ClF_3

The Lewis structure of ClF_3 shows five sets of electron pairs: three bonding pairs and two lone pairs.



We again expect a distorted trigonal bipyramidal geometry of the five sets of electron pairs, but now we must determine whether the two lone pairs occupy axial or equatorial positions.

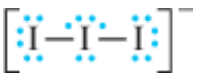
We can immediately discount placing one lone pair axial and the other equatorial, as this would lead to a LP–LP repulsion, the largest possible, at 90°. You might imagine that placing the lone pairs in the axial positions would be preferred, as it places them furthest away, but it also leads to a total of six LP–BP repulsions at 90°. In fact, experiments show that the two lone pairs are equatorial; this leads to four LP–BP repulsions at 90° and is energetically preferred, despite the fact that there is a LP–LP repulsion at 120°. Thus, ClF_3 is T-shaped with two equatorial lone pairs.



It is sometimes difficult to determine which of the possible structures is correct using simple VSEPR theory, and we must then resort to experimental results for definitive answers.

The Triiodide Ion, I_3^-

The Lewis structure shows five sets of electron pairs around the inner I atom: two bonding and three lone pairs.



We have seen in the previous examples that lone pairs prefer to be in equatorial positions in trigonal bipyramidal geometries, and the same principle applies here. All three lone pairs are equatorial, as this is the only way to avoid any highly destabilising LP–LP repulsions at 90°.

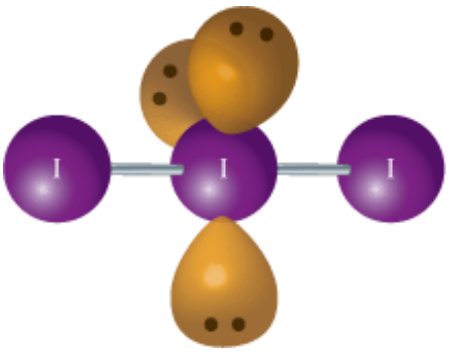


Figure 5.16 summarises the different possible shapes of species with five sets of electron pairs.

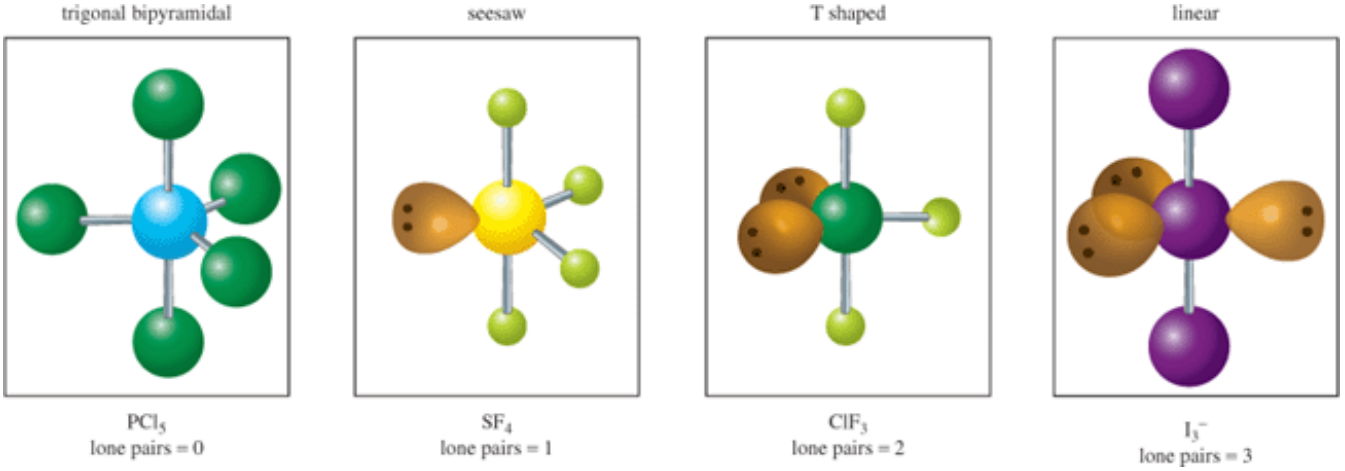


FIGURE 5.16 The different possible shapes of species with five sets of electron pairs.

Six Sets of Electron Pairs: Octahedral Geometry

Sulfur Hexafluoride, SF_6

The Lewis structure of SF_6, shown in figure 5.17a, indicates that sulfur has six S—F bonds and no lone pairs, and therefore has six sets of electron pairs around the inner S atom. An **octahedral** geometry of the six sets (table 5.2) places them as far apart as possible, as shown in figure 5.17b. This gives an octahedral shape; each F atom lies at one of the six vertices of an octahedron, with possible F—S—F bond angles of 90° and 180°. An octahedron is so called because it has eight triangular faces, as shown in figure 5.17c.

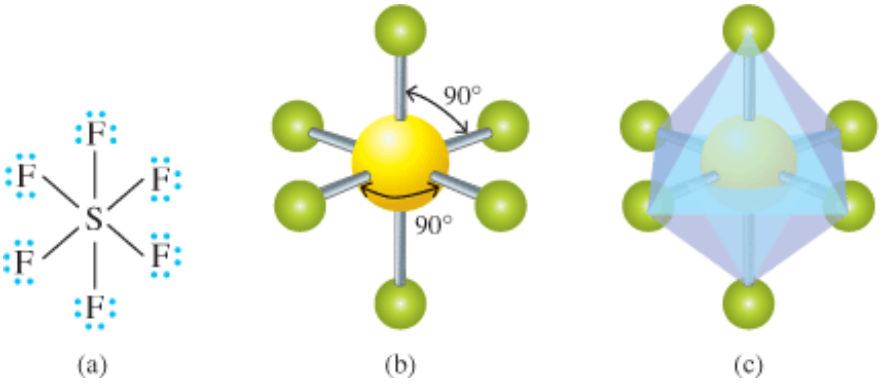


FIGURE 5.17 Views of sulfur hexafluoride:
(a) Lewis structure
(b) ball-and-stick model and
(c) ball-and-stick model showing the triangular faces of the octahedron.

All six positions around an octahedron are equivalent, as figure 5.18 demonstrates. Replacing one fluorine atom in SF_6 with a chlorine atom gives SF_5Cl. No matter which fluorine is replaced, the SF_5Cl molecule has four fluorine atoms in a square, with the fifth fluorine and the chlorine atom on opposite sides, at right angles to the plane of the square.

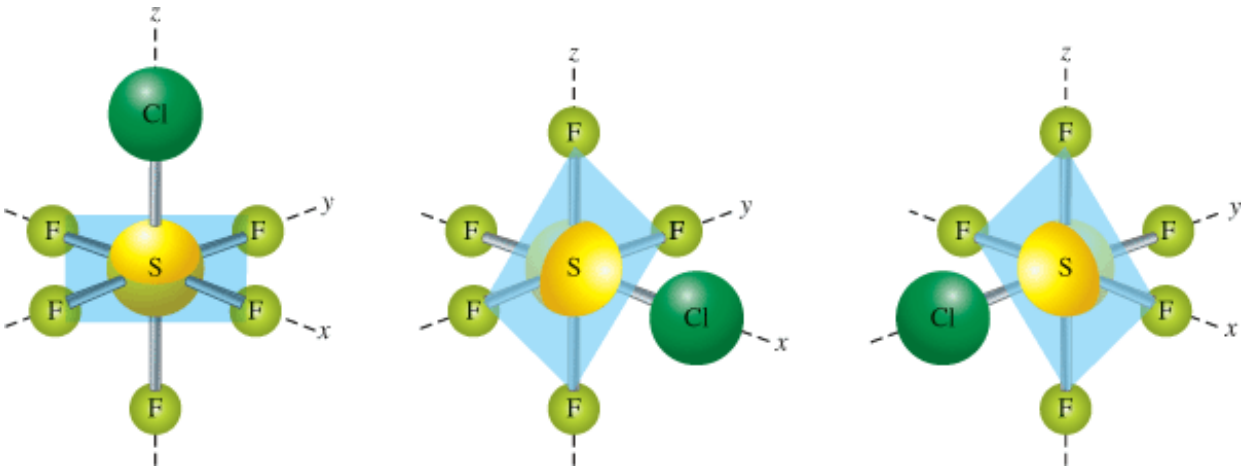
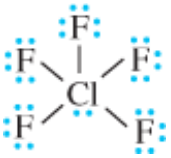


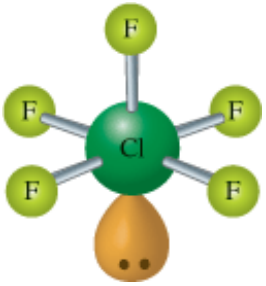
FIGURE 5.18 Replacing any of the fluorine atoms of SF_6 with a chlorine atom gives a molecule with a square of fluorine atoms capped by one fluorine and one chlorine. This shows that all six positions of the octahedron are equivalent.

Chlorine Pentafluoride, ClF_5

The Lewis structure of ClF_5 shows a total of six sets of electron pairs: five bonding pairs and one lone pair.

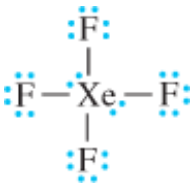


We again expect an octahedral geometry of the six sets of electron pairs, and, in this case, all six possible positions of the lone pair are equivalent. Therefore, ClF_5 adopts a square pyramidal shape.



Xenon Tetrafluoride, XeF_4

The Lewis structure of this molecule shows six sets of electron pairs: four bonding pairs and two lone pairs.



We therefore expect an octahedral geometry of the sets of electron pairs, but, as always, we must determine how to arrange the lone pairs. In XeF_4, both lone pairs must be opposite each t other because any other arrangement would lead to highly destabilising LP–LP repulsions at 90°. This leaves the four fluorine atoms in a square plane around xenon.

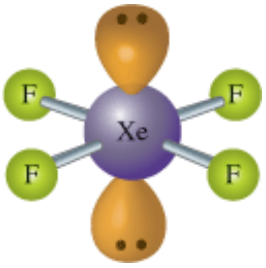


Figure 5.19 summarises the shapes of molecules with six sets of electron pairs. This completes our inventory of molecular shapes.

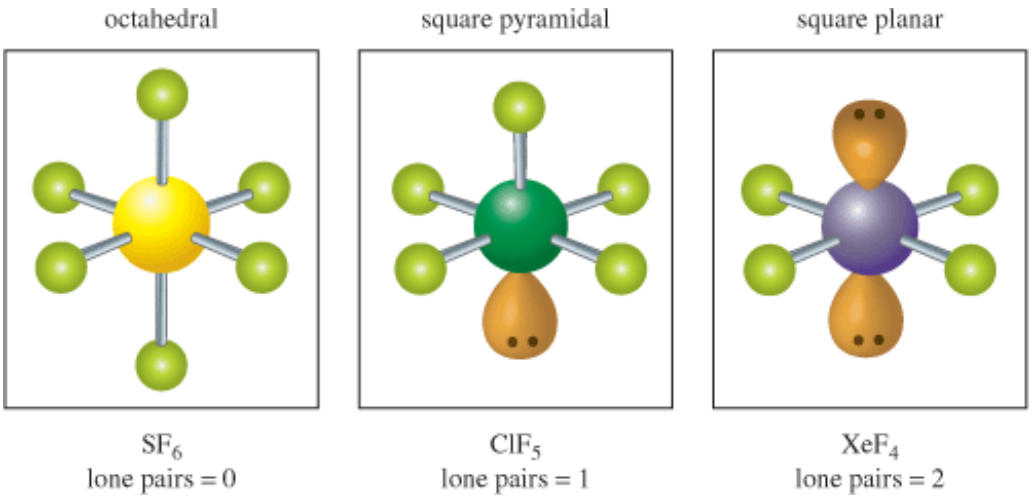


FIGURE 5.19 The different possible shapes of some molecules with six sets of electron pairs.

The most common mistake made when determining a molecular shape using VSEPR theory is to count the number of *atoms* surrounding an inner atom, rather than the number of *sets of electron pairs*. For example, a molecule such as SF_4 may be easily mistaken as tetrahedral, by analogy with tetrahedral CH_4, as both molecules have four outer atoms surrounding an inner atom. However, we have shown previously that SF_4 has five sets of electron pairs and its shape is based on a trigonal bipyramidal arrangement of these. While VSEPR theory often gives remarkably accurate results, it does not necessarily work for all molecules. In cases where repulsion between the electron pairs is not the dominant factor in determining molecular geometry, VSEPR theory fails. You will encounter some examples of this in chapter 13.

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5.5 Properties of Covalent Bonds

Having developed ideas about Lewis structures and shapes of molecules, we can now explore some of the important features of covalent bonds. These features provide revealing information about molecular shapes.

Dipole Moments

As described in section 5.1, most chemical bonds are polar, meaning that one end of the bond is slightly negative, and the other is slightly positive. Bond polarities can lead to molecules with negative ends and positive ends. A molecule with this type of electron density distribution is said to have a **dipole moment**, μ (the lower-case Greek letter mu).

The dipole moment of a polar molecule can be measured by placing a sample in an electric field. For example, figure 5.20 shows a schematic diagram of hydrogen fluoride, HF, molecules between a pair of metal plates. In the absence of an applied field, the molecules are oriented randomly throughout the volume of the device. When an electric potential is applied across the plates, the HF molecules align spontaneously according to the principles of electrostatic force. The positive ends of the molecules (the hydrogen atoms) point towards the negative plate, and the negative ends (the fluorine atoms) point towards the positive plate. The extent of alignment depends on the magnitude of the dipole moment. The SI unit for the dipole moment is the coulomb metre (C m). Bond dipole moments span the range from 0 to about 7×10^{-30} C m. Hydrogen fluoride has $\mu = 5.95 \times 10^{-30}$ C m, while a nonpolar molecule like F_2 has no dipole moment, $\mu = 0$ C m. Experimental values are also often reported in units of debyes, D (1 D = 3.34×10^{-30} C m).

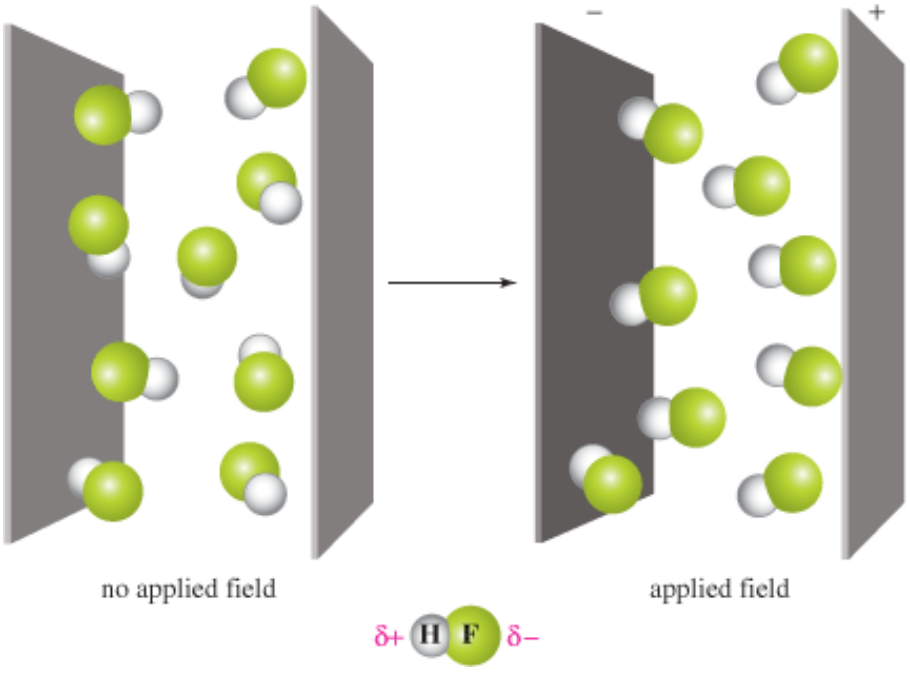
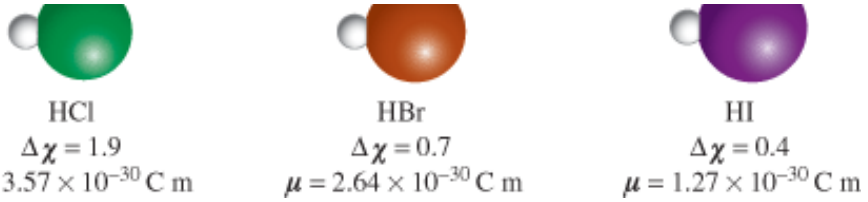


FIGURE 5.20 An applied electric field causes an alignment of polar HF molecules. The extent of alignment depends on the magnitude of the dipole moment.

Dipole moments depend on bond polarities. For example, the trend in dipole moments for the hydrogen halides follows the trend in electronegativity differences; the more polar the bond (indicated by the difference in electronegativity, Δχ, the larger the dipole moment, μ.



Dipole moments also depend on molecular shape. Any diatomic molecule composed of atoms with different electronegativities has a dipole moment. For more complex molecules, we must evaluate dipole moments using both bond polarity and molecular shape. A molecule with polar bonds will have no dipole moment if its shape causes the dipole moments of individual bonds to cancel one another, which is more likely for small symmetrical molecules.

Figure 5.21 illustrates the dramatic effect of shape on the dipole moments of triatomic molecules. Recall from section 5.1 that an arrow can be used to represent a dipole moment. The head of the arrow points to the partial positive end (δ+) of the polar bond. Figure 5.21a shows that, although both bonds in linear CO_2 are polar ($\Delta\chi = 1.0$), the two arrows indicating individual bond polarities point in exactly opposite directions. Thus, the effect of one polar bond exactly cancels the effect of the other. For bent H_2O, in contrast, figure 5.21b shows that the effects of the two polar bonds do not cancel. Water has a partial negative charge on its oxygen atom and partial positive charges on its hydrogen atoms. The resulting dipole moment of the molecule is $\mu = 6.18 \times 10^{-30}$ C m, with the direction of the dipole moment shown by the coloured arrow in figure 5.21b.

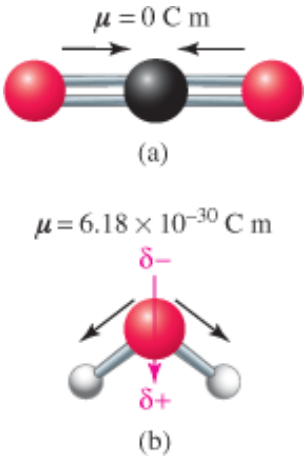


FIGURE 5.21

(a) When identical polar bonds point in opposite directions, as in CO_2, their polarity effects cancel, giving zero net dipole moment.

(b) When two identical polar bonds do not point in exactly opposite directions, as in H_2O, there is a net dipole moment.

Molecules containing polar bonds whose dipole moments cancel each other do not have overall dipole moments. Such molecules tend to have highly symmetrical geometries. Phosphorus pentachloride, for example, has μ = 0 C m. The two axial P—Cl bonds point in opposite directions, and, although three P—Cl bonds arranged in a trigonal plane have no counterparts pointing in opposite directions, trigonometric analysis shows that the polar effects of three identical bonds in a trigonal plane cancel exactly. Likewise, the bonds in a tetrahedron are arranged so that their polarities cancel exactly; i.e. the tetrahedral molecule CCl_4 has no dipole moment.

The perfect symmetry of these geometric forms is disrupted when a lone pair replaces a bond, giving a molecule with a dipole moment. Examples include SF_4 (seesaw), ClF_3 (T shape), NH_3 (trigonal pyramid) and H_2O (bent), all of which have dipole moments. Replacing one or more bonds with a bond to a different kind of atom also introduces a dipole moment because the symmetry is lowered. Thus, chloroform, $CHCl_3$, has a dipole moment but CCl_4 does not. The carbon atom of chloroform has four

bonds in a near-regular tetrahedron, but the four bonds are not identical. The C—Cl bonds are more polar than the C—H bond, so the polarities of the four bonds do not cancel. Figure 5.22 shows the magnitude and direction of the dipole moment in chloroform ($\mu = 3.47 \times 10^{-30}$ C m).

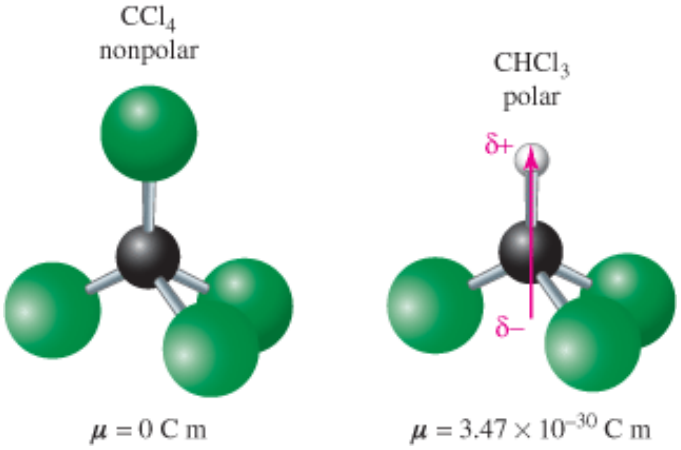


FIGURE 5.22 Carbon tetrachloride, CCl_4, is a symmetrical tetrahedral molecule, so the individual bond polarities cancel. Chloroform, $CHCl_3$, is also a tetrahedral molecule, but the four bonds are not identical, so the bond polarities do not cancel.

In a symmetrical octahedral system such as SF_6, each polar S—F bond has a counterpart pointing in the opposite direction. The bond polarities cancel in pairs, leaving this molecule without a dipole moment.

WORKED EXAMPLE 5.5

Predicting Dipole Moments

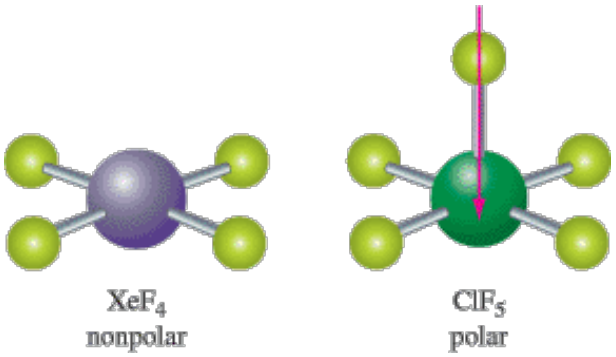
Does either ClF_5 or XeF_4 have a dipole moment?

Analysis

Molecules composed of atoms with different electronegativities have dipole moments unless their symmetries are sufficient to cancel their bond polarities. Therefore, we must examine each molecular structure and the orientation of the bonds in each molecule.

Solution

The molecular structures of chlorine pentafluoride and xenon tetrafluoride are shown in figure 5.19. Each has six sets of electron pairs around an inner atom, but these include lone pairs. As a result, ClF_5 has a square pyramidal shape, whereas XeF_4 has a square planar shape. Pictures can help us determine whether or not the bond polarities cancel.



Each molecule has four fluorine atoms at the corners of a square. The Xe—F bond polarities cancel in pairs, leaving XeF_4 without a dipole moment. Four bond polarities also cancel in ClF_5, but the fifth Cl—F bond has no counterpart in the opposing direction, so ClF_5 has a dipole moment that points along the axis containing the lone pair and the fifth Cl—F bond.

Is our answer reasonable?

Any molecule in which individual dipole moments do not cancel will have an overall dipole moment. It is therefore reasonable that XeF_4 will have no dipole moment while the less symmetric ClF_5 molecule will.

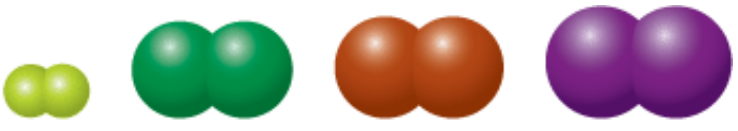
PRACTICE EXERCISE 5.5

Determine whether ethane, C_2H_6, and ethanol, C_2H_5OH, have dipole moments.

Bond Length

As we described in section 5.1, the bond length of a covalent bond is the nuclear separation distance at which the molecule is most stable. The H—H bond length in molecular hydrogen is 74 pm. At this distance, attractive interactions are maximised relative to repulsive interactions (see figure 5.2). Having developed ideas about Lewis structures and molecular shapes, we can now examine bond lengths in more detail.

Table 5.3 lists average bond lengths for the most common chemical bonds. The table displays several trends. One trend is that bonds become longer as atom size increases, as shown by bond lengths of the diatomic halogens.



	F_2	Cl_2	Br_2	I_2
Bond length (pm)	142	199	228	267
Atomic radius (pm)	72	100	114	133

TABLE 5.3 Average bond lengths (all values are in picometres, 1 pm = 10^{-12} m)

n_a[a]	n_b[a]	Bond lengths

H—X bonds									
1	1	H—H	74						
1	2	H—C	109	H—N	101	H—O	96	H—F	92
1	3	H—Si	148	H—P	144	H—S	134	H—Cl	127
1	4							H—Br	141
Second-row elements									
2	2	C—C	154	C—N	147	C—O	143	C—F	135
2	2			N—N	145	O—O	148	F—F	142
2	3	C—Si	185	C—P	184	C—S	182	C—Cl	177
2	3	O—Si	166	O—P	163	O—S	158	N—Cl	175
2	3	F—Si	157	F—P	157	F—S	156		
2	4,5			F—Xe	190	C—Br	194	C—I	214
Larger elements									
3	3	Si—Si	235	P—P	221	S—S	205	Cl—Cl	199
3	3	Si—Cl	202	P—Cl	203	S—Cl	207		
4	4							Br—Br	228
5	5							I—I	267
Multiple bonds									
		C═C	133	C═N	138	C═O	120	O═O	121
		P═O	150	S═O	143				
		C≡C	120	C≡N	116	C≡O	113	N≡N	110

(a) n_a is the principal quantum number for the first named atom and is the principal quantum number for the first named atom and n_b is for the second atom. is for the second atom.

The trend is consistent with our introduction to orbital overlap. Recall that bonding involves valence orbitals, and it is the occupied valence orbitals that determine the size of an atom.

Bond polarity also contributes to bond length because partial charges generate electrostatic attraction that pulls the atoms closer together. For example, notice in Table 5.3 that C—N bonds are slightly shorter than the average of C—C and N—N bonds. This is a result of the polarity of the C—N bond.

The bond lengths in Table 5.3 show one final feature: a multiple bond is shorter than the single bond between the same two atoms. This is because placing additional electrons between atoms decreases internuclear repulsion, leading to an increase in net attraction, thereby allowing the atoms to come closer together. Thus, triple bonds are the shortest of all bonds among second-row elements.

Because bond lengths depend on the number of electrons involved in the bond, we can use bond lengths to decide which Lewis structure best represents the actual electron distribution in a molecule. Sulfur–oxygen bonds provide a good example. Figure 5.23 shows two possible sets of Lewis structures for species that contain sulfur–oxygen bonds. One set, the ‘unoptimised structures’, places octets of electrons on the inner sulfur atom, while the other set, the optimised structures, reduces the formal charge on sulfur to zero at the expense of exceeding the octet on the S atom. As the figure shows, the two sets of structures predict different bond types.

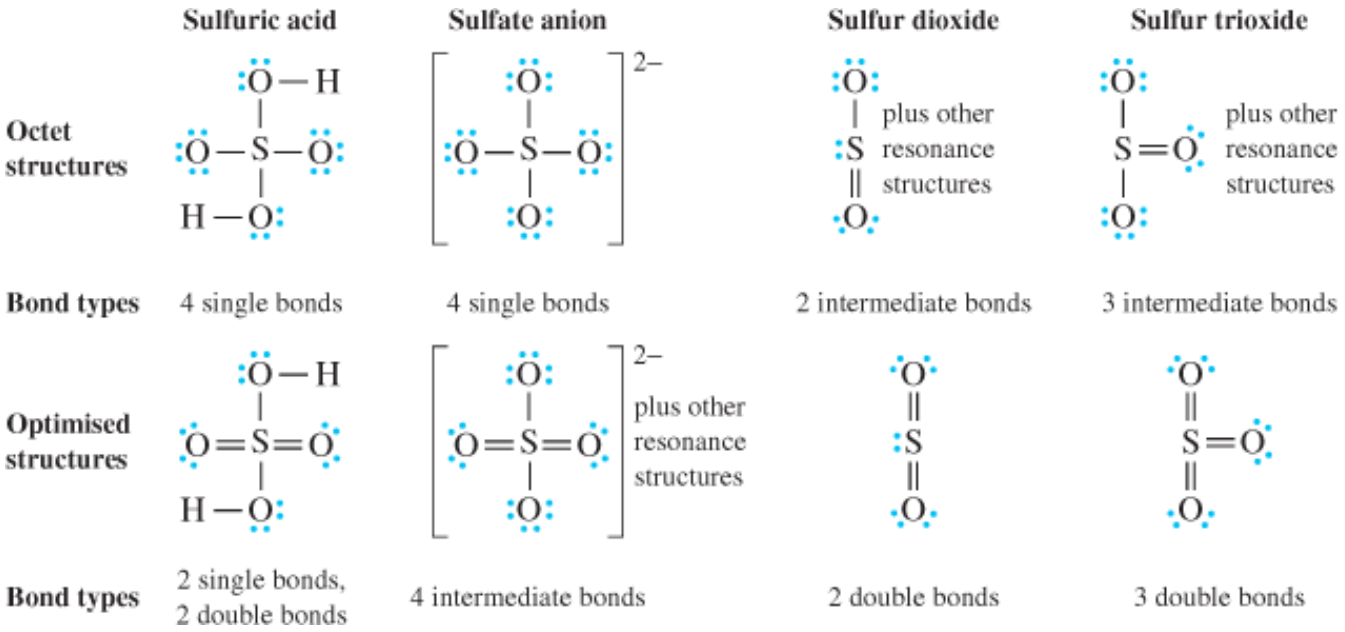


FIGURE 5.23 'Unoptimised structures' and optimised structures predict different bond types for sulfur–oxygen bonds.

We can use experimental bond length values to support the optimised Lewis structures. In sulfuric acid, there are two distinctly different bond types with bond lengths of 157 pm and 142 pm. In the sulfate anion, all the bond lengths are 147 pm, while the bond lengths in SO_2 and SO_3 are 143 pm and 142 pm, respectively. These values indicate that a bond length of 157 pm is consistent with an S—O single bond, and 142 pm with an S═O double bond. A bond length of 147 pm indicates an intermediate bond character (see Table 5.3). These values support the optimised Lewis structures, as shown in figure 5.22, which predict double bonds only for SO_2 and SO_3, double and single bonds for H_2SO_4 and intermediate bonds for SO_4^{2-}.

To summarise, generally the following factors influence bond lengths:

1. For a given pair of atoms, the more electrons in the bond between them, the shorter the bond.
2. For two atoms joined by the same type of bond (single, double or triple), the larger the electronegativity difference between the bonded atoms, the shorter the bond.

WORKED EXAMPLE 5.6

Bond Lengths

What factor accounts for each of the following differences in bond length?

(a) I_2 has a longer bond than Br_2.

(b) C—N bonds are shorter than C—C bonds.

(c) H—C bonds are shorter than the C≡O bond.

(d) The carbon–oxygen bond in formaldehyde, $H_2C{=}O$, is longer than the bond in carbon monoxide, C≡O.

Analysis

Bond lengths are controlled by three factors, some of which are more influential than others. To explain a difference in bond length, we need to determine the way that the factors are

balanced.

Solution

(a) I—I > Br—Br. Iodine is just below bromine in the periodic table, so the valence orbitals of iodine are larger than the valence orbitals of bromine. Thus, the I_2 bond is longer than the Br_2 bond because iodine has a larger atomic radius.

(b) C—N < C—C. Carbon and nitrogen are both second-row elements. However, nitrogen has a higher effective nuclear charge than carbon, so nitrogen has the smaller radius. This makes C—N bonds shorter than C—C bonds. In addition, a C—N bond is polar, which contributes to the shortening of the C—N bond.

(c) H—C < C≡O. Here, we are comparing bonds in which the atomic radii and the amount of multiple bonding influence bond length. The experimental fact that H—C bonds are shorter than the triple C≡O bond indicates that the size of the hydrogen orbital is a more important factor than the presence of multiple bonding in this case.

(d) C═O > C≡O. Both bonds are between carbon and oxygen, so n (the principal quantum number, which determines size), atomic number (Z) and electronegativity difference ($\Delta\chi$) are the same. However, carbon monoxide contains a triple bond, whereas formaldehyde has a double bond. The triple bond in CO is shorter than the double bond in H_2CO because more shared electrons means a shorter bond.

Is our answer reasonable?

When factors work in the same direction (effective nuclear charge and bond polarity in the case of C—N < C—C), we can make confident predictions. When factors work in the opposite direction (n value and bond multiplicity in the case of H—C < C≡O), we can explain the observed values but cannot confidently predict them.

PRACTICE EXERCISE 5.6

What factor accounts for each of the following differences in bond length? (a) The C═C bond is longer than the C≡C bond. (b) The C—Cl bond is shorter than the Si—Cl bond. (c) The C—C bond is longer than the O—O bond.

Bond Energy

Bond energies are defined as the amount of energy that must be supplied to break a particular chemical bond. Bond energies, like bond lengths, vary in ways that can be traced to atomic properties, and there are three consistent trends in bond energies:

1. *Bond energies increase as more electrons are shared between the atoms*. Shared electrons are the ‘glue’ of chemical bonding, so sharing more electrons strengthens the bond.
2. *Bond energies increase as the electronegativity difference* ($\Delta\chi$) *between bonded atoms increases*. Polar bonds gain stability from the electrostatic attraction between the negative and positive partial

charges around the bonded atoms. Bonds between oxygen and other second-period elements exemplify this trend (note that the bond lengths also change slightly).

Bond	Difference in electronegativity (Δχ)	Bond energy (kJ mol^{-1})
O—O	0.0	145
O—N	0.5	200
O—C	1.0	360

3. *Bond energies decrease as bonds become longer*. As atoms become larger, the electron density of a bond is spread over a wider region. This decreases the net attraction between the electrons and the nuclei. The following table of bond energies illustrates this effect (note that the electronegativity difference also changes, strengthening the trend).

Bond	Bond length (pm)	Bond energy (kJ mol^{-1})
H—F	92	565
H—Cl	127	430
H—Br	141	360
H—I	161	295

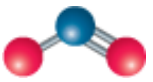
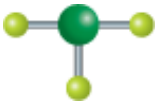
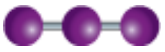
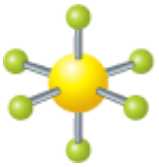
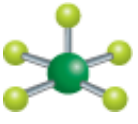
Like bond lengths, bond energies result from the interplay of several factors, including effective nuclear charge, principal quantum number, electrostatic forces and electronegativity. Thus, it is not surprising that there are numerous exceptions to these three trends in bond energies as, in most cases, more than one of the determining factors changes at the same time (see tables above) and often not with the same influence on bond energies. Although it is possible to *explain* many differences in bond energy, it frequently is not possible to *predict* differences with confidence. *t*

Summary of Molecular Shapes

Table 5.4 summarises the relationships between number of sets of electron pairs, the geometry of the sets of electron pairs and molecular shape. If you remember the geometry associated with each number of sets of electron pairs, you can deduce molecular shapes, bond angles and the existence of dipole moments.

TABLE 5.4 Features of molecular geometries

Number of sets of electron pairs	Number of outer atoms	Lone pairs	Geometry of sets of electron pairs	Molecular shape	Bond angles	Dipole moment[(a)]	Example
2	2	0	linear	linear	180°	no	 CO_2
3	3	0	trigonal planar	trigonal planar	120°	no	 BF_3
	2	1	trigonal	bent	<120°	yes	

			planar				 NO_2 - (plus other resonance structures)
4	4	0	tetrahedral	tetrahedral	109.5°	no	 CH_4
	3	1	tetrahedral	trigonal pyramidal	<109.5°	yes	 NH_3
	2	2	tetrahedral	bent	<109.5°	yes	 H_2O
5	5	0	trigonal bipyramidal	trigonal bipyramidal	90°, 120°	no	 PCl_5
	4	1	trigonal bipyramidal	seesaw	<90°, <120°	yes	 SF_4
	3	2	trigonal bipyramidal	T shaped	<90°, <120°	yes	 ClF_3
	2	3	trigonal bipyramidal	linear	180°	no	 I_3^-
6	6	0	octahedral	octahedral	90°	no	 SF_6
	5	1	octahedral	square pyramidal	<90°	yes	 ClF_5
	4	2	octahedral	square planar	90°	no	

(a) Applies only to molecules with identical outer atoms.

This relatively small catalogue of molecular shapes accounts for a remarkable number of molecules. Even complicated molecules such as proteins and other polymers have shapes that can be traced back to these relatively simple templates. The overall shape of a large molecule is a composite of the shapes associated with its inner atoms, with the shape around each inner atom determined by the number of sets of surrounding bonding electron pairs and the number of lone pairs.

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5.6 Valence Bond Theory

Lewis structures are blueprints that show the distribution of valence electrons in molecules. However, the dots and lines of a Lewis structure do not show how bonds form, how molecules react or the shape of a molecule. In this respect, a Lewis structure is like the electron configuration of an atom; both tell us about electron distributions, but neither provides detailed descriptions. Just as we need atomic orbitals to understand how electrons are distributed in an atom, we need an orbital view to understand how electrons are distributed in a molecule.

In the remainder of this chapter we describe two ways to think about covalent bonding: valence bond theory, which uses **localised bonds**, and molecular orbital theory, which uses **delocalised bonds**. The valence bond approach to molecules assumes that electrons are either localised in bonds between two atoms or localised on a single atom, usually in pairs. Accordingly, the localised bonding model develops orbitals of two types. One type is a bonding orbital that has high electron density between two atoms. The other type is an orbital located on a single atom. In other words, any electron is restricted to the region around a single atom, either in a bond to another atom or in a nonbonding orbital.

Localised bonds are easy to apply, even to very complex molecules, and they do an excellent job of explaining much chemical behaviour. In many instances, however, localised bonds are insufficient to explain molecular properties and chemical reactivity. We therefore also show how to construct delocalised bonds that spread over several atoms using molecular orbital theory. Delocalisation requires a more complicated analysis, but it explains chemical properties that localised bonds cannot.

Orbital Overlap

As described earlier in this chapter, the electrons in a hydrogen molecule are located between the two nuclei in a way that maximises electron–nucleus attraction. To understand chemical bonding, we must develop a new orbital model that accounts for shared electrons. In other words, we need to develop a set of **bonding orbitals**.

The model of bonding used by most chemists is an extension of the atomic theory that incorporates a number of important ideas from chapters 1 and 4. Bonding orbitals are created by combining atomic orbitals. Remember that orbitals have wave-like properties. Waves interact, resulting in addition of their amplitudes. Two waves that occupy the same region of space will be superimposed, generating a new wave that is a composite of the original waves. In regions where the amplitudes of the superimposed waves have the same phase, addition of the amplitudes of the waves leads to constructive overlap. This gives a new wave amplitude that is larger than either original wave in that region, as figure 5.24a shows. In regions where the amplitudes have opposite phases, addition of the amplitudes of the waves leads to destructive overlap, giving a new wave amplitude that is smaller than either of the original waves, as illustrated in figure 5.24b.



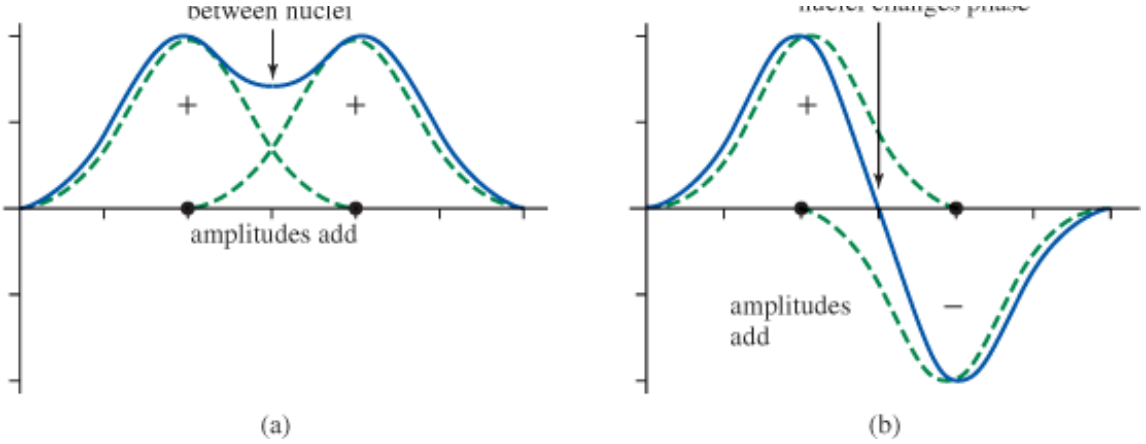


FIGURE 5.24 (a) When two waves (dashed lines) have amplitudes of the same phase, addition gives a new wave (solid line) with a large amplitude in the overlap region.
(b) When two waves (dashed lines) have amplitudes of opposite phases, addition gives a new wave (solid line) with a small amplitude in the overlap region.

Because electrons have wave-like properties, orbital interactions involve similar addition or subtraction of wavefunctions. When two orbitals of the same phase are superimposed, the result is a new orbital that is a composite of the originals, as shown for molecular hydrogen in figure 5.25. This interaction is called **orbital overlap**, and is the foundation of the bonding models we will describe.

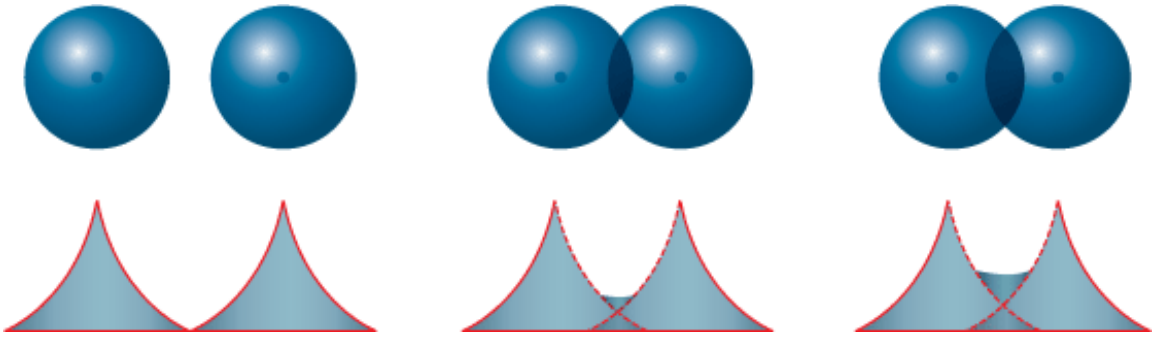


FIGURE 5.25 As two hydrogen atoms approach each other, the overlap of their 1*s* atomic orbitals increases. The wave amplitudes add to generate a new orbital with high electron density between the nuclei.

Conventions of the Orbital Overlap Model

Orbital overlap models proceed from the following assumptions:

1. Each electron in a molecule is assigned to a specific orbital.
2. No two electrons in a molecule have identical descriptions because the Pauli exclusion principle (chapter 4) applies to electrons in molecules as well as in atoms.
3. The electrons in molecules obey the Aufbau principle (chapter 4), meaning that, in the ground state, they occupy the lowest energy orbitals available to them.
4. Only the valence orbitals are needed to describe bonding.

Bonding involves the valence orbitals exclusively in this model, because these orbitals have the appropriate sizes and energies to interact strongly. We have already seen examples of the overlap of valence atomic orbitals in the H_2 and F_2 molecules earlier in this chapter, and this simple approach is perfectly adequate for these small diatomic molecules. There are, however, instances where this simple model does not reproduce the experimentally determined structures of certain molecules. For example, if we consider the bonding in a water molecule to arise from overlap of the valence atomic orbitals on O and H, we find that we cannot reproduce the 104.5° H—O—H bond angle. The two singly occupied *p* orbitals on oxygen lie at 90° to each other, and overlap of these with the H 1*s* orbitals should give a bond angle of 90°.

Valence bond theory recognises this problem, and attempts to solve it by constructing hybrid orbitals from valence atomic orbitals. This approach gives much better agreement with experiments, and is outlined in detail on the following pages, with particular emphasis on the tetrahedral molecule methane.

Hybridisation of Atomic Orbitals

The experimentally determined structure of methane is shown in figure 5.26. Methane adopts a tetrahedral molecular geometry with H—C—H bond angles of 109.5° and the H atoms situated at the vertices of a tetrahedron. If we consider the bonding in methane solely in terms of the overlap of atomic valence orbitals, we quickly come to the conclusion that such a model could not reproduce these bond angles; the three 2*p* orbitals on C are at 90° to each other, while the 2*s* orbital has no directional preference, and we would therefore expect a structure with three of the four C—H bonds at 90° to each other. Obviously this simple model is inadequate to describe the bonding in methane. We can, however, use the individual valence atomic orbitals as a starting point to construct **hybrid orbitals**. These are combinations of atomic orbitals and the process by which we combine them is called **hydridisation**. We illustrate this with methane.

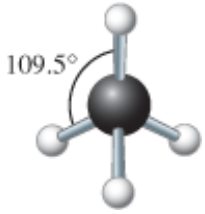


FIGURE 5.26 The experimentally determined structure of methane. The molecule has a tetrahedral geometry with 109.5° bond angles.

Methane: sp^3 Hybrid Orbitals

To construct hybrid orbitals, we first need to identify the valence atomic orbitals that we will use. Carbon has the electron configuration $1s^2 2s^2 2p^2$, which means that the valence orbitals of interest are the one 2*s* and three 2*p* orbitals. We then 'mix' these four atomic orbitals to form four new hybrid orbitals that are called **sp^3 hybrid orbitals**. Recall from chapter 4 that a *p* orbital has two lobes of opposite phase (indicated in figure 5.27a as pink and blue lobes). If we imagine placing an *s* and a *p* orbital such that their centres coincide, one of these lobes will interact constructively with the *s* orbital and will therefore be enhanced, while the other will interact destructively and be diminished. The name sp^3 refers to the fact that the four hybrid orbitals are constructed from one *s* and three *p* atomic orbitals. Equally, and possibly more instructively, it can also be interpreted as each individual sp^3 hybrid orbital having $\frac{1}{4}s$ character and $\frac{3}{4}p$ character. Figure 5.27a shows the shape of sp^3 hybrid orbitals, and also shows diagrammati-cally the process by which they are formed.

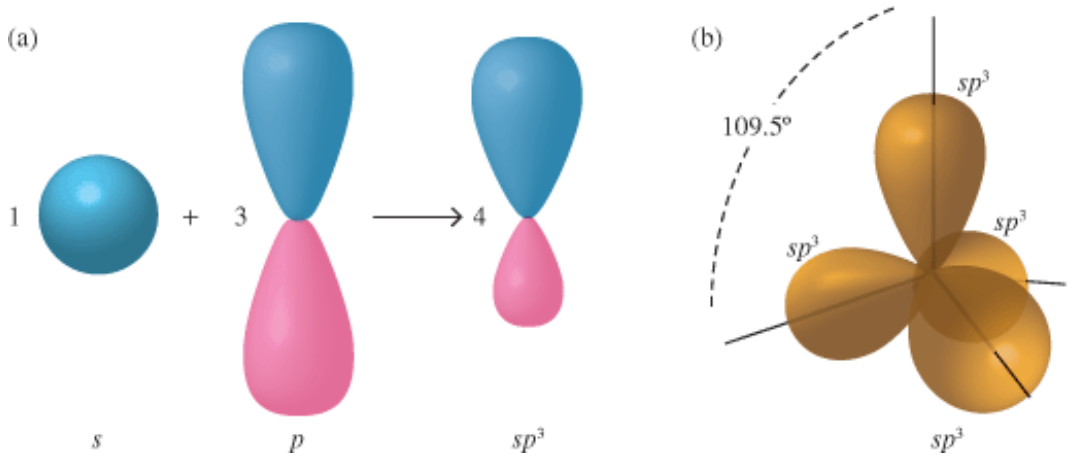


FIGURE 5.27 (a) The formation of four sp^3 hybrid orbitals from one *s* orbital and three *p* orbitals.

(b) The tetrahedral arrangement of the four sp^3 hybrid orbitals. The smaller lobes of opposite phase have been omitted for clarity as they are not significantly involved in any major bonding interactions.

The energy level diagram for this process is shown in figure 5.28.

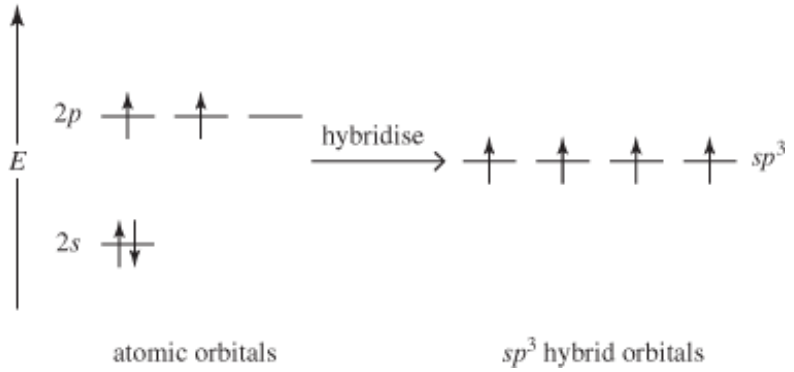


FIGURE 5.28 Energy level diagram for the formation of four sp^3 hybrid orbitals from one 2*s* and three 2*p* atomic valence orbitals.

Because we can neither create nor destroy energy, the total energy of the four atomic orbitals must equal the total energy of the four hybrid orbitals. This means that the energy of the sp^3 hybrid orbitals must lie between the energies of the 2*s* and 2*p* atomic orbitals. Specifically, the energy of each sp^3 hybrid orbital must be $\frac{1}{4}E_{2s} + \frac{3}{4}E_{2p}$. As the four hybrid orbitals are degenerate, each of them accommodates one valence electron.

The four sp^3 hybrid orbitals are arranged such that their electrons undergo the minimum repulsion. This results in a tetrahedral arrangement in which each hybrid orbital points towards a different corner of a tetrahedron. Every hybrid orbital is directional, with a lobe of high electron density pointing in one specific direction, as shown in figure 5.27b.

We can now complete our model of methane. We overlap each singly occupied sp^3 hybrid orbital with one singly occupied 1*s* orbital of a H atom. This leads to the formation of four identical σ bonds and a regular tetrahedral shape for the molecule, as shown in figure 5.29.

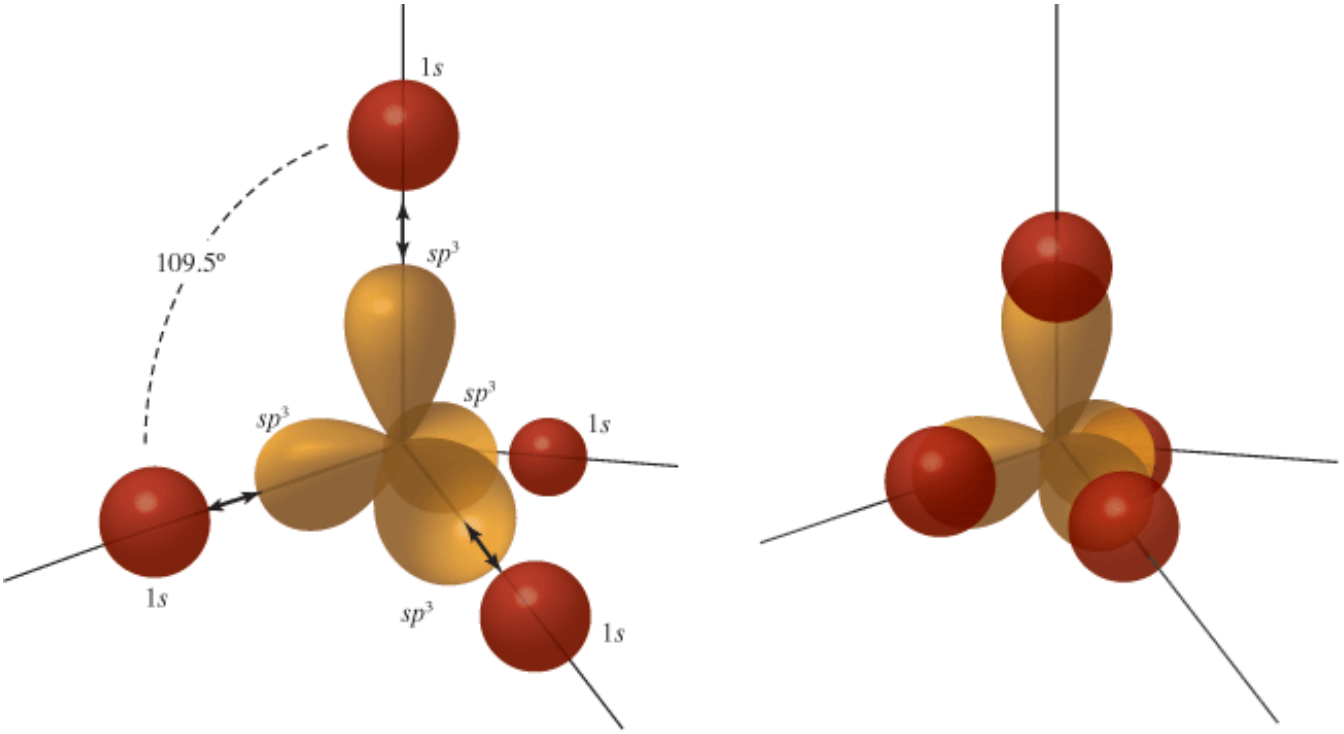


FIGURE 5.29 Methane forms from orbital overlap between the hydrogen 1*s* orbitals and the sp^3 hybrid orbitals of the carbon atom. *Note:* The large lobes of the sp^3 orbitals and the hydrogen *s* orbitals shown are of the same phase. The different colours are used for clarity only. Diminished lobes of opposite phase for the sp^3 hybrid orbitals have been omitted.

Note that sp^3 hybridisation is not limited to C atoms. In fact, any atom which exhibits a tetrahedral (or nearly so) arrangement of electron pairs can be considered to be sp^3 hybridised. This is illustrated in worked example 5.7 for the hydronium ion in which the O atom is sp^3 hybridised.

WORKED EXAMPLE 5.7

Bonding in the Hydronium Ion

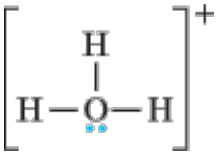
Describe the bonding of the hydronium ion, H_3O^+, in terms of hybrid orbitals.

Analysis

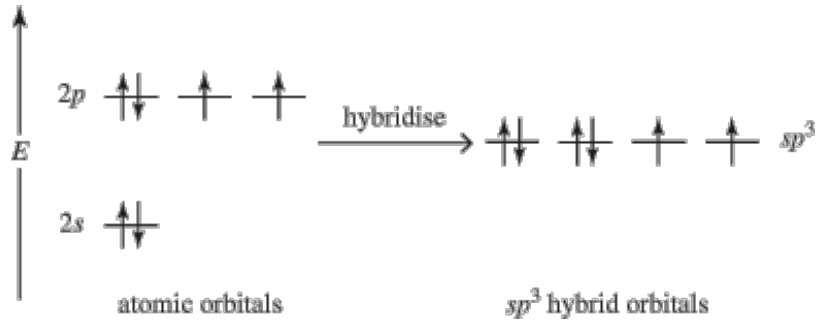
Determine the Lewis structure to confirm that the inner O atom is surrounded by four sets of electron pairs, which will adopt a nearly tetrahedral geometry. This suggests sp^3 hybridisation of the O atom. Then construct the four sp^3 hybrid orbitals from the appropriate atomic orbitals on the O atom.

Solution

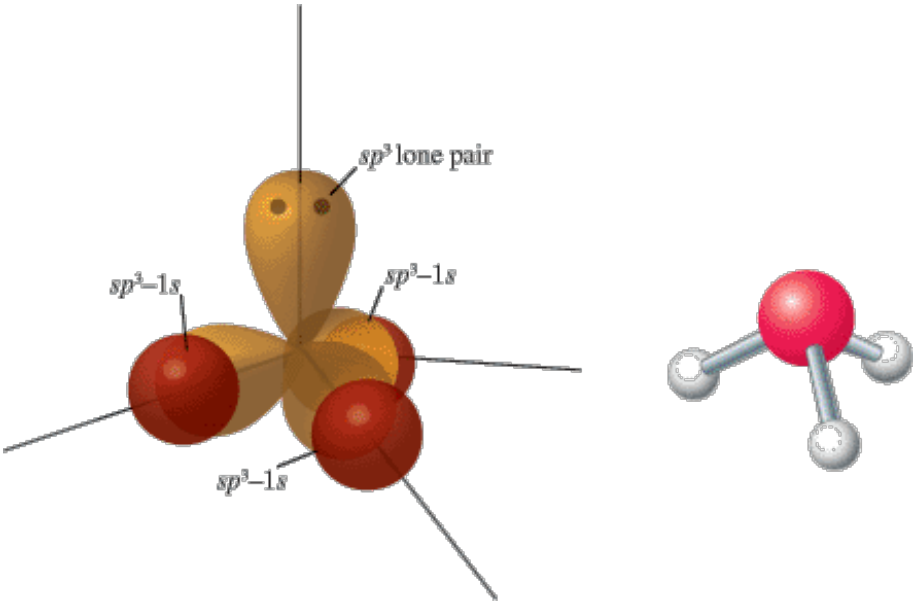
We have determined the Lewis structure of the hydronium ion before (worked example 5.4).



As the inner atom is O, we use the 2*s* and 2*p* atomic orbitals to construct the sp^3 hybrid orbitals. These will contain a total of six electrons.



We have two half-occupied sp^3 hybrid orbitals that can overlap with two half-occupied 1*s* orbitals on H to form two O—H σ bonds. We form the third bond by overlapping one of the *full* sp^3 orbitals with an empty 1*s* orbital on an H^+ ion. Although both electrons in this bond derive formally from the O atom, the bond is identical to the other two O—H bonds. This leaves an sp^3 hybrid orbital not involved in bonding, which contains two electrons. These electrons constitute a lone pair on the O atom. We can visualise the bonding situation as:



Note: The large lobes of the sp^3 orbitals and the hydrogen *s* orbitals shown are of the same phase. The different colours are used for clarity only. Diminished lobes of opposite phase for the sp^3 hybrid orbitals have been omitted.

Is our answer reasonable?

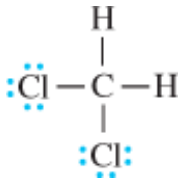
Our bonding description accounts for the trigonal pyramidal shape of the hydronium ion. This example provides an excellent illustration of how valence bond theory can account for the presence of lone pairs in a molecule. The actual H—O—H bond angles in the hydronium ion will be slightly less than the idealised 109.5^o due to the presence of the lone pair.

PRACTICE EXERCISE 5.7

Describe the bonding in a water molecule in terms of hybrid orbitals.

Note that, in methane, the number of hybridised valence atomic orbitals equals the number of valence atomic orbitals participating in hybridis ation. This is always the case, regardless of the nature of the hybridisation. For example, as we will see later, hybridisation of three atomic orbitals gives three sp^2 hybrid orbitals, while hybridisation of two atomic orbitals gives two *sp* hybrid orbitals.

To this point, we have considered only molecules in which hybrid orbitals on the inner atom overlap with H 1 *s* atomic orbitals. In cases where the outer atoms are not hydrogen, we also hybridise these atoms to obtain a better description of the geometry of any lone pairs present. We can illustrate this with reference to the dichloromethane molecule, CH_2Cl_2, the Lewis structure of which is:



We hybridise the inner C atom to generate four singly occupied sp^3 hybrid orbitals, and we can generate two C—H σ bonds by overlapping these with two singly occupied H 1*s* orbitals. We could also form the C—Cl σ bonds by overlapping the remaining two hybrid orbitals with the singly occupied *p* orbital on each of two Cl atoms. However, the problem with this approach is the same as that which led us to hybridise atomic orbitals in the first place — it leads to an incorrect geometry of electron pairs (in this case, the three lone pairs on each Cl atom). We can hybridise the valence orbitals on Cl in the same way as we have done previously for C, as shown in figure 5.30.

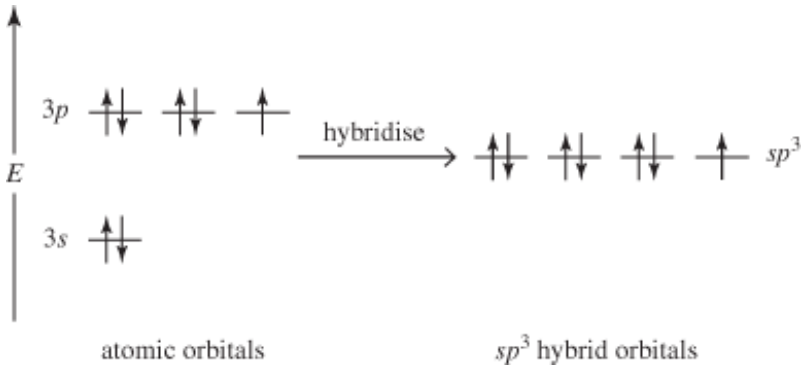
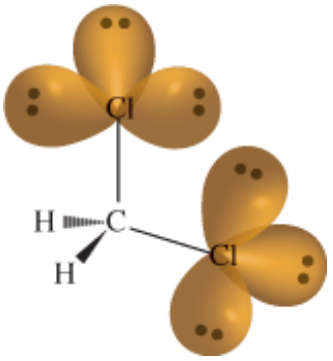


FIGURE 5.30 Energy level diagram for the formation of sp^3 hybrid orbitals on Cl from the 3*s* and 3*p* valence atomic orbitals.

This hybridisation gives one singly occupied sp^3 hybrid orbital on each Cl atom, which can overlap with the sp^3 hybrid orbitals on the carbon atom to form two C—Cl σ bonds. Given that the sp^3 hybrid orbitals on the chlorine atom are tetrahedrally disposed, the three lone pairs will be at approximately 109.5° to each other.



sp^2 hybrid orbitals

Boron trifluoride appears in section 5.4 as an example of a molecule where the inner atom has three sets of electron pairs in a trigonal planar geometry, with 120° angles separating the three B—F bonds. If we were to treat the bonding in BF_3 solely in terms of overlap of atomic valence orbitals, we would predict bond angles close to 90°. A set of sp^3 hybrids is also not appropriate, because these would give F—B—F bond angles of 109.5° rather than 120°. We need a different set of hybrid orbitals to represent an atom with trigonal planar geometry. In this case we can generate a set of three **sp^2 hybrid orbitals** by mixing the 2*s* orbital with two 2*p* orbitals on the boron atom. We represent this process in figure 5.31, in which each resulting sp^2 hybrid orbital has $\frac{1}{3}s$ and $\frac{2}{3}p$ character.

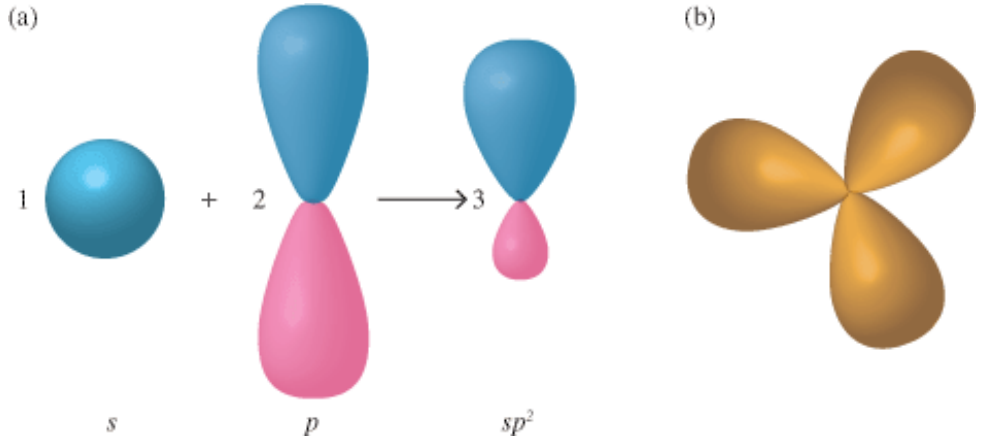


FIGURE 5.31

(a) The formation of three sp^2 hybrid orbitals from one *s* orbital and two *p* orbitals.

(b) The orientation of the three sp^2 hybrid orbitals. They lie in the same plane at an angle of 120° to each other. The smaller lobes of opposite phase have been omitted for clarity as they are not involved in the major bonding interaction.

Although an individual sp^2 hybrid orbital looks very much like its sp^3 counterpart, the energetics of the hybridisation process are quite different, as shown in figure 5.32.

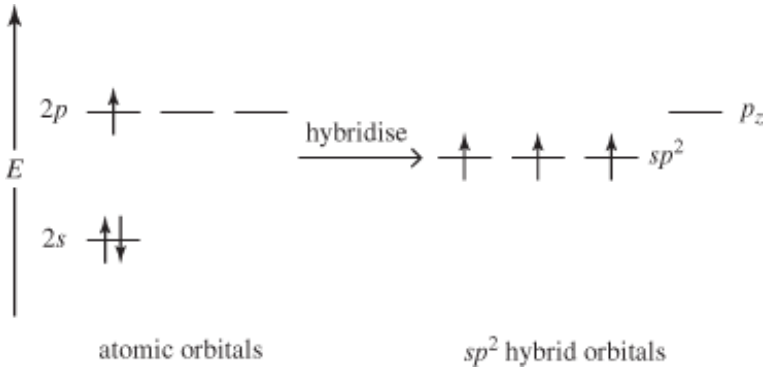


FIGURE 5.32 Energy level diagram for the formation of sp^2 hybrid orbitals from the 2*s* and 2*p* valence atomic orbitals on a B atom.

The three sp^2 hybrid orbitals are coplanar, and are positioned at angles of 120° to each other around the B atom. As we use only two of the three 2*p* orbitals in constructing the sp^2 hybrid orbitals, this leaves one orbital (by convention, the p_z) unhybridised. Figure 5.33 shows the arrangement of all the orbitals.

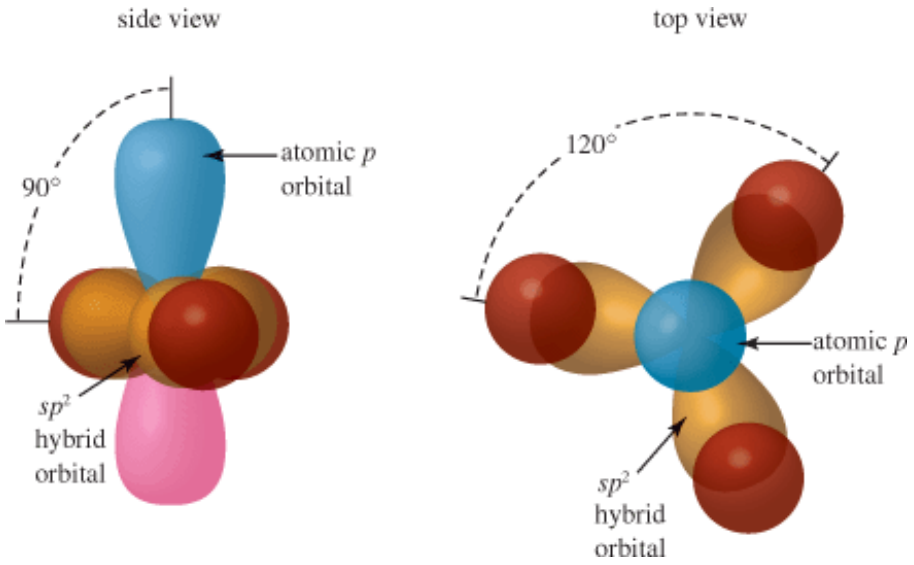
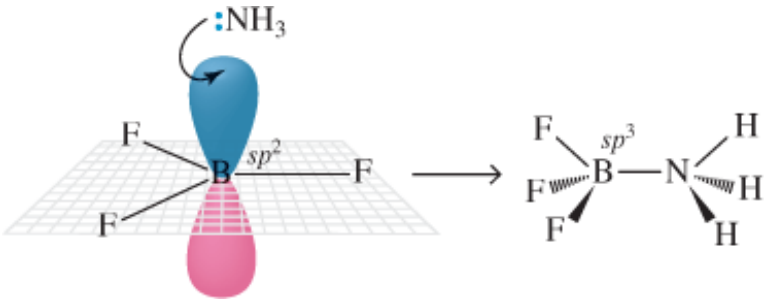


FIGURE 5.33 An sp^2 hybridised atom has three coplanar hybrid orbitals separated by 120° angles. One unchanged *p* orbital is perpendicular to the plane of the hybrid orbitals. Note: Apart from one half (pink or blue) of the unhybridised p_z atomic orbital, all orbitals are of the same phase. The different colours are used for clarity only. Diminished lobes of opposite phase have been omitted.

We also hybridise the F atoms. Each F atom is surrounded by four electron pairs, which means the atoms will be sp^3 hybridised, and the process is entirely analogous to that used previously for the Cl atoms in CH_2Cl_2. We now overlap each of the three singly occupied sp^2 hybrid orbitals with a singly occupied sp^3 hybrid orbital on a fluorine atom to form the three identical σ B—F bonds.

The presence of the unoccupied p_z orbital on the B atom has significant consequences for the reactivity of BF_3. BF_3 often reacts very easily with molecules that have a lone pair of electrons, such as NH_3. The p_z orbital serves to accept the pair of electrons from such molecules, thereby giving the B atom an octet and converting it to sp^3 hybridisation in the process.



sp Hybrid Orbitals

Beryllium hydride appears in section 5.4 as an example of a molecule with linear geometry. There are two bonds to the beryllium atom and a H—Be—H bond angle of 180°. To describe linear orbital geometry, we need a hybridisation scheme that generates two orbitals pointing in opposite directions. We do this by hybridising the 2*s* orbital of Be with one of the 2*p* orbitals to generate a pair of ***sp* hybrid orbitals**. We represent this process in figure 5.34, in which each *sp* hybrid orbital has $\frac{1}{2}s$ character and $\frac{1}{2}p$ character.

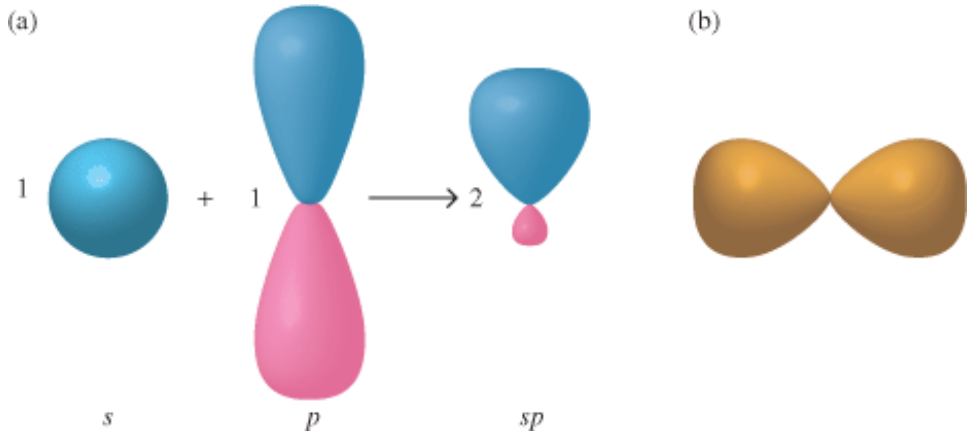


FIGURE 5.34

(a) The formation of two *sp* hybrid orbitals from one *s* orbital and one *p* orbital.

(b) The orientation of the two s*p* hybrid orbitals. They lie at an angle of 180° to each other. The smaller lobes have been omitted for clarity as they are not involved in the major bonding interaction.

Figure 5.35 shows the energetics of the hybridisation process. In this case, we use only one of the *p* orbitals, which leaves two of them unhybridised.

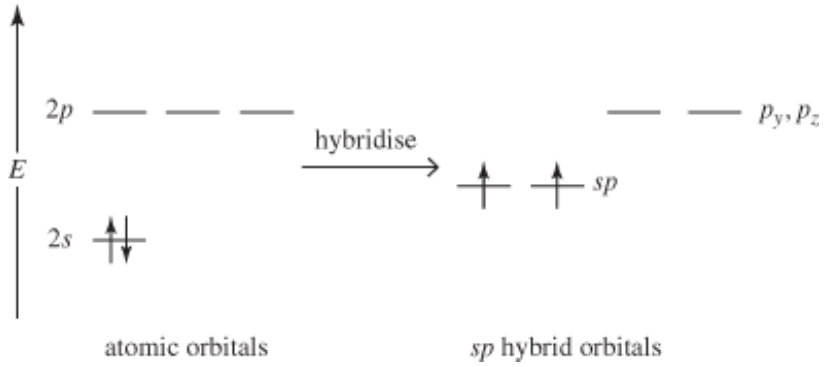


FIGURE 5.35 Energy level diagram for the formation of *sp* hybrid orbitals from the 2*s* and 2*p* valence atomic orbitals on Be.

The two *sp* hybrid orbitals are oriented at 180° from each other, which leads to a linear shape for the molecule. We form two identical Be—H σ bonds by overlapping each half-filled hybrid orbital with one half-filled 1*s* orbital on a H atom. Note that we cannot hybridise the outer H atoms, as they have only a 1*s* orbital each. Figure 5.36 shows a diagram of the bonding for BeH_2. Note that the two unoccupied and unhybridised *p* orbitals lie perpendicular to each other. We will see how such orbitals can participate in bonding when we consider triply bonded molecules later in this chapter.

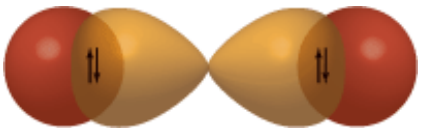
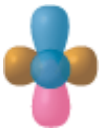


FIGURE 5.36 The bonding in BeH_2. Note: The large lobes of the sp^3 orbitals and the hydrogen *s* orbitals shown are of the same phase. The different colours are used for clarity only. Diminished lobes of opposite phase in the *sp* hybrid orbitals have been omitted.

Table 5.5 summarises the hybridisation schemes we have encountered so far. While other hybridisation schemes are required to describe the bonding in molecules with coordination numbers higher than 4, *sp*, sp^2 and sp^3 are by far the most useful, particularly to describe the bonding in organic molecules. Multiple bonding is one of the features of many organic molecules. On the following pages, we will look at this phenomenon from a valence bond point of view.

TABLE 5.5 A summary of valence orbital hybridisation

Number of sets of electron pairs	Electron group geometry	Hybridisation	Number of hybrid orbitals	Number of unused *p* orbitals	Diagram[(a)]
2	linear	*sp*	2	2	
3	trigonal planar	sp^2	3	1	
4	tetrahedral	sp^3	4	0	

(a) Apart from one half (pink or blue) of the unhybridised p_z atomic orbital, all orbitals are of the same phase. The different colours are used for clarity only. Diminished lobes of opposite phase have also been omitted.

Multiple Bonds

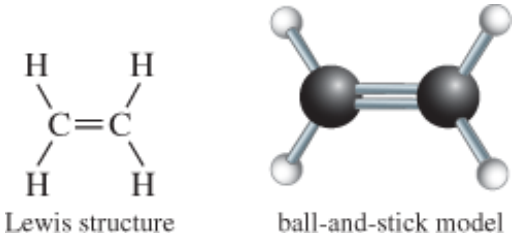
Many of the Lewis structures in this book represent molecules that contain double and triple bonds. From simple molecules such as ethene and ethyne, to complex compounds such as chlorophyll and vitamin B_{12}, multiple bonds are abundant in chemistry. Double and triple bonds can be described by extending the valence bond model. We begin with ethene, a simple hydrocarbon with the formula C_2H_4.

Bonding in Ethene

Ethene (ethylene) is a colourless, flammable gas with a boiling point of -104°C that is predominantly used in the manufacture of plastics such as polyethylene (see chapter 26). Because ethene stimulates the breakdown of cell walls, it is used commercially to speed up the ripening of fruit, particularly bananas.

Every description of bonding starts with a Lewis structure. Ethene has 12 valence electrons. The bond framework of the molecule has one C—C bond and four C—H bonds, requiring 10 of these electrons. If we place the final two electrons as a lone pair on one of the carbon atoms, this gives a formal charge of -1 on

one carbon atom and +1 on the other. These charges can be minimised by forming a double bond between the carbon atoms, leaving them both with an octet of electrons.



Each carbon atom is thus surrounded by three sets of electron pairs, which implies that the carbon atoms are sp^2 hybridised, with a trigonal planar geometry. (Recall from p. 176 that double bonds and triple bonds are treated as being a single set of electron pairs.)

To develop a bonding picture for molecules with multiple bonds, we start by considering *only* the singly bonded σ framework of the molecule, which we construct using hybrid orbitals. The orbital diagram for an sp^2 hybridised C atom is shown in figure 5.37 and the σ framework is shown in figure 5.38. Note that the electron configuration on the right-hand side of figure 5.37 violates the Aufbau principle. This is justified as the energy difference between the sp^2 orbitals and the p_z orbital is small, and therefore the energy required to populate the p_z orbital is smaller than the spin-pairing energy that would otherwise be required to occupy one of the hybrid orbitals with two electrons. Such an electron configuration provides us with results that agree with experiments.

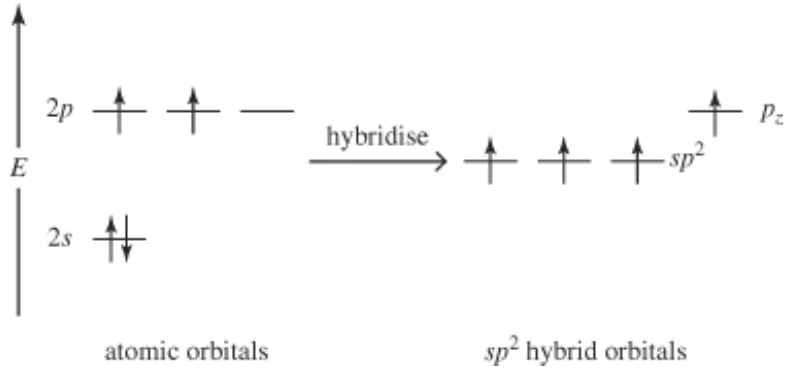


FIGURE 5.37 Energy level diagram for the formation of sp^2 hybrid orbitals from the 2*s* and 2*p* valence atomic orbitals on C.

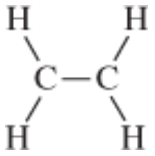


FIGURE 5.38 The σ framework of the ethene molecule.

For the σ framework, we must form four C—H bonds and one C—C bond. We can do this, as shown in figure 5.39, by using two sp^2 hybrid orbitals on each carbon to form two C—H σ bonds, with the C—C bond formed by overlap of the remaining sp^2 hybrid orbital on each C atom.

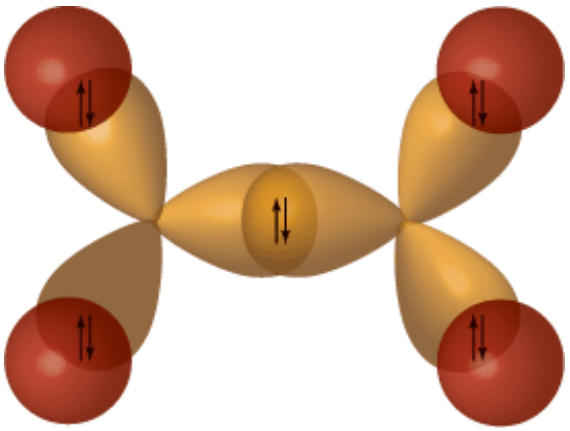


FIGURE 5.39 Orbital overlaps used to form the σ framework of ethene. Note that all orbitals shown are of the same phase and colours are used for clarity only.

Having constructed the σ framework, we are left with one half-occupied p_z orbital on each C atom, which is used to construct the double bond. As we have seen earlier, a σ bond has its maximum electron density along the internuclear axis between the two nuclei. To construct the double bond, we overlap the two p_z orbitals in a side-by-side fashion to form a **pi (π) bond**, as shown in figure 5.40. A π bond has its maximum electron density above and below the plane of the nuclei, and has zero electron density along the inter-nuclear axis between the nuclei. A double bond always consists of one σ bond and one π bond. The σ bond forms from the end-on overlap of two hybrid orbitals, and the π bond forms from the side-by-side overlap of two atomic *p* orbitals. As the side-by-side overlap is not as efficient as the end-on overlap, double bonds are not twice as strong as single bonds between the same atoms. Figure 5.40 shows the complete orbital picture of the bonding in ethene. Ethene is the simplest of a class of molecules, the alkenes, which contain C═C double bonds.

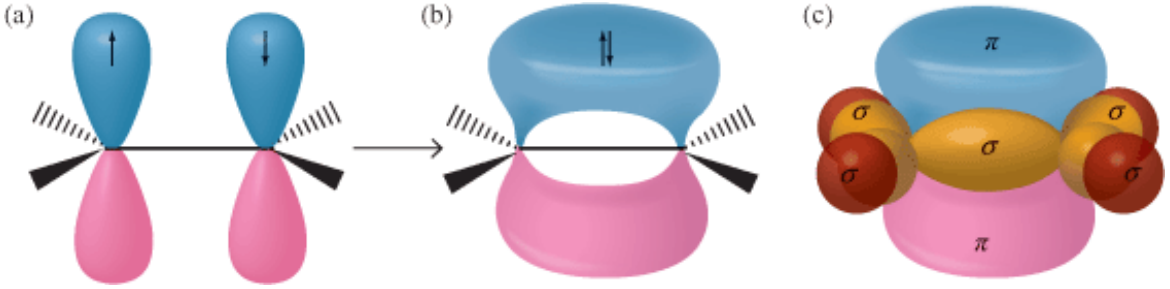


FIGURE 5.40 Orbital pictures of the bonding in ethene from three perspectives:
(a) view of the p_z atomic orbitals which overlap to form the π bond,
(b) view of the π bond formed from the overlap of the p_z atomic orbitals and
(c) the π bond superimposed on the σ framework. Note that the pink and blue lobes together represent a single π bond, which is occupied by two electrons.

The availability of an unhybridised valence *p* orbital to form π bonds is characteristic of sp^2 hybridis ation and is not restricted to carbon atoms. Many organic molecules contain C═N and C═O double bonds and we can describe the bonding in such compounds in a similar fashion to the above description of a C═C double bond.

To summarise, we can construct the valence bond description of any double bond using the following four-step procedure:

1. Determine the Lewis structure.
2. Use the Lewis structure to determine the type of hybridisation.
3. Construct the σ bond framework.
4. Add the π bonds.

Bonding in Ethyne

The ethyne molecule may be familiar to you by its more common name acetylene, the gas used in oxyacetylene welding torches. Ethyne has 10 valence electrons, and we use six of these to form one C—C bond and two C—H bonds. This leaves each C atom in the molecule with a share of only four electrons. We can complete the octet of one of the C atoms by allocating the remaining four electrons to it in the form of two lone pairs. However, this leads to a -2 charge on this and a formal charge of +2 on the other C atom. Converting the two lone pairs on the C atom to two bonding pairs situated between the two C atoms, we obtain formal charges of zero for all atoms in the molecule. This produces the following Lewis structure in which the carbon atoms are joined by a triple bond.

$$H—C\equiv C—H$$

Each carbon atom is surrounded by two sets of electron pairs, and we would predict a linear geometry for this molecule. We can therefore use *sp* hybrid orbitals to describe the bonding in ethyne.

As we did for ethene, we first construct the singly bonded σ framework using the hybrid orbitals. The orbital diagram for an *sp* hybridised C atom is shown in figure 5.41, and the σ framework of ethyne is shown in figure 5.42.

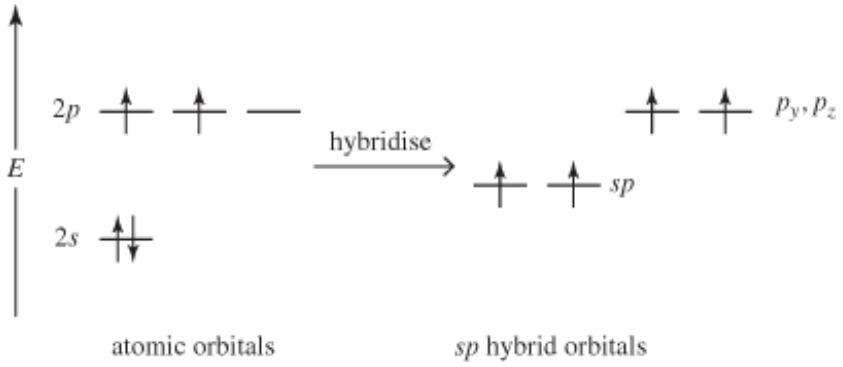


FIGURE 5.41 Energy level diagram for the formation of *sp* hybrid orbitals from the 2*s* and 2*p* valence atomic orbitals on C.

$$H—C—C—H$$

FIGURE 5.42 The σ framework of the ethyne molecule.

We form the σ framework by forming two C—H bonds and one C—C bond using the *sp* hybrid orbitals, as shown in figure 5.43.

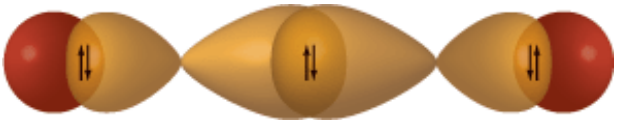


FIGURE 5.43 Orbital overlaps used to form the σ framework of ethyne. All orbitals are in the same phase; different colours are used for clarity only.

This then leaves two singly occupied *p* orbitals on each C atom. We can form two π bonds by overlapping the p_y and p_z orbitals on each C atom in a side-by-side fashion, as shown in figure 5.44.

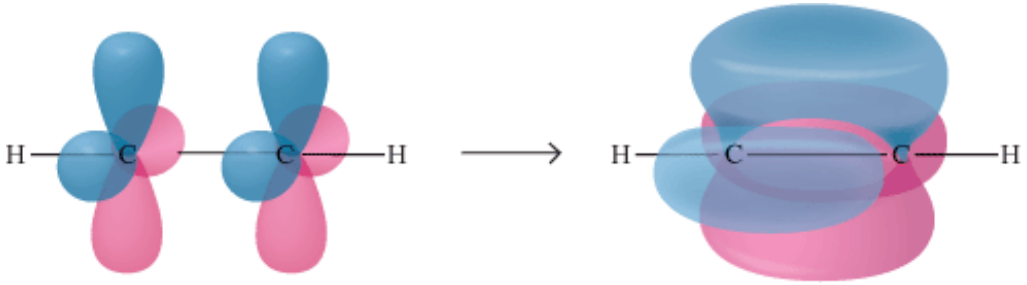


FIGURE 5.44 Overlapping nonhybridised *p* orbitals form the π framework of ethyne.

Thus, each triple bond has one C—C σ bond and two C—C π bonds perpendicular to each other, which is always the case in any alkyne. Worked example 5.8 treats another molecule with bonding that can be described by *sp* hybrid orbitals.

WORKED EXAMPLE 5.8

Orbital Overlap in Triple Bonds

Hydrogen cyanide, HCN, is an extremely poisonous gas. Approximately half a million tonnes of HCN is produced each year, most of which is used to prepare starting materials for polymers. Construct a complete bonding picture for HCN and sketch the various orbitals.

Analysis

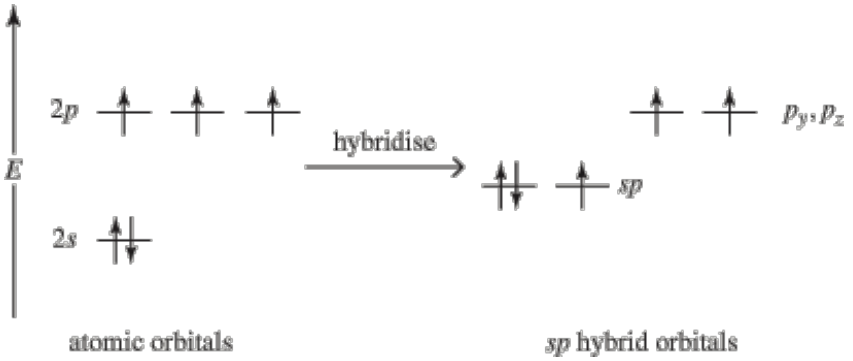
Use the four-step procedure described previously. Begin with the Lewis structure for the molecule, and then identify the appropriate hybrid orbitals. Construct a σ bond framework, and complete the bonding picture by assembling the π bonds from the unhybridised *p* orbitals.

Solution

The five steps of our procedure for writing Lewis structures lead to a triple bond between carbon and nitrogen.



The inner C atom is surrounded by two sets of electron pairs, as is the N atom. These atoms can therefore be considered to be *sp* hybridised. We have derived the orbital diagram for an *sp* hybridised C atom previously, while that for an *sp* N atom is shown below.

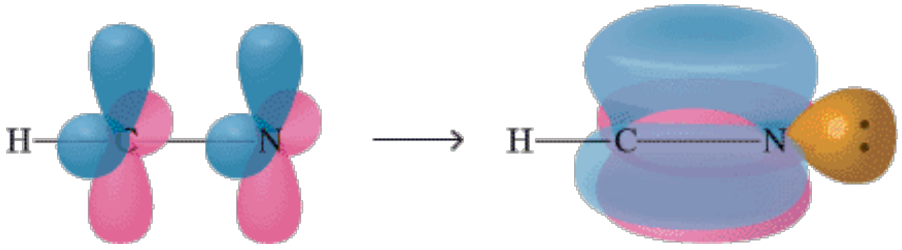


We form the linear singly bonded σ framework shown below by overlapping one of the *sp* hybrid

orbitals on C with the 1*s* orbital on the H atom to give a C—H σ bond. Similarly, we form a C—N σ bond by overlapping the other *sp* hybrid orbital on the C atom with the singly occupied *sp* hybrid orbital on the N atom.

H—C—N

This leaves two singly occupied *p* orbitals on C and two singly occupied *p* orbitals on the N atom with which we can construct the C≡N triple bond, in the same way as described previously for ethyne. We are then left with an *sp* hybrid orbital containing two electrons situated on the N atom. This is a non-bonding lone pair and is shown in the diagram below in gold, for clarity.



Is our answer reasonable?

We have already shown that a triple bond consists of one σ and two π bonds, which is what we have derived. Our bonding scheme also accounts for the presence of a lone pair on the N atom, so it is consistent with the experimentally determined structure.

PRACTICE EXERCISE 5.8

Describe the bonding in the but-2-yne molecule, $CH_3C{\equiv}CCH_3$, using valence bond theory, and sketch the orbitals involved.

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5.7 Molecular Orbital Theory: Diatomic Molecules

Hybrid orbitals and localised bonds provide a model of bonding that can be easily applied to a wide range of molecules. Using this model we do an excellent job of rationalising and predicting chemical structures, but localised bonds cannot predict or interpret all aspects of bonding and reactivity. For example, while valence bond theory predicts the geometry of the methane molecule perfectly, it cannot explain the fact that the four valence orbitals in this molecule are not degenerate. It also fails to explain why there are unpaired electrons in a molecule of O_2. In this section we introduce **molecular orbital theory**, a powerful theory of bonding that is more successful than valence bond theory in predicting and explaining molecular properties. Molecular orbital theory differs fundamentally from valence bond theory in that the electrons within a molecule are not localised either on one atom or between two atoms; instead they occupy **molecular orbitals (MOs)** that can cover the entire molecule.

Although molecular orbital theory is more complex than the hybrid orbital approach, we can illustrate the fundamentals of the theory with reference to simple diatomic molecules.

Molecular Orbitals of H_2 and He_2

Molecular orbital theory considers the formation of molecular orbitals from the overlap of atomic orbitals on all of the individual atoms in the molecule. The overlap of *N* atomic orbitals will always lead to the formation of *N* molecular orbitals. Because of the large number of possible overlaps in even quite small molecules, we will restrict our discussion to diatomic molecules, and will first consider the molecular orbital treatment of the H_2 molecule.

We can consider the MOs of H_2 to be formed from the overlap of the 1*s* orbitals on the H atoms. As each atomic orbital can have either a positive or negative phase, there are two possible ways in which these atomic orbitals can overlap — both orbitals can have the same phase (in-phase overlap) or they can have opposite phases (out-of-phase overlap). In-phase overlap is constructive and results in the formation of a molecular orbital with a large amplitude, and consequently high electron density, between the nuclei. Out-of-phase overlap is destructive and gives a molecular orbital with zero amplitude, and therefore zero electron density, exactly halfway between the nuclei. As for atomic orbitals, this position where the amplitude changes phase is called a **node**. These overlaps and the resulting molecular orbitals are shown in figures 5.24 and 5.45.

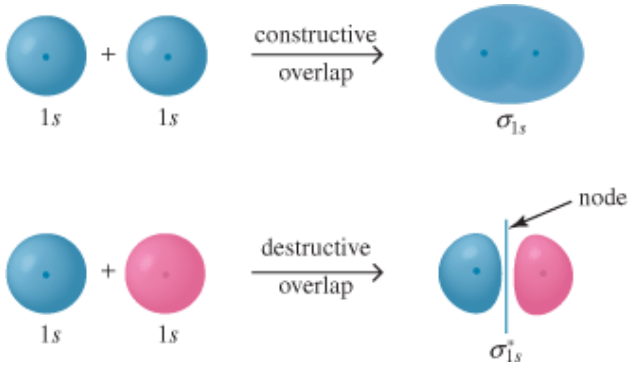


FIGURE 5.45 When two hydrogen 1*s* atomic orbitals interact, they generate two molecular orbitals, one bonding (σ_{1s}) and one anti bonding (σ^*_{1s}).

Constructive overlap gives a **bonding molecular orbital**, in which electron density is maximised between the two nuclei. Such an arrangement of electrons minimises internuclear repulsions. The orbital is completely symmetric with respect to rotation around the internuclear axis and is therefore a σ orbital. We use a 1*s* subscript to show that it derives from the overlap of two 1*s* atomic orbitals, and the complete description of this orbital is therefore σ_{1s}.

Destructive overlap gives an **antibonding molecular orbital** in which electron density is minimised between the nuclei and is zero at the node between the nuclei (all antibonding orbitals have more nodes than the corresponding bonding orbitals and are therefore of higher energy.). Internuclear repulsions are therefore significant as they are not mediated by the electrons. As the orbital is completely symmetric with respect to rotation about the internuclear axis, it is a σ orbital. We use a superscript asterisk (*) to denote its antibonding nature and again use a subscript 1*s* to show that it is derived from two 1*s* atomic orbitals. The complete description of this orbital is therefore σ^*_{1s}.

The relative energies of atomic orbitals and the molecular orbitals they form are shown in a **molecular orbital diagram**. Figure 5.46 shows the molecular orbital diagram for H_2. It shows that the bonding orbital is of lower energy than the orbitals from which it is formed, whereas the antibonding orbital is of higher energy. When a hydrogen molecule forms, its two electrons obey the same principles for distributing electrons as described in chapter 4. The lowest energy arrangement of electrons requires adherence to the Aufbau principle, the Pauli exclusion principle and Hund's rule, no matter what types of orbitals they occupy. The two valence electrons of molecular hydrogen therefore fill the lowest energy orbital, the σ_{1s} orbital, with their spins paired, leaving the σ^*_{1s} orbital empty.

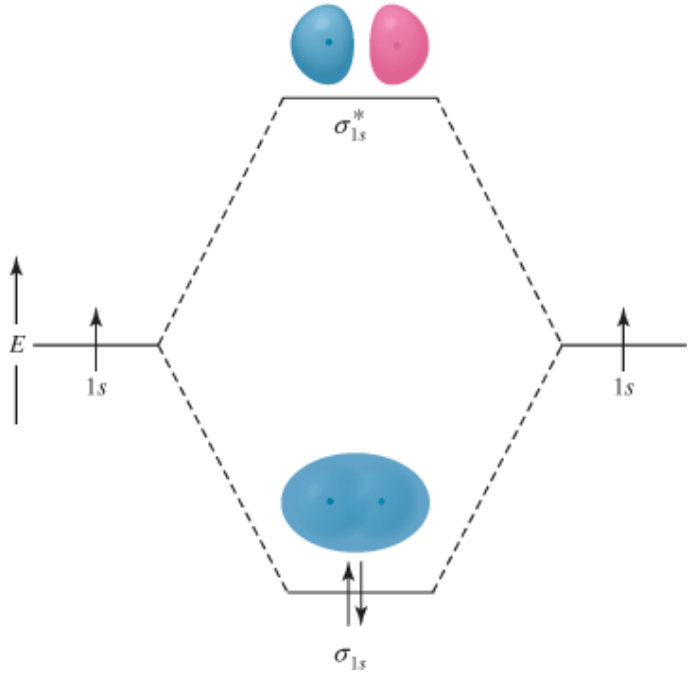


FIGURE 5.46 Molecular orbital diagram for molecular hydrogen.

The molecular orbital diagram shown in figure 5.46 applies to all diatomic species from the first row of the periodic table, except that the electron occupancy and the absolute energies involved are different. We can, for instance, use molecular orbital theory to rationalise why two helium atoms do not combine to form a molecule of He_2. The electron configuration of He is $1s^2$ and therefore the hypothetical He_2 molecule would have four electrons. Two of these would populate the bonding σ_{1s} orbital, while the remaining two electrons would have to occupy the antibonding σ^*_{1s} orbital, as shown in figure 5.47. The total electronic energy of the He_2 molecule would therefore be exactly the same as that of two isolated He atoms, as the destabilising effect of the electrons in the antibonding orbital cancels out any stabilisation due to the electrons in the bonding orbital. As there is no energetic advantage, a molecule is not formed (see the discussion of entropy in chapter 8 for an explanation). A convenient way to summarise this argument is by calculating the **bond order**, which represents the net amount of bonding between two atoms.

$$\text{Bond order} = \frac{1}{2}(\text{number of electrons in bonding orbitals} - \text{number of electrons in antibonding molecular orbitals})$$

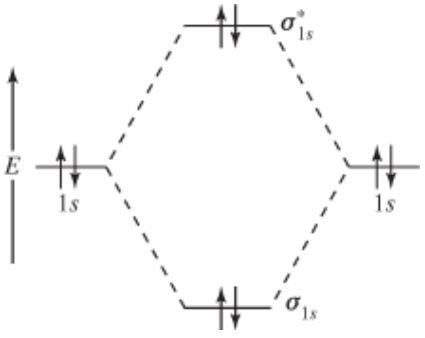


FIGURE 5.47 Diatomic He_2 does not exist because the stability imparted by the electrons in bonding orbitals is offset by the destabilisation due to the electrons in antibonding orbitals.

Bond orders usually have integer or half-integer values: the larger the bond order, the stronger the bond (for the same

type of atom).

For molecular hydrogen, with two bonding electrons and no electrons in the antibonding orbitals, the bond order is $\frac{1}{2}(2-0)=1$. A bond order of 1 corresponds to a single bond, consistent with the Lewis structure of H_2. For the hypothetical He_2 molecule, two bonding and two antibonding electrons give a bond order of $\frac{1}{2}(2-2)=0$, so no bond forms and helium does not form stable diatomic molecules.

WORKED EXAMPLE 5.9

Does He_2^+ Exist?

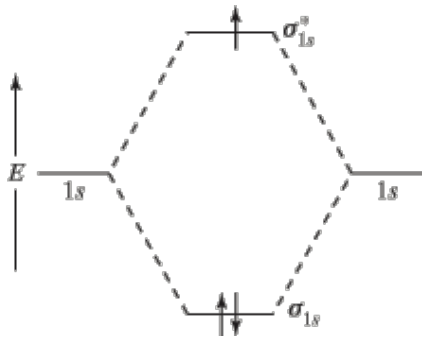
Use a molecular orbital diagram to predict if it is possible to form the He_2^+ cation.

Analysis

The schematic MO diagram shown in figure 5.46 can be applied to any of the possible diatomic molecules or ions formed from the first-row elements, hydrogen and helium. Count the electrons of He_2^+, place the electrons in the molecular orbital diagram and calculate the bond order. If the bond order is greater than zero, the species can potentially form under the right conditions.

Solution

One He atom has two electrons, so a He_2^+ cation has three electrons. Following the Aufbau principle, two electrons fill the lower-energy σ_{1s} orbital, so the third must be placed in the antibonding σ_{1s}^* orbital in either spin orientation.



The bond order of the cation is therefore $\frac{1}{2}(2-1)=\frac{1}{2}$. Although a bond order of $\frac{1}{2}$ might sound unusual, it is greater than zero and therefore we predict that He_2^+, with a net bond order of $\frac{1}{2}$, can be prepared in the laboratory under appropriate conditions.

Is our answer reasonable?

Up until this point, we have discussed only single, double and triple bonds, and have not encountered bonds with non-integer orders. In fact, such bonds are quite common in chemistry. He_2^+ can be prepared by passing an electrical discharge through a sample of helium gas. The He_2^+ ion is unstable but survives long enough to allow its study. The bond dissociation energy of He_2^+ is 250 kJ mol^{-1}, approximately 60% as strong as the bond in the H_2 molecule, which has a bond order of 1.

PRACTICE EXERCISE 5.9

Which species has the stronger bond, H_2 or H_2^-? Use a molecular orbital diagram to support your answer.

Molecular Orbitals of O_2

The next step in the development of molecular orbital theory is to consider the molecular orbitals formed by constructive and destructive overlap of atomic *p* orbitals. We use molecular oxygen, O_2, as a case study.

The Lewis structure of O_2 shows the two atoms connected by a double bond, with two non-bonding electron pairs on each atom. Note that there are no unpaired electrons in the Lewis structure.



We derive the molecular orbital diagram for the O_2 molecule by considering overlap of only the valence atomic orbitals on the two oxygen atoms; an exact treatment would also include the core 1*s* orbitals, but we will ignore these in the interests of clarity. Each oxygen atom has four valence orbitals, so the molecular orbital diagram for O_2 will contain eight molecular orbitals. The first interaction involves the 2*s* atomic orbitals. This pair interacts in exactly the same way as the 1*s* orbitals described previously for H_2. The constructive overlap generates a bonding σ_s orbital, and the destructive overlap forms an antibonding σ_s^* orbital. Because of the larger size of the 2*s* atomic orbitals, these two molecular orbitals are larger than their hydrogen σ_{1s} and σ_{1s}^* counterparts, but their overall appearances are similar.

Figure 5.48 shows the construction of the 2*p*-based molecular orbitals. One pair of molecular orbitals forms from end-on constructive and destructive overlap of the p_z orbitals that point towards each other along the bond axis (by convention, the bond axis is chosen to be the *z*-axis). These end-on overlaps give a pair of σ orbitals, the bonding σ_p and the antibonding σ_p^* as shown in figure 5.48a. (Note that here we have simply labelled the molecular orbitals as σ_p and σ_p^*, rather than σ_{2p} and σ_{2p}^* for reasons we will explain on p. 203.) The remaining sets of *p* orbitals undergo constructive and destructive overlap in a side-by-side fashion to form pairs of molecular orbitals with electron density located primarily above and below the internuclear axis. Such molecular orbitals are called orbitals. Constructive overlap gives a bonding π orbital, while destructive overlap gives an antibonding π* orbital. One of these pairs comes from overlap of the p_y orbitals, while the other comes from overlap of the p_x orbitals. Figure 5.48b shows only the p_y pair of π orbitals, which we label π_y — the π_x pair of orbitals derived from the p_x atomic orbitals has the same appearance, but is perpendicular to the π_y orbitals. Note that the antibonding π^* orbital contains a node between the two O atoms.

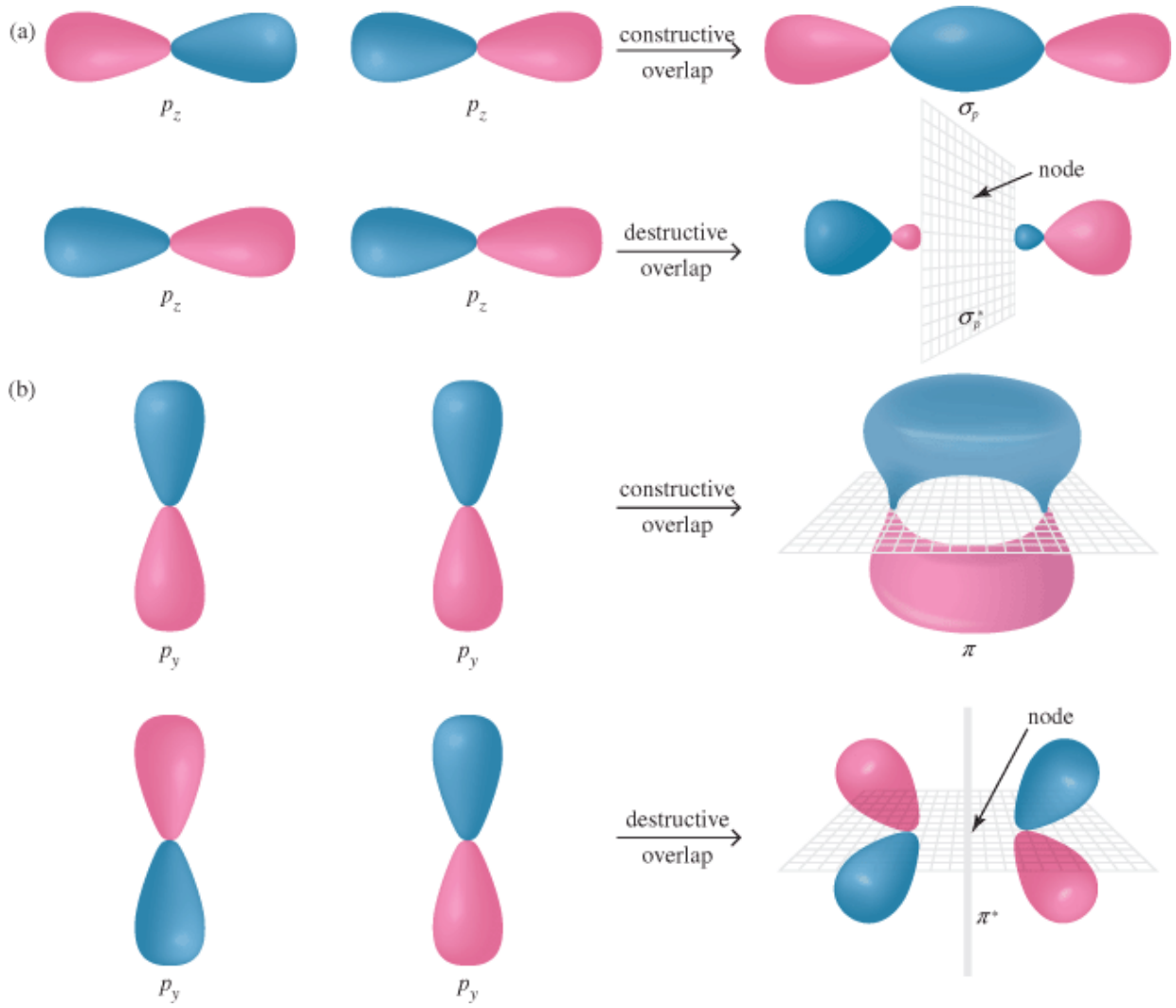


FIGURE 5.48 Constructive and destructive overlap of *p* orbitals lead to bonding and antibonding orbitals

(a) End-on overlap of the p_z orbitals gives σ orbitals.

(b) Side-by-side overlap of the p_y atomic orbitals gives π_y and π_y^* molecular orbitals. Similar combinations of p_x orbitals would give π_x and π_x^* MOs.

To draw the molecular orbital diagram for O_2, we must first determine the relative energies of the molecular orbitals. We can do this with the following rules:

1. The core σ_s and σ_s^* orbitals derived from the overlap of the 1*s* atomic orbitals are of lowest energy and contribute little to bonding. For this reason, they are not shown explicitly.
2. The bonding σ_s and antibonding σ_s^* orbitals derived from the overlap of the 2*s* orbitals are of lower energy than any of the six molecular orbitals derived from the 2*p*orbitals. This is because the 2*s* orbitals that generate the σ_s and σ_s^* orbitals are of lower energy than the 2*p* atomic orbitals.
3. The π_x and π_y bonding orbitals are degenerate, because the corresponding atomic *p* orbitals from which they are derived are degenerate. The π_x^* and π_y^* orbitals are degenerate for the same reason.

4. The antibonding orbitals formed from the atomic 2*p* orbitals are highest in energy, with the σ_p^* orbital higher than the degenerate π_x^* and π_y^* pair of orbitals.

After applying these features, we are left with the bonding σ_p and π molecular orbitals. These must be placed between σ_s^* and π*, but which of them is lower in energy? It can be shown mathematically that end-on overlap is more efficient than side-by-side overlap, which suggests that the σ_p orbital should be of lower energy than the π orbitals. This is the case for the O_2 molecule and figure 5.49 shows the complete diagram. To obtain the ground state electron configuration, we place the 12 valence electrons in the molecular orbitals in accordance with the Pauli and Aufbau principles and Hund's rule. We can describe the resulting electron configuration by naming the orbitals (σ_s, π_x etc.), and using superscripts to show how many electrons each orbital contains. Therefore, the configuration for the ground state of O_2 is:

$$(\sigma_s)^2(\sigma_s^*)^2(\sigma_p)^2(\pi_x)^2(\pi_y)^2(\pi_x^*)^1(\pi_y^*)^1$$

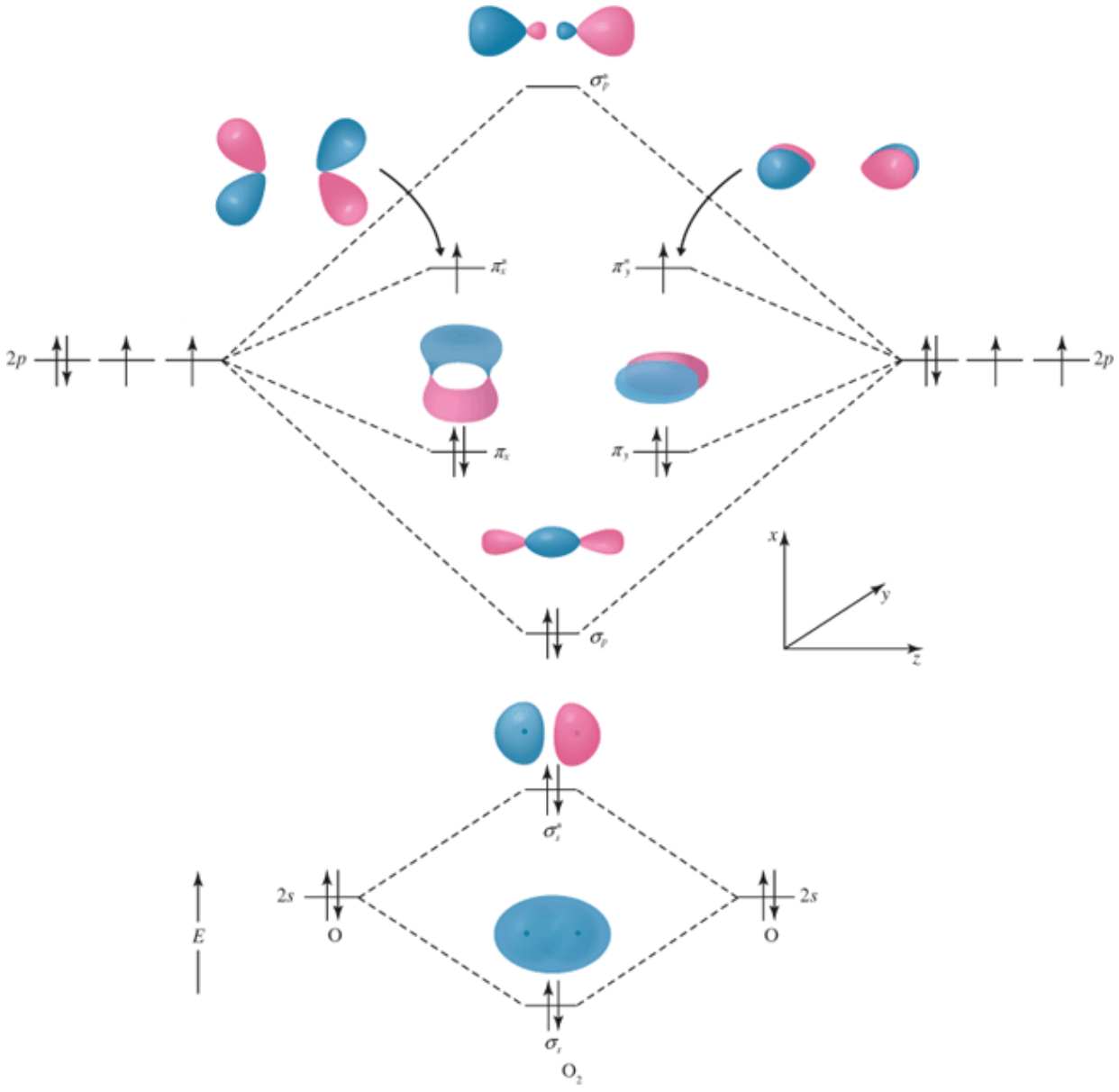


FIGURE 5.49 The molecular orbital diagram for O_2. The energy ordering of the MOs applies to second-row diatomic molecules with $Z > 7$.

Note that, to satisfy Hund's rule, we must place one electron in each of the two π* orbitals with parallel spins. Therefore, this model of bonding predicts that O_2 should contain two unpaired electrons, in contrast to both the Lewis structure and the valence bond theory. Which model agrees with experiment?

Figure 5.50 shows that liquid oxygen adheres to the poles of a magnet. Attraction to a magnetic field shows that

molecular oxygen is paramagnetic. Recall from chapter 4 that paramagnetism arises when the electron configuration includes unpaired electrons. Neither the Lewis structure of O_2 nor the valence bond model predicts the presence of unpaired electrons. However, the molecular orbital description shows that the two highest energy electrons of the oxygen molecule occupy the two degenerate π^*_x and π^*_y antibonding orbitals (figure 5.50). So, molecular orbital theory gives us a more appropriate model of the bonding in O_2 than either the Lewis or the valence bond theories. This does not necessarily mean that the molecular orbital theory is 'correct', just that it gives better agreement with experiment than the other models.



FIGURE 5.50 Molecular oxygen is paramagnetic, so it clings to the poles of a magnet.

Bond length and bond energy measurements on oxygen and its cation provide evidence that the π^* orbitals are indeed antibonding. The bond order of the O_2 molecule is $\frac{1}{2}(8-4)=2$. If we remove an electron from O_2, we form the O_2^+ cation. Experimental measurements show that this species has a larger bond energy and shorter bond length than O_2, both observations consistent with an increased bond order. This indicates that the electron removed must be antibonding in character, as its removal has reduced the amount of antibonding and strengthened the bond.

Species	Bond length	Bond energy	Configuration	Bond order
O_2	121 pm	496 kJ mol^{-1}	… $(\sigma_p)^2 (\pi_x)^2 (\pi^*_x)^1 (\pi^*_y)^1$	2
O_2^+	112 pm	643 kJ mol^{-1}	… $(\sigma_p)^2 (\pi_x)^2 (\pi_y)^2 (\pi^*_{x,y})^1$	2.5

Molecular orbital theory predicts the observed increase in bond order, with the calculated bond order of O_2^+ being $\frac{1}{2}(8-3)=2.5$. The experimental data show that the highest energy orbital of O_2 is antibonding in character and the theoretical molecular orbital predictions are in good agreement.

Our treatment of O_2 shows that the extra complexity of the molecular orbital approach explains features that a simpler description of bonding cannot. The Lewis structure of O_2 does not reveal its two unpaired electrons, but a molecular orbital approach does. The simple σ–π description of the double bond in O_2 does not predict that the bond in O_2^+ is stronger than that in O_2, but a molecular orbital approach does. We now extend our discussion to include all of the homonuclear diatomic molecules formed by elements in the second row of the periodic table.

Homonuclear Diatomic Molecules

We saw previously that very similar molecular orbital diagrams can describe the bonding in H_2, He_2^+ and He_2. Can we use the molecular orbital diagram for O_2 to explain the bonding in all of the second-row diatomic molecules (Li_2, Be_2, B_2, C_2, N_2, O_2, F_2 and Ne_2)? Consider the B_2 molecule, which can be formed in the gas phase by strong heating of solid boron. If we use the molecular orbital diagram for O_2 and insert the six valence electrons of B_2, we would

predict the electron configuration $(\sigma_s)^2(\sigma_s^*)^2(\sigma_p)^2$ for this molecule. With all its electrons paired, B_2 should be diamagnetic. However, experiments show that B_2 molecules are paramagnetic, with two unpaired electrons. When theory and experiment conflict, theory must be revised. The molecular orbital diagram we used for O_2 must be revised to account for the paramagnetism of B_2.

The view of molecular orbital theory that leads to the molecular orbital diagram in figure 5.49 assumes that the 2*s* and 2*p* orbitals act independently. A more refined treatment considers interactions between the 2*s* and 2*p* orbitals. Recall from chapter 4 that the 2*s* and 2*p* orbitals have similar radii. Consequently, when two atoms approach each other, the 2*s* orbital on one atom will overlap not only with the 2*s* orbital, but also with the 2*p* 2 *z* orbital of the other atom. This mixed interaction of 2*s* and 2*p* 2 *z* stabilises the σ_s molecular orbital and destabilises the σ_p molecular orbital. In other words, **orbital mixing** causes the σ_s and σ_p molecular orbitals to move further apart in energy. In this more refined treatment, the resulting molecular orbitals are therefore not derived solely from two atomic orbitals, and hence we do not use specific labels, such as σ_{1s}, as we did for the hydrogen and helium cases. Labels of the type σ_s and π_y show the *pre-dominant* type of overlap that contributes to the *t* molecular orbital. The amount of mixing depends on the difference in energy between the 2*s* and 2*p* atomic orbitals. Mixing is largest when the energies of the orbitals are nearly the same. As figure 5.51 shows, the energies of the 2*s* and 2*p* atomic orbitals diverge as *Z* increases across the second row, so mixing is large for B_2 but small for F_2. Figure 5.52 shows how mixing affects the energies of the σ_s and σ_p molecular orbitals.

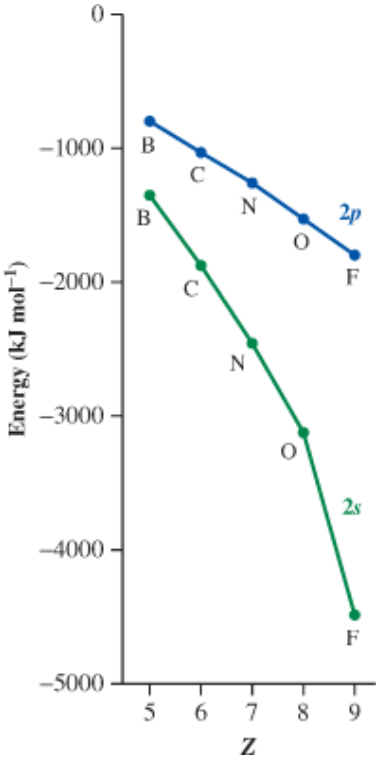


FIGURE 5.51 Energies of the *n* = 2 valence orbitals as a function of *Z*.

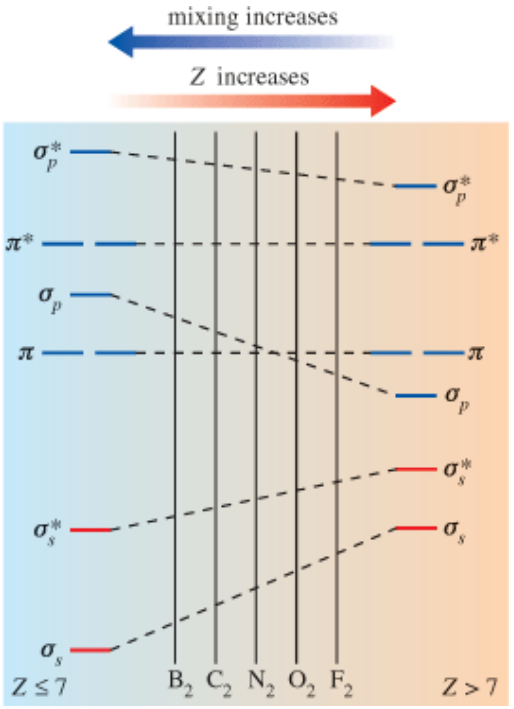


FIGURE 5.52 Mixing of the 2*s* and 2p_z orbitals causes the σ_s MOs to become lower in energy and the σ_p MOs to increase in energy. The amount of mixing decreases across the second row of the periodic table.For B_2, C_2 and N_2, the π MOs are of lower energy than the σ_p orbitals. For O_2 and F_2, the opposite is true.

The main effect of mixing is to make the σ_p molecular orbital of higher energy than the degenerate π orbitals for the B_2, C_2 and N_2 molecules. There-fore, according to the Aufbau principle, we first fill the π orbitals and then the σ_p orbital for these molecules. Following Hund's rule, this means that B_2 is paramagnetic, as it has the electron configuration $(\sigma_s)^2(\sigma_s^*)^2(\pi_x)^1(\pi_y)^1$, in agreement with experiment. Notice that crossover of the σ_p and π energy levels takes place between molecular nitrogen and molecular oxygen. Because of orbital mixing, we therefore require two generalised molecular orbital diagrams for diatomic molecules, one for B_2, C_2 and N_2, and the other for O_2 and F_2. Figure 5.52 shows both diagrams.

These molecular orbital diagrams help to rationalise experimental observations about molecules.

WORKED EXAMPLE 5.10

Trends in Bond Energy

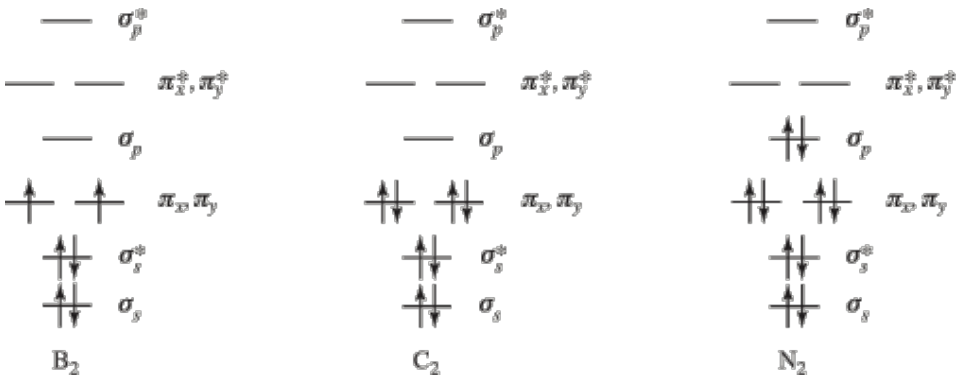
Use molecular orbital diagrams to explain the trend in the following bond energies: B_2 = 290 kJ mol^{-1}, C_2 = 600 kJ mol^{-1} and N_2 = 942 kJ mol^{-1}.

Analysis

The data show that bond energies for these three diatomic molecules increase as we move across the second row of the periodic table. We must construct molecular orbital diagrams for the three molecules and use the results to interpret the trend.

Solution

The crossover point for the σ_p /π energy levels takes place between N_2 and O_2, so the general diagram for *Z* ≤ 7 in figure 5.52 applies to all three molecules. The valence electron counts are B_2 = $6e^-$, C_2 = $8e^-$, and N_2 = $10e^-$. Place these electrons in the MO diagram following the Pauli exclusion and Aufbau principles and Hund's rule. Here are the results.



The diagrams show that the increasing electron counts as we progress from boron to carbon to nitrogen result in the filling of bonding molecular orbitals. This is revealed most clearly by calculating the bond orders for the three molecules: $B_2 = \frac{1}{2}(4-2) = 1$, $C_2 = \frac{1}{2}(6-2) = 2$ and $N_2 = \frac{1}{2}(8-2) = 3$. Increasing bond order corresponds to stronger bonding between the atoms and therefore greater bond energies.

Is our answer reasonable?

Our predicted bond orders correlate perfectly with the experimental bond energies, and therefore our answer is reasonable. Of these three diatomic molecules, only N_2 exists under normal conditions. Boron and carbon form nonmolecular solids rather than isolated diatomic mol ecules. However, molecular orbital theory predicts that B_2 and C_2 may exist under the right conditions, and in fact both molecules can be generated in the gas phase by vaporising solid boron or solid carbon.

PRACTICE EXERCISE 5.10

Use molecular orbital diagrams to explain the trend in bond energies for the following diatomic molecules: N_2 = 942 kJ mol^{-1}, O_2 = 495 kJ mol^{-1} and F_2 = 155 kJ mol^{-1}.

Heteronuclear Diatomic Molecules

Nitrogen oxide (NO) is an example of a heteronuclear diatomic molecule. This interesting molecule has been in the news in recent years because of important discoveries about the role of NO as a biological messenger. A molecular orbital diagram of NO is shown in figure 5.53.

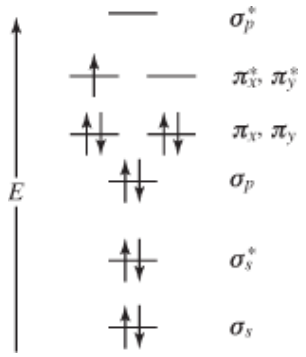


FIGURE 5.53 Molecular orbital diagram of NO.

Because the qualitative features of orbital overlap do not depend on the identity of the atoms, the bonding in NO can be described by the same sets of orbitals that describe homonuclear diatomic molecules. Which of the two general MO diagrams for diatomic molecules applies to nitrogen oxide? The crossover point for the energy rankings of the σ_p and π molecular orbitals falls between N and O, so we expect the orbital energies to be nearly equal. Experiments have shown that the σ_p MO is slightly more stable than the π MO. Consequently, the MO configuration for the 11 valence electrons of NO mirrors that for the 12 valence electrons of O_2, except that there is a single electron in the π^* orbital:

$$(\sigma_s)^2(\sigma_s^*)^2(\sigma_p)^2(\pi_x)^2(\pi_y)^2(\pi_x^*)^1$$

There are eight bonding electrons and three antibonding electrons, so the bond order of NO is 2.5. This bond is stronger and shorter than the double bond of O_2 but weaker and longer than the triple bond of N_2.

Species	Bond length	Bond energy	Configuration	Bond order
O_2	121 pm	495 kJ mol^{-1}	$\ldots(\sigma_p)^2(\pi_x)^2(\pi_y)^2(\pi_x^*)^1(\pi_y^*)^1$	2
NO	115 pm	605 kJ mol^{-1}	$\ldots(\sigma_p)^2(\pi_x)^2(\pi_y)^2(\pi_{xy}^*)^1$	2.5
N_2	110 pm	945 kJ mol^{-1}	$\ldots (\pi_x)^2 (\pi_y)^2 (\sigma_p)^2$	3

Electron configurations for these molecules lead to a guideline for molecular orbital configurations based on average nuclear charge, $Z_{average}$:

For second-row diatomic molecules and ions:

- *σ_p is lower in energy than π_x, π_y when $Z_{average} > 7$*
- *π_x, π_y is lower in energy than σ_p when $Z_{average} \leq 7$.*

Worked example 5.11 compares the ionisation energies of three diatomic molecules and uses MO theory to explain the differences.

WORKED EXAMPLE 5.11

Comparing Ionisation Energies

The first ionisation energy of NO is 891 kJ mol^{-1}, that of N_2 is 1500 kJ mol^{-1}, and that of CO is 1350 kJ mol^{-1}. Use electron configurations to explain why NO ionises more easily than either N_2 or CO.

Analysis

Recall from chapter 4 that ionisation energy refers to the removal of an electron from an atom, or, in this case, from a molecule. We must count the valence electrons, choose the correct MO diagram, follow the Aufbau principle in placing the electrons, and then use the configurations to explain the ionisation energy data.

Solution

Begin with a summary of the important information for each molecule: NO has 11 valence electrons and $Z_{average} = 7.5$; N_2 has 10 valence electrons and $Z_{average} = 7$; CO has 10 valence electrons and $Z_{average} = 7$. Applying the general diatomic MO diagrams of figure 5.52 gives the following configurations:

$$\text{NO} = (\sigma_s)^2(\sigma_s^*)^2(\pi_x)^2(\pi_y)^2(\sigma_p)^2\left(\pi_{x,y}^*\right)^1$$

$$\text{N}_2 = (\sigma_s)^2(\sigma_s^*)^2(\sigma_p)^2(\pi_x)^2(\pi_y)^2(\sigma_p)^2$$

$$\text{CO} = (\sigma_s)^2(\sigma_s^*)^2(\pi_x)^2(\pi_y)^2(\sigma_p)^2$$

CO and N_2 are isoelectronic species, meaning they have the same number of electrons (see p. 145), and each has a bond order of 3. It makes sense that these two molecules have comparable ionisation energies. NO has one electron more than N_2 and CO, and this electron occupies one of the antibonding π* orbitals. It is much easier to remove this antibonding electron from NO than it is to remove a bonding electron from either of the other two species.

PRACTICE EXERCISE 5.11

Use electron configurations to predict which of the following is the most stable diatomic combination of carbon and nitrogen: CN^-, CN or CN^+.

For diatomic molecules composed of atoms that have very different energies of their atomic orbitals, the MO diagram becomes slightly more complicated. We will use HF as an example and show the energy levels for both atomic orbitals and molecular orbitals in figure 5.54.

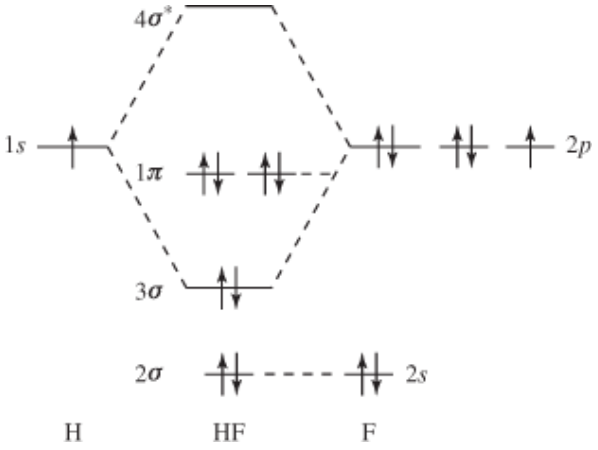
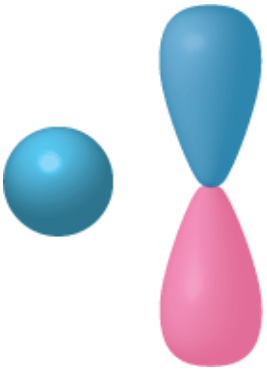


FIGURE 5.54 The molecular orbital diagram of HF.

Generally, orbitals are of lower energy in a more electronegative atom and orbitals with the same designation are lower in energy if the nuclear charge is larger. Armed with these rules we can understand that the 1*s* orbital in the F atom is much lower in energy than the 1*s* orbital of H.

Molecular orbitals can form only when there is net overlap between the constituent atomic orbitals and when the atomic orbitals are relatively close in energy. We can illustrate this by considering the approach of the hydrogen 1*s* orbital with either the $2p_x$ or $2p_y$ orbital of the fluorine atom.



As these orbitals approach each other in a ‘side-on’ manner, there will be constructive interference, and hence a bonding interaction, between the *s* orbital and the same phased lobe of the *p* orbital, but there will be an equal and opposite destructive interference, and hence an antibonding interaction, between the *s* orbital and the opposite phased lobe of the *p* orbital (figure 5.54). Therefore, there is no net overlap between an *s* orbital and a p_x or p_y orbital when they approach in this manner, and no molecular orbitals are formed. Instead, the $2p_x$ and $2p_y$ orbitals are located primarily on the fluorine atom as essentially nonbonding molecular orbitals. While overlap of the hydrogen 1*s* and fluorine 2*s* orbitals can, in theory, occur, the energies of the orbitals are too different to permit effective overlap, and for this reason, the fluorine 2*s* orbital remains essentially nonbonding. The 1*s* orbital of hydrogen and the $2p_z$ orbital of fluorine overlap effectively and form two MOs. The 3σ orbital is much closer in energy to the $2p_y$ orbital of fluorine and therefore has more $2p_y$ character and is closer to the fluorine nucleus, while the antibonding 4σ orbital has more hydrogen 1*s* character. The MO diagram in figure 5.54 shows the sequence of the valence molecular orbitals.

The CO molecule is another heteronuclear diatomic molecule that can serve to illustrate features of MO theory. Both C and O have 2*s* and 2*p* valence orbitals and therefore can form π bonds. Given that O is more electronegative than C, the valence orbitals on O will be of lower energy than the corresponding orbitals on C.

Figure 5.55 shows the energy level diagram for CO. The 2*s* and the $2p_z$ orbitals on both C and O overlap to form four σ molecular orbitals, while the other two *p* orbitals on C and O overlap to form two bonding and two antibonding π orbitals. The bonding π orbitals are lower in energy than the σ bonding orbital with mainly *p* character due to *s*–*p* mixing, which is generally large in heteronuclear diatomic molecules.

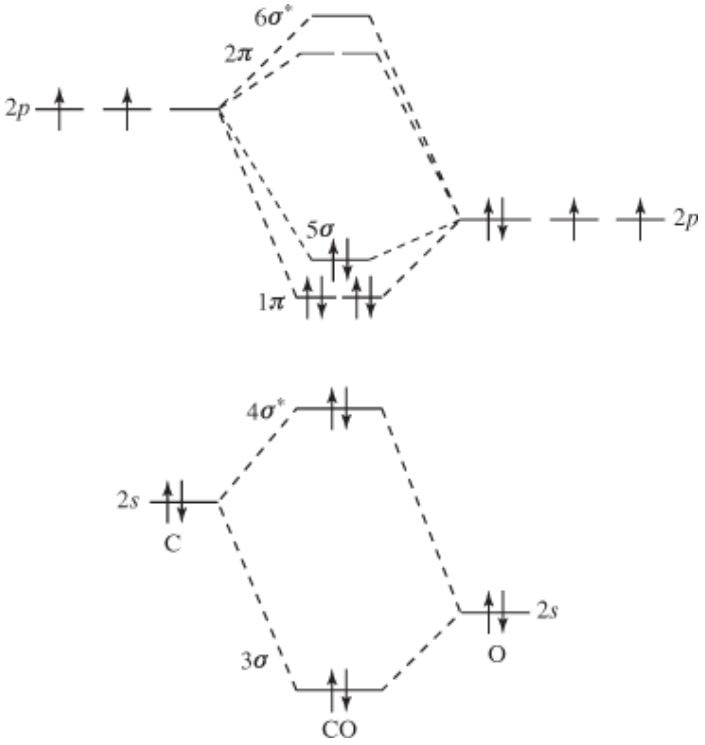


FIGURE 5.55 The molecular orbital diagram of CO.

We have barely scratched the surface of molecular orbital theory. More complicated systems (three or more atoms) require the use of powerful computers to adequately treat the bonding. Indeed, even the simple diatomic systems we have discussed have involved huge simplifications; it is, in fact, currently impossible to exactly describe a molecule containing more than one electron, as the mathematics of such a system have so far defied solution. We have discussed a number of ways to describe the bonding in molecules; although each of them has particular shortcomings, if applied appropriately, we can use them to satisfactorily explain the bonding in virtually all chemical systems.

Chemistry Research

Asymmetric Organocatalysis — a computational approach

Professor (Richard) Ming Wah Wong, National University of Singapore

In this chapter we have discussed how the electrons on atoms in molecular compounds can interact and be shared between atoms to form bonds. Understanding how electrons in specific orbitals in a group of atoms interact with other electrons from another group of atoms can assist us in determining methods by which complex molecules might be syntesised. This can be carried out using the principles of quantum mechanics and solutions of the Schrödinger equation (see chapter 4). However, practical means to achieve this have only recently become available through the development of sophisticated computers and intelligent programs. With the latest advances in computer hardware and computational methodologies, highly accurate theoretical calculations of chemical processes can now be carried out routinely.

Professor (Richard) Ming Wah Wong is one researcher who uses computational methods to study how molecules react. His theoretical studies showed for the first time that argon and helium are capable of forming chemical bonds and predicted that their compounds can exist in the gas phase. These predictions have subsequently been confirmed by experimental chemists and this shows how using a computer can guide practical research towards new discoveries.

Professor Wong's recent research has focused on understanding the detailed pathways involved in reactions where two smaller molecules join to make more complicated structures. Importantly, some of these reactions can be influenced by the presence of other small molecules. These additives can control the speed of the reaction and influence the orientation of the reactants. For instance, Wong and co-workers have investigated the use of BF_3 as a catalyst for a reaction between two alkene molecules that creates a new cyclic structure. Figure 5.56 is a representation of how BF_3 binds to propenal to control the orientation of the orbital overlap between propenal and buta-1,3-diene, which leads ultimately to the cyclic product. The diagram also shows the transition state, which is the momentary arrangement of bonds and atoms that exists as reactants are converted to products. You will see in chapter 15 that transition states have no measurable lifetime and consequently their nature cannot be determined experimentally but must be inferred from other observations. Wong's theoretical calculations also give insight into the nature of the transition state and allow us to understand how the reaction occurs and predict the nature of the observed product.

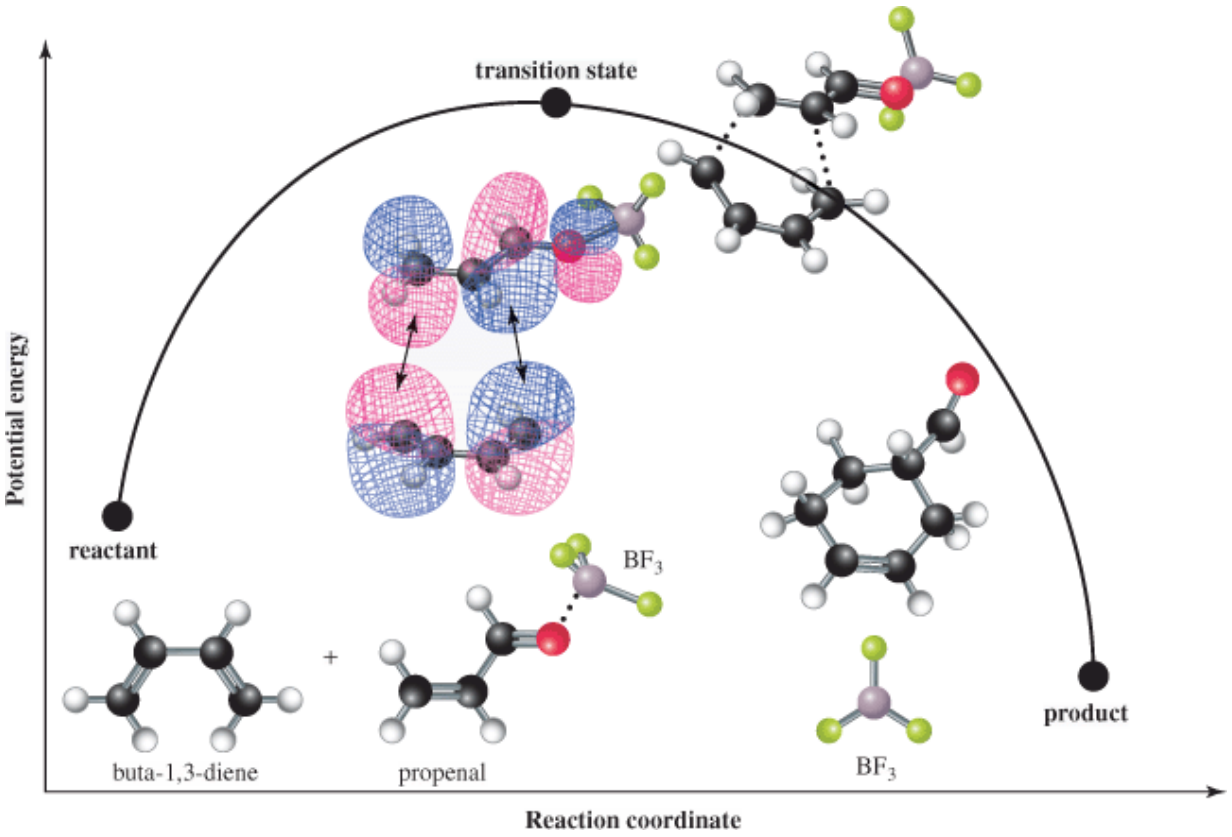


FIGURE 5.56 A graphical description of the manner by which buta-1,3-diene and propenal are converted into a cyclic alkene. The transformation goes through an energy peak, which is called the transition state, where the orbitals in the alkenes begin to overlap to form the new carbon–carbon bonds found in the product.

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SUMMARY

Fundamentals of Bonding

Covalent bonds are formed as a result of the sharing of electrons between nuclei in a way that balances attractive and repulsive forces. In the hydrogen molecule, H_2, this leads to a lowest energy inter nuclear separation of 74 pm. This distance is called the bond length, and the energy difference between the molecule at this distance and the separated atoms is called the bond energy. The single bond in H_2 is an example of a σ bond, a bond that is totally symmetric with respect to rotation about the internuclear axis. In simple diatomic molecules such as H_2 and F_2 we can describe bonding in terms of overlap of atomic orbitals containing single electrons. When the two atoms in a diatomic molecule are different, the electron pair will tend to be attracted more to one atom, resulting in unequal sharing of the electrons and a polar covalent bond. The unequal sharing is a consequence of the different electronegativity values of the atoms in the molecule; the greater the electronegativity difference between the atoms, the more polar the bond. Electronegativities generally increase across a period and decrease down a group in the periodic table.

Ionic Bonding

Compounds formed between elements with very different electro-negativities are often ionic in character. Ionic compounds generally consist of alternating positively and negatively charged ions that are held together by attractive electrostatic forces between the oppositely charged ions. The magnitude of the attractive forces is dependent on the charge of the ions and the separation between them, as well as a number of other factors. The total energy that must be supplied to break the crystal lattice into its gaseous ions is called the lattice energy. Trends in lattice energy values for ionic compounds can be explained in terms of ionic charge and separation.

Lewis Structures

Lewis structures show the distribution of valence electrons within a molecule. Bonding electrons are found in single bonds (1 electron pair), double bonds (2 electron pairs) or triple bonds (3 electron pairs) and these are represented as 1, 2 and 3 lines respectively between the bonded atoms. Nonbonding electrons, called lone pairs, are indicated as dots next to the elemental symbol for the atom on which they are located. Lewis structures may be drawn using the following five-step procedure:

Step 1: Count the valence electrons.

Step 2: Assemble the bonding framework using single bonds.

Step 3: Place three nonbonding pairs of electrons on each outer atom, except H.

Step 4: Assign the remaining valence electrons to inner atoms.

Step 5: Minimise formal charges on all atoms.

An atom has an octet if it is surrounded by four pairs of electrons. This arrangement is often found for elements in the second period of the periodic table. When there is a choice of electron arrangement, the one which minimises the formal charge on all atoms will be preferred. In some cases, two or more energetically equivalent Lewis structures for a molecule can be drawn which differ only in the position of one electron pair. Such structures are called resonance structures. We can also have energetically inequivalent resonance structures; in these cases, the preferred structure will again be that with the lowest possible formal charge on each atom.

Valence-Shell-Electron-Pair Repulsion (Vsepr) Theory

VSEPR theory states that a molecule will adopt a shape in which electron-pair repulsions are minimised. This is achieved by placing electron pairs as far apart as possible. We can predict the structure of a molecule by using the following three-step procedure:

1. Draw the Lewis structure of the molecule.
2. Count the number of sets of bonding pairs and lone pairs of electrons around any inner atom, and use the following table to determine the optimum geometry of these sets.

Number of sets of electron pairs	Geometry of sets of electron pairs
2	linear
3	trigonal planar
4	tetrahedral
5	trigonal bipyramidal
6	octahedral

3. Modify the geometry, if necessary, to take account of the fact that the magnitudes of repulsions between sets of electron pairs depend on whether the electron pairs involved are bonding pairs (BP) or lone pairs (LP). The repulsions are in the order:

$$\mathrm{LP-LP} > \mathrm{BP-LP} > \mathrm{BP-BP}$$

The idealised electron pair geometries will be slightly distorted whenever lone pairs are present, because lone pairs occupy more space than bonding pairs.

Properties of Covalent Bonds

Molecules where the centres of partial negative and partial positive changes do not coincide have a dipole moment. The magnitudes of dipole moments are measured in C m (coulomb metres). Molecules containing polar bonds do not necessarily have a dipole moment, as the polarities of such bonds can cancel each other. Carbon dioxide provides such an example.

Bond lengths in molecules are dependent on the atomic radii of the bonded atoms, which themselves are dependent on effective nuclear charge. A multiple bond between two atoms is shorter than a single bond between the same atoms. Bond energies increase as the number of electrons in the bond increases, and also as the electronegativity difference between the bonded atoms increases. The length of a bond is inversely proportional to its bond energy — as a bond lengthens, its energy becomes less.

Valence Bond Theory

Valence bond theory describes bonding in molecules using localised bonds formed from orbital overlap of hybrid orbitals. As the name suggests, valence bond theory considers only valence orbitals in the formation of bonds. Valence atomic orbitals undergo hybridisation to form hybrid orbitals, with the orbitals involved depending on the type of hybrid orbital required. Hybridisation of one *s* and three *p* orbitals gives four sp^3 hybrid orbitals, hybridising one *s* and two *p* orbitals gives three sp^2 hybrid orbitals, and hybridising one *s* and one *p* orbital gives two *sp* hybrid orbitals. These processes leave zero, one and two *p* orbitals, respectively, unhybridised. The sp^3 hybrid orbitals are positioned tetrahedrally, sp^2 hybrid orbitals are arranged in a trigonal plane, and *sp* hybrid orbitals adopt a linear arrangement. The hybrid orbitals form σ bonds by overlapping with either atomic orbitals or hybrid orbitals on adjacent atoms. Multiple bonds can be described in terms of one σ bond plus one π bond (double bond) or one σ bond plus two π bonds (triple bond); π bonds are formed by overlap of the unhybridised *p* orbitals on adjacent sp^2 or *sp* hybridised atoms.

Molecular Orbital Theory: Diatomic Molecules

Molecular orbital theory considers all possible overlaps between atomic orbitals in a molecule and describes bonding in terms of delocalised bonds. Overlap of two atomic orbitals gives the formation of

molecular orbitals that can cover the entire molecule. Atomic orbitals can overlap in phase (constructive overlap) to give a low energy bonding molecular orbital, or out of phase (destructive overlap) to give a high energy antibonding molecular orbital. Electron density is maximised between the nuclei in bonding MOs, while antibonding MOs contain a node, a position where the amplitude changes sign, between the nuclei. The relative energies of the resulting orbitals are shown on a molecular orbital diagram. Electrons are placed into a molecular orbital diagram following the same rules as used in an atomic energy level diagram. The bond order of a simple diatomic molecule can be calculated from the expression:

$$\text{Bond order} = \frac{1}{2}(\text{number of electrons in bonding molecular orbitals} - \text{number of electrons in antibonding molecular orbitals})$$

While bond orders are generally 1, 2 or 3, it is possible to have non-integer bond orders. Molecular orbital theory can account for the observed paramagnetism of O_2 while valence bond theory cannot. However, to account for the observed properties of other diatomic molecules, orbital mixing, the overlap of *s* atomic orbitals with p_z atomic orbitals, must be considered.

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KEY CONCEPTS AND EQUATIONS

Periodic trends in electronegativity *(section 5.1)*

These trends allow us to use the positions of elements in the periodic table to estimate the degree of bond polarity and to estimate which atom in a bond is the most electronegative.

Method for drawing Lewis structures *(section 5.3)*

Lewis structures show the distribution of valence electrons in a molecule or ion and are drawn according to the following conventions.

1. Each atom is represented by its elemental symbol.
2. Only the valence electrons appear in a Lewis structure.
3. A line joining two elemental symbols represents one pair of electrons shared between two atoms.
4. Dots placed next to an elemental symbol represent nonbonding electrons on that atom.

Formal charges *(section 5.3)*

By assigning formal charges, we can select the best Lewis structure for a molecule or poly atomic ion.

Method for determining resonance structures *(section 5.3)*

By distributing multiple bonds over atoms in a molecule, we obtain a better description of the bonding.

VSEPR theory *(section 5.4)*

This theory enables us to predict the shape of a molecule or polyatomic ion when its Lewis structure is known.

1. Draw the Lewis structure of the molecule.
2. Count the number of sets of bonding pairs and lone pairs of electrons around any inner atom, and use the following table to determine the optimum geometry of these sets.

Number of sets of electron pairs	Geometry of sets of electron pairs
2	linear
3	trigonal planar
4	tetrahedral
5	trigonal bipyramidal
6	octahedral

3. Modify the geometry, if necessary, to take account of the fact that the magnitudes of repulsions between sets of electron pairs depend on whether the electron pairs involved are bonding pairs (BP) or lone pairs (LP). The repulsions are in the order:

$$\mathrm{LP-LP} > \mathrm{BP-LP} > \mathrm{BP-BP}$$

Hybrid orbitals *(section 5.6)*

Hybrid orbitals help to explain the bonding in molecules, and in particular can be used to rationalise the shapes of molecules.

Molecular orbital diagrams *(section 5.7)*

By placing electrons in molecular orbital diagrams we are able to obtain bond orders that agree with

experiments for simple diatomic molecules.

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REVIEW QUESTIONS

Fundamentals of Bonding

5.1 For the following atoms, write the complete electron configuration and identify which of the electrons will be involved in bond formation:

(a) O

(b) P

(c) B

(d) Br.

5.2 Describe bond formation between a hydrogen atom and an iodine atom to form a molecule of HI, and include a diagram of the overlapping orbitals.

5.3 Give the group number and the number of valence electrons for the following elements:

(a) aluminium

(b) arsenic

(c) fluorine

(d) tin.

5.4 Hydrogen forms diatomic molecules with elements from group 1 of the periodic table. Describe the bonding in LiH and include a diagram of the overlapping orbitals.

5.5 For each of the following pairs, identify which element tends to attract electron density from the other in a covalent bond:

(a) C and N

(b) S and H

(c) Zn and I

(d) S and As.

5.6 Show the direction of bond polarity for the following bonds using δ+/δ- notation:

(a) Si—O

(b) N—C

(c) Cl—F

(d) Br—C.

5.7 Arrange the following molecules in order of increasing bond polarity: H_2O, NH_3, PH_3 and H_2S.

Ionic Bonding

5.8 From the following list, select the elements that form ionic compounds: Ca, C, Cu, Cs, Cl and Cr. Indicate whether each forms a stable cation or a stable anion.

5.9 From the following list, select the elements that form ionic compounds: B, Ba, Be, Bi and Br. Indicate whether each forms a stable cation or a stable anion.

5.10 Consider three possible ionic compounds formed by barium and oxygen: $Ba^{+}O^{-}$, $Ba^{2+}O^{2-}$ and $Ba^{3+}O^{3-}$.

(a) Which would have the greatest lattice energy?

(b) Which would require the least energy to form the ions?

(c) Which compound actually exists, and why?

Lewis Structures

5.11 Count the total number of valence electrons in the following species:

(a) H_3PO_4

(b) $(C_6H_5)_3C^+$

(c) $(NH_2)_2CO$

(d) SO_4^{2-}.

5.12 Convert the following formulae into molecular frameworks. For each molecule, calculate how many valence electrons are required to construct the framework:

(a) $(CH_3)_3CBr$

(b) $(CH_3CH_2CH_2)_2NH$

(c) $HClO_3$

(d) $OP(OCH_3)_3$.

5.13 Determine the Lewis structures of:

(a) NH_3

(b) NH_4^+

(c) H_2N^-.

5.14 Determine the Lewis structures of:

(a) PBr_3

(b) SiF_4

(c) BF_4^-.

5.15 Use the standard procedures to determine the Lewis structures of:

(a) H_3CNH_2

(b) CF_2Cl_2

(c) OF_2.

5.16 Determine the Lewis structures of:

(a) IF_5

(b) SO_3

(c) $OPCl_3$

(d) XeF_2.

5.17 Determine the Lewis structure of each of the following polyatomic ions. Include all resonance structures and formal charges where appropriate.

(a) NO_3^-

(b) HSO_4^-

(c) CO_3^{2-}

(d) ClO_2^-

Valence-shell-electron-pair Repulsion (VSEPR) Theory

5.18 Sketch the following molecular shapes and give the various bond angles in the structures:

(a) trigonal planar,

(b) tetrahedral,

(c) octahedral.

5.19 Sketch and name the shapes of the following molecules:

(a) CF_2Cl_2

(b) SiF_4

(c) PBr_3.

5.20 Draw a ball-and-stick model that shows the geometry of 1,2-dichloroethane, ClH_2CCH_2Cl.

5.21 Write the Lewis structure of dimethylamine, $(CH_3)_2NH$. Determine its geometry, and draw a ball-and-stick model of the molecule; show it as an ammonia molecule with the two hydrogen atoms replaced by CH_3 groups.

5.22 Iodine forms three compounds with chlorine:

(a) ICl

(b) ICl_3

(c) ICl_5.

Determine the Lewis structure, describe the shape and draw a ball-and-stick model of each compound.

5.23 Determine the molecular shape and the ideal bond angles for each of the following:

(a) SO_2

(b) SbF_5

(c) ClF_4^+

(d) ICl_4^-.

Properties of Covalent Bonds

5.24 Determine the Lewis structures of the following compounds, and determine which have dipole moments. For each molecule that has a dipole moment, draw a ball-and-stick model and include an arrow to indicate the direction of the dipole moment.

(a) SiF_4

(b) H_2S

(c) XeF_2

(d) $GaCl_3$

(e) NF_3

5.25 Carbon dioxide has no dipole moment, but sulfur dioxide has $\mu = 5.44 \times 10^{-30}$ C m. Use Lewis structures to account for this difference in dipole moments.

5.26 Which of the following molecules would you expect to have bond angles that deviate from the ideal VSEPR values? For the molecules that do, make sketches that illustrate the deviations.

(a) PF_5

(b) CH_3I

(c) BrF_5

5.27 Use Table 5.3 to arrange the following bonds in order of increasing bond strength (weakest first). List the single most important factor for each successive increase in strength.

C═C, H—N, C═O, N≡N and C—C

Valence Bond Theory

5.28 Describe the bonding between fluorine and chlorine atoms in the mixed halogen FCl.

5.29 Describe the bonding between hydrogen and chlorine atoms in HCl and include a picture of the overlapping orbitals.

5.30 The bond angles in antimony trifluoride are 87°. Describe the bonding in SbF_3, including a picture of the orbital overlap interaction that creates the Sb—F bonds.

5.31 Determine the hybridisation of an inner atom in a molecule that has each of the following characteristics:

(a) 2 lone pairs and 2 ligands

(b) 3 ligands and 1 lone pair

(c) 3 ligands and no lone pairs.

5.32 Name the hybrid orbitals formed by combining each of the following sets of atomic orbitals:

(a) 3*s* and three 3*p* orbitals

(b) 2*s* and one 2*p* orbital.

5.33 Identify the hybridisation of the bolded atom in each of the following species:

(a) $(CH_3)_2\mathbf{N}H$

(b) $\mathbf{S}O_2$

(c) $\mathbf{C}S_2$.

5.34 Describe the bonding in the chloroform molecule, $CHCl_3$. Sketch an orbital overlap diagram of the molecule.

5.35 Describe the bonding in the hydrazine molecule, H_2NNH_2. Sketch an orbital overlap diagram of the molecule.

5.36 Describe the bonding in the common solvent acetone, $(CH_3)_2CO$, and include sketches of all the bonding orbitals.



acetone

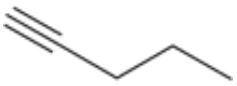
5.37 The carbon compounds penta-1,4-diene, pent-1-yne and cyclopentene all have the molecular formula C_5H_8. Use the number of sets of electron pairs and hybridisation to develop bonding pictures of these three molecules.

(a)



penta-1,4-diene

(b)



pent-1-yne

(c)



cyclopentene

5.38 Decide if the following pairs of orbitals overlap to form a σ bond, π bond, or no bond at all. Explain your reasoning in each case, including a sketch of the orbitals. Assume the bond lies

along the *z*-axis.

(a) $2p_z$ and $2p_z$

(b) $2p_y$ and 2_{px}

(c) sp^3 and $2p_z$

(d) $2p_y$ and $2p_y$

Molecular Orbital Theory: Diatomic Molecules

5.39 Use molecular orbital diagrams to rank the bond energies of the following diatomic species from weakest to strongest: H_2, H_2^- and H_2^{2-}.

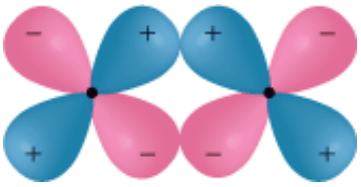
5.40 Which of N_2 or N_2^+ has the stronger bond? Use orbital configurations to justify your selection.

5.41 For each of the following interactions between orbitals of two different atoms, sketch the resulting molecular orbitals. Assume that the nuclei lie along the *z*-axis, and include at least two coordinate axes in your drawing. Label each MO as bonding or antibonding and σ or π.

(a) $2s$ and $2p_z$

(b) $2p_x$ and $2p_x$

5.42 Below is an illustration showing two 3*d* orbitals about to overlap. The drawings also show the algebraic signs of the wavefunctions for both orbitals in this combination. Will this combination of orbitals produce a bonding or an antibonding MO?



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REVIEW PROBLEMS

5.43 Determine the molecular geometries of the following molecules:

(a) $SiCl_4$,

(b) SeF_4 and

(c) CI_4.

5.44 Determine the molecular geometries of the following ions:

(a) ClF_2^-,

(b) BF_4^- and

(c) PF_4^+.

5.45 How many different structural isomers are there for octahedral molecules with the general formula AX_3Y_3? Draw three-dimensional structures of each.

5.46 Using information in Table 5.1, determine the average difference in lattice energy between group 1 fluorides and group 1 chlorides, and the average difference in lattice energy between group 1 bromides and group 1 iodides. Is there a trend in the individual values? If so, describe and explain it.

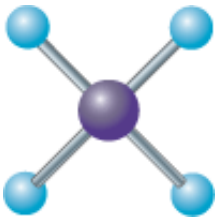
5.47 Carbon, nitrogen and oxygen form two different polyatomic ions: the cyanate ion, NCO^-, and the isocyanate ion, CNO^-. Write Lewis structures for each anion; include near-equivalent resonance structures and indicate formal charges.

5.48 Species with the general chemical formula XY_4 can have the shapes shown in the following diagrams. For each, name the molecular geometry, identify the ideal VSEPR bond angles, give the number of lone pairs present in the structure and provide a specific example.

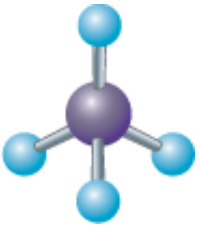
(a)



(b)



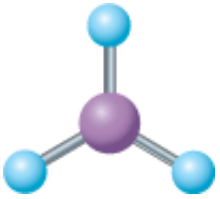
(c)



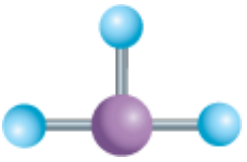
5.49 Species with the general chemical formula XY_3Y can have the shapes shown in the following diagrams. For each, name the molecular geometry, identify the ideal VSEPR bond angles, give the number of lone pairs present in the structure and provide a specific example.

(a)

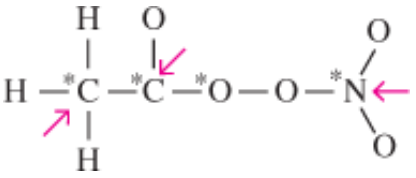
(b)



(c)



5.50 In the lower atmosphere, NO_2 participates in a series of reactions in air that is also contaminated with unburned hydrocarbons. One product of these reactions is peroxyacetyl nitrate (PAN). The skeletal arrangement of the atoms in PAN appears below.



(a) Complete the Lewis structure of this compound.

(b) Determine the geometry around each atom marked with an asterisk.

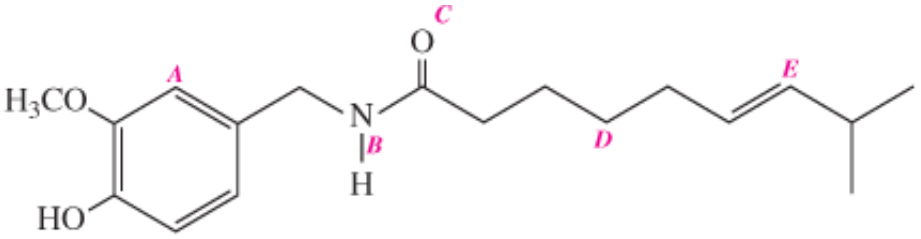
(c) Give the approximate values of the bond angles indicated with arrows.

5.51 The H—O—H bond angle in a water molecule is 104.5°. The H—S—H bond angle in hydrogen sulfide is only 92.2°. Explain these variations in bond angles using orbital sizes and electron–electron repulsion arguments. Draw space-filling models to illustrate your explanation.

5.52 List the following *X*—H bonds from smallest bond polarity to largest bond polarity: C—H, F—H, N—H, O—H and Si—H.

5.53 Sulfur forms two stable oxides, SO_2 and SO_3. Describe the bonding and geometry of these compounds.

5.54 Capsaicin is the molecule responsible for the hot spiciness of chillies:



capsaicin, $C_{18}H_{27}O_3N$

(a) How many π bonds does capsaicin have?

(b) Which orbitals are used for bonding by each of the labelled atoms?

(c) What are the bond angles around each of the labelled atoms?

(d) Redraw the structure of capsaicin adding the lone pairs.

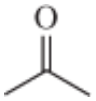
5.55 Use electron configurations to decide if the following species are paramagnetic or diamagnetic:

(a) N_2^+

(b) O_2^+.

5.56 Determine the type of orbitals (atomic, sp^3 or sp^2) used by each atom in the molecules shown below.

(a)



(b) H_3CNH_2

(c)



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ADDITIONAL EXERCISES

5.57 Determine the Lewis structures for the two possible arrangements of the N_2O molecule: N—N—O and N—O—N. Experiments show that the molecule is linear and has a dipole moment. What is the arrangement of atoms? Justify your choice.

5.58 The inner atom of a triatomic molecule can have any of four different geometries for the surrounding sets of electron pairs. Identify the four, describe the shape associated with each and give a specific example of each.

5.59 Both PF_3 and PF_5 are known compounds. NF_3 also exists, but NF_5 does not. Why is there no molecule with the formula NF_5?

5.60 Phosphorus acid, H_3PO_3, is an exception to the rule that hydrogen always bonds to oxygen in oxoacids. In this compound, one of the hydrogen atoms bonds to phosphorus. Determine the Lewis structure of phosphorus acid and determine the geometry around the phosphorus atom. Draw a ball-and-stick model of the molecule.

5.61 Nitrogen molecules can absorb photons to generate excited-state molecules. Construct an energy level diagram and place the valence electrons so that it describes the most stable excited state of an N_2 molecule. Is the N—N bond in this excited-state N_2 molecule stronger or weaker than the N—N bond in ground-state nitrogen? Explain your answer.

5.62 Chlorine forms one neutral oxide, ClO_2. Describe the bonding in this unusual compound. Explain why it is considered unusual.

5.63 Dilithium molecules can be generated by vaporising lithium metal at very low pressure. Do you think it is possible to prepare diberyllium? Explain your reasoning using MO diagrams for Li_2 and Be_2.

5.64 When an oxalate anion, $C_2O_4^{2-}$, adds two protons to form oxalic acid, two C—O bonds become longer and two become shorter than the bonds in oxalate anions. Which bonds get longer and which shorter? Use bonding principles to explain the changes.

5.65 Consider the bond lengths of the following diatomic molecules: N_2, 110 pm; O_2, 121 pm; F_2, 143 pm. Explain the variation in length in terms of the molecular orbital descriptions of these molecules.

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KEY TERMS

antibonding molecular orbital
bond energy
bond length
bond order
bonding molecular orbital
bonding orbital
covalent bond
delocalised bond
dipole moment
double bond
electronegativity
formal charge
hybrid orbital
hydration
ionic compounds
lattice energy
Lewis structure
linear
localised bond
lone pair
molecular orbital diagram
molecular orbital theory
molecular orbital (MO)
node
octahedral
orbital mixing
orbital overlap
pi (π) bond
polar covalent bond
resonance structure
seesaw shape
sigma (σ) bond
single bond
sp hybrid orbitals
sp^2 hybrid orbitals
sp^3 hybrid orbitals
tetrahedral
trigonal bipyramidal
trigonal planar
triple bond
valence-shell-electron-pair-repulsion (VSEPR)

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CHAPTER

6 Gases

We are all familiar with the three common states of matter — gas, liquid and solid — in, for example, the air we breathe, the water of the ocean and the sand of the beach. All three states are composed of atoms, ions or molecules. The strength of the attractive forces between these constituents influences which particular state of matter a compound displays. In this chapter we will focus on the characteristics and behaviour of gases, and in chapter 7 we will deal with liquids and solids.

Although few chemical elements occur naturally as gases, we spend almost all of our time immersed in them. The Earth's atmosphere is made up mainly of nitrogen, N_2, (˜78%) and oxygen, O_2, (˜21%) with some other species in trace amounts. The exact composition and temperature of this gas mixture is responsible for our weather. The photo on this page shows hot-air balloons over the Melbourne Cricket Ground (MCG) and reminds us that hot-air balloonists exploit the fact that hot air rises.

We begin this chapter with a discussion of the variables that characterise gases. Then we develop a molecular description that explains gas behaviour. Next, we explore additional gas properties and show how to carry out stoichiometric calculations for reactions involving gas-phase species. We then explore the kinds of attractions that exist between molecules and how these attractions affect the physical properties of gases.



KEY TOPICS

6.1 The states of matter
6.2 Describing gases
6.3 Molecular view of gases

6.4 Gas mixtures
6.5 Applications of the ideal gas equation
6.6 Gas stoichiometry
6.7 Real gases
6.8 Intermolecular forces

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6.1 The States of Matter

It is remarkable that essentially all of the matter in the universe exists in only three states: solid, liquid or gas. A fourth state of matter, plasma, exists only under extreme conditions such as those found in the interiors of stars, while the Bose–Einstein condensate, a recently discovered state of matter, is found only at temperatures approaching absolute zero. We will also encounter supercritical fluids, which have properties of both liquids and gases, in chapter 7.

It is also interesting that most substances can exist in any of these three states, and we can change the most stable state of a particular substance by varying the temperature and/or pressure; for example, cooling liquid water to below 0 °C at ambient pressure will produce solid water (ice).

Why, at 25 °C and atmospheric pressure, does water exist as a liquid, while oxygen is a gas and gold is a solid? The answer lies in the forces that occur between individual atoms, molecules or ions in a substance. Solids are held together by relatively strong forces between their components, while the corresponding forces in gases are relatively weak. This chapter and chapter 7 focus on the different possible states of matter. In this chapter, we concentrate on the gaseous state of matter, and investigate the different types of forces that can occur between atoms, ions and molecules. Chapter 7 is primarily concerned with liquids and solids (the so-called condensed phases), and also looks at the processes involved when substances undergo changes of state.

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6.2 Describing Gases

Gases are characterised by the fact that, in contrast to liquids and solids, they expand to occupy all the space of their container. For example, gaseous water (water vapour) will be found in all parts of any flask it is in, but, if the temperature is lowered, the resulting liquid water occupies only the bottom of the flask. Lowering the temperature further to below the freezing point produces ice, which also occupies only the bottom of the flask. The fact that gases fill all available space implies that the individual gas atoms or molecules are free to move anywhere within their container (figure 6.1), and therefore the forces between them must be very weak. One of the defining characteristics of gases is the pressure they exert. This results from the rapid motion of individual gas atoms or molecules and their collisions with the walls of the container. The pressure (p) exerted by a gas is dependent on the amount of gas present (n), the volume in which it is contained ($V!$) and its temperature (T). On the following pages, we derive a relationship relating all of these variables.

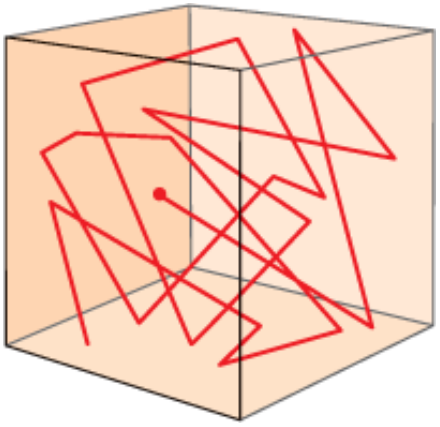


FIGURE 6.1 Molecules or atoms of a gas move freely throughout the entire volume of a container, changing direction whenever they collide with other molecules or atoms or with a wall. The line traces a possible path of a single molecule or atom.

Pressure (p)

Any object that strikes a surface exerts a force against that surface. In the same way that a ball exerts a force against the ground when it strikes it, the gas molecules inside the ball also exert pressure through collisions with the walls of the ball. At any temperature above absolute zero, atoms and molecules are always in motion. At the molecular level, atoms and molecules exert forces through never-ending collisions with each other and with the walls of their container (e.g. the inside surface of the ball). The collective result of these collisions is what we call **pressure**. We experience pressure as a macroscopic property.

We can get a feel for the macroscopic characteristics of gas pressure by examining the Earth's atmosphere. The atmosphere is a huge reservoir of gas that, due to Earth's gravity, exerts pressure on the Earth's surface. The pressure of the atmosphere can be measured with an instrument called a **barometer**. Figure 6.2 shows a schematic view of a simple mercury barometer. A long glass tube, closed at one end, is filled with liquid mercury. The filled tube is inverted carefully into a dish that is partially filled with more mercury. The force of gravity pulls downwards on the mercury in the tube. With no opposing force, all the mercury would run out of the tube and mix with the mercury in the dish. The mercury does fall, but the flow stops at a certain height. The column of mercury stops falling because the atmosphere exerts pressure on the mercury in the dish, pushing the column up the tube. When the height of the mercury column generates a downward force on the inside of the tube that exactly balances the force exerted by the atmosphere on the outside of the tube, the column of mercury will remain steady.

FIGURE 6.2 A mercury barometer. The pressure of the atmosphere on the surface of the mercury balances the pressure of the column of mercury.

At sea level, atmospheric pressure supports a mercury column approximately 760 mm high. Changes in altitude and weather cause fluctuations in atmospheric pressure. At sea level the height of the mercury column seldom varies by more than 10 mm, except under extreme conditions, such as in the eye of a cyclone, when it may fall below 740 mm.

A **manometer** is similar to a barometer, but in a manometer gases exert pressure on both liquid surfaces. Consequently, a manometer measures the difference in pressures exerted by two gases. A simple manometer, shown in figure 6.3, is a U-shaped glass tube containing mercury. One side of the tube is exposed to the atmosphere and the other to a gas whose pressure we want to measure. In figure 6.3, the pressure exerted by the atmosphere (p_{atm}) is less than the pressure exerted by the gas in the bulb (p_{gas}). The difference in heights of mercury between the two sides of the manometer depends on the difference in the pressures exerted by the gas and the atmosphere (equal to p_{Hg}).

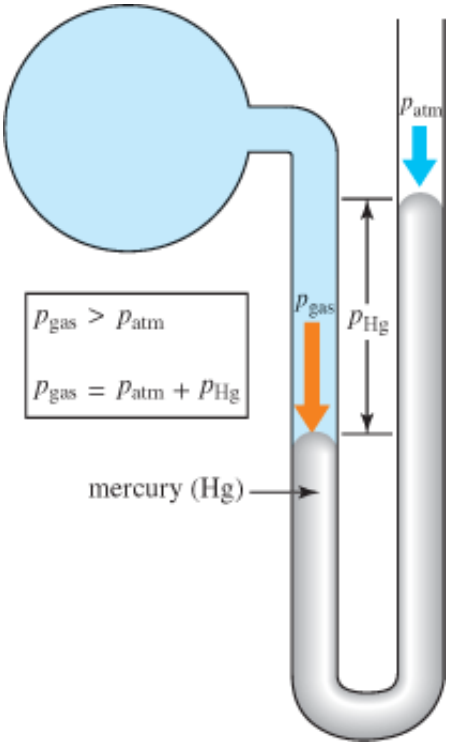


FIGURE 6.3 The difference in heights of liquid on the two sides of a manometer is a measure of the difference in gas pressures applied to the two sides.

As we learned in chapter 2, the SI unit for pressure is the **pascal (Pa)**. Pressure is defined as force per unit area, so the pascal is expressed by combining the SI units for these two variables. The SI unit of force is the newton (N), and the unit of area is square metres (m^2). Thus 1 Pa = 1 N m^{-2} = 1 kg m^{-1} s^{-2} = 1 J m^{-3} (with 1 N = 1 kg m s^{-2} and 1 J = 1 kg m^2 s^{-2}).

A number of non-SI units for pressure are also commonly used:

- One standard atmosphere (1 atm) is the pressure that will support a column of mercury 760 mm in height (i.e. average atmospheric pressure at sea level); 1 atm = 1.013 25 × 10^5 Pa.
- One torr is the pressure exerted by a column of mercury 1 mm in height; 1 atm = 760 torr.
- 1 bar = 1 × 10^5 Pa.

In this textbook we will always express pressure in the SI unit: the pascal (Pa). In chapter 8, we will encounter standard pressure, $p^{\ominus}$, which is 1×10^5 Pa, very slightly different from one standard atmosphere. It is important not to confuse the two.

The Gas Laws

The volume occupied by a gas changes in response to changes in pressure, temperature and amount of gas. The relationships among these are known as the gas laws.

Boyle'S Law: the Relationship Between Volume and Pressure

Figure 6.4a illustrates experiments conducted at constant temperature by the English scientist Robert Boyle in about 1660. Boyle added liquid mercury to the open end of a J-shaped glass tube, trapping a fixed amount of air on the closed side. When Boyle added additional mercury to the open end of the tube, the pressure exerted by the weight of the additional mercury compressed the trapped gas into a smaller volume. For example, as shown in figure 6.4a, Boyle found that doubling the total pressure on the trapped air by the addition of mercury halved its volume. In more general terms, Boyle's experiments showed that the volume of the trapped air was inversely proportional to the total pressure applied by the mercury plus the atmosphere.

$$V_{\text{gas}} \propto \frac{1}{P_{\text{gas}}} \quad \text{(fixed temperature and amount of gas)}$$

or, alternatively:

$$P_{\text{gas}} V_{\text{gas}} = \text{k} \quad \text{(fixed temperature and amount of gas)}$$

where k is a constant. This is shown graphically in figure 6.4b.

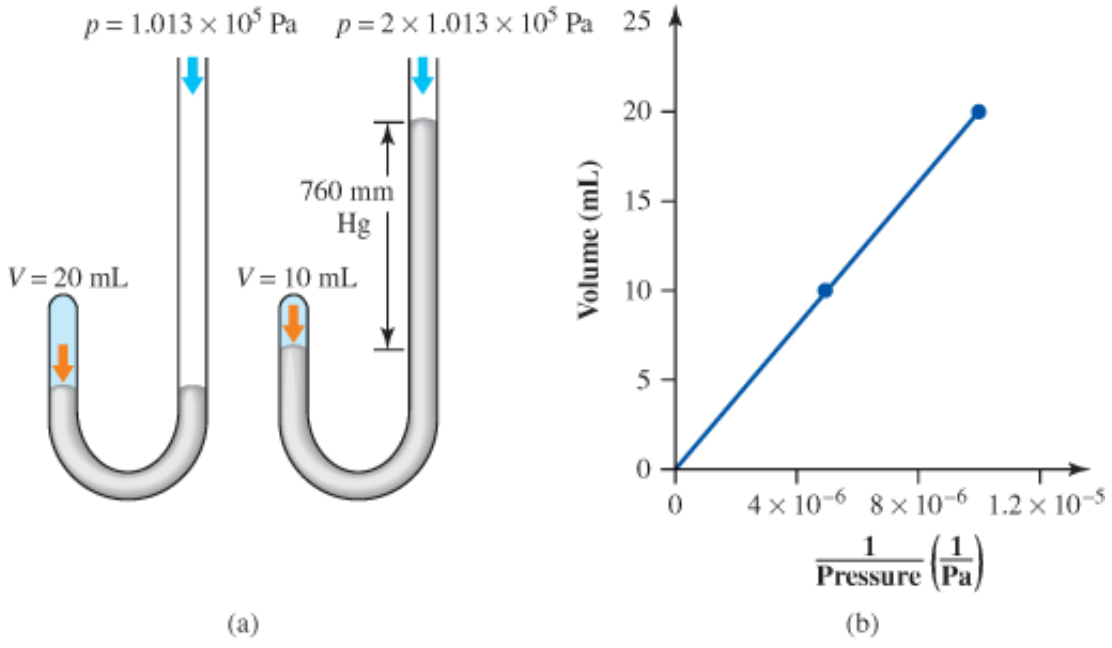


FIGURE 6.4

(a) Schematic illustration of Boyle's experiments on air trapped in J-shaped tubes. The pressure on the enclosed gas in the right-hand tube is twice that in the left-hand tube, and the volume of the enclosed gas is halved.

(b) Graph showing the linear variation of V versus $\frac{1}{p}$.

Charles' Law: the Relationship Between Volume and Temperature

Boyle also observed that heating a gas causes it to expand in volume, but more than a century passed before Jacques-Alexandre-César Charles reported the first quantitative studies of gas volume as a function of temperature. Charles found that, for a fixed amount of gas, a graph of gas volume versus temperature gives a straight line, as shown in figure 6.5. In other words, the volume of a gas is directly proportional to its temperature.

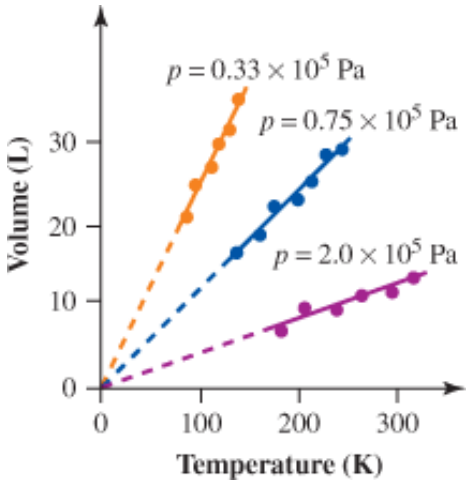


FIGURE 6.5 Plots of volume versus temperature for 1 mole of air at three constant pressures. The dots represent experimental data, with dashed lines of best fit extrapolated to 0 K.

$$V_{gas} \propto T_{gas} \quad \text{(fixed pressure and amount of gas)}$$

or, alternatively:

$$V_{gas} = k' T_{gas} \quad \text{(fixed pressure and amount of gas)}$$

where k′ is a constant.

Avogadro's Law: the Relationship Between Volume and Amount

The volume of a gas also changes when the amount of the gas changes. If we double the amount of a gas while keeping the temperature and pressure fixed, the gas volume doubles. In other words, gas volume is proportional to the amount of gas.

$$V_{gas} \propto n_{gas} \quad \text{(fixed pressure and temperature of gas)}$$

or, alternatively:

$$V_{gas} = k'' n_{gas} \quad \text{(fixed pressure and temperature of gas)}$$

where k″ is a constant.

The Ideal Gas Equation

The work of Boyle, Charles, Avogadro and other early scientists showed that the volume of any gas is proportional to the temperature and amount of the gas, and inversely proportional to the pressure of the

gas. Combining these observations, we find that:

$$V \propto \frac{nT}{p}$$

This proportionality is converted into an equality by introducing the **gas constant**, represented by the symbol *R*. Introducing *R* and multiplying both sides of the equation by *p* gives:

$$pV = nRT$$

This is known as the **ideal gas equation**, because it describes the behaviour of an **ideal gas**. While no gas is truly ideal, the ideal gas equation is adequate to describe most real gases provided that their pressure is relatively low. The temperature in the ideal gas equation is expressed in kelvin, with T (K) = T (°C) + 273.15. The gas constant is defined in SI units as $R = 8.314$ J mol^{-1} K^{-1}. Pressure is expressed in Pa, volume is expressed in m^3 (1 m^3 = 1 × 10^3 L) and amount (n) is expressed in moles. There is a second version of the gas constant that is expressed in non-SI units: $R = 0.082\ 06$ L atm^{-1} K^{-1} mol^{-1}. This is used frequently and so it is important to always confirm that the value and units of the gas constant are chosen appropriately for a given problem. Worked example 6.1 shows the calculations for both gas constants.

It follows naturally from the ideal gas equation that all ideal gases have the same molar volume under a given set of standard conditions. In chemistry, the generally accepted standard conditions are 0 °C and 1 × 10^5 Pa, leading to a molar volume under these conditions of 22.71 L.

WORKED EXAMPLE 6.1

Calculation of Gas Pressure

A 1.000 × 10^3 L steel storage tank contains 88.5 kg of methane, CH_4. If the temperature is 25 °C, what is the pressure inside the tank?

Analysis

The problem asks for the pressure exerted by a gas. The gas is stored in a steel tank, so the volume of the gas cannot change. No chemical changes are described in the problem. We can therefore solve this problem using the ideal gas equation.

Solution

We are told that:

$$V = 1.000 \times 10^3\ \text{L} = 1.000\ \text{m}^3 \quad T = 25°\text{C} \quad m = 88.5\ \text{kg of methane}$$

We can calculate the pressure of the gas using the ideal gas equation, but we need to make sure all the variables are expressed in appropriate units. Temperature must be in kelvin, amount of methane in moles, and volume in m^3.

We rearrange the ideal gas equation by dividing both sides by V, thus making pressure the subject of the equation.

$$pV = nRT$$

$$P = \frac{nRT}{V}$$

Add 273.15 to the temperature in °C to convert to kelvin.

$$T = 25 + 273.15 = 298 \text{ K}$$

Note that, when we add numbers, the result has the same number of decimal places as the number with the fewest decimal places (zero in this example).

Use the molar mass of methane to calculate the amount of gas.

$$n_{CH_4} = \frac{88.5 \times 10^3 \text{ g}}{16.04 \text{ g mol}^{-1}} = 5.52 \times 10^3 \text{ mol}$$

Now substitute this into the rearranged ideal gas equation and calculate the pressure.

$$p = \frac{(5.52 \times 10^3 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1.000 \text{ m}^3} = 1.37 \times 10^7 \text{ Pa}$$

If we use the non-SI version of the gas constant, 0.082 06 L atm K^{-1} mol^{-1}, we need to express the volume in litres (L):

$$p = \frac{(5.52 \times 10^3 \text{ mol})(0.082\ 06 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{1000 \text{ L}} = 135 \text{ atm}$$

Is our answer reasonable?

It is important to check that the units cancel properly, giving a result in pressure units (recall that 1 Pa = 1 J m^{-3}). The problem describes a large amount of methane in a relatively small volume, so a high pressure (over 100 times atmospheric pressure) is reasonable. This high value indicates why gases must be stored in tanks made of materials such as steel that can withstand high pressures.

PRACTICE EXERCISE 6.1

Determine the new pressure if the tank in worked example 6.1 is stored in a hot shed where the temperature reaches 42 °C.

During chemical and physical transformations, any of the four variables in the ideal gas equation (*p*, *V*, *n*, *T*) may change, and any of them may remain constant. The ideal gas equation can be rearranged as:

$$R = \frac{pV}{nT}$$

Then, for different initial and final conditions, we have:

$$\frac{p_i V_i}{n_i T_i} = \frac{p_f V_f}{n_f T_f}$$

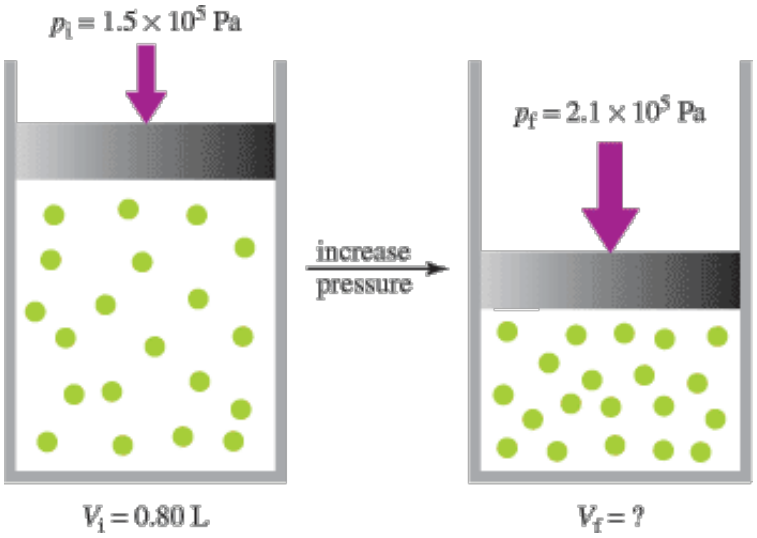
WORKED EXAMPLE 6.2

Pressure–Volume Variations

A sample of helium gas is held at constant temperature inside a cylinder with a volume of 0.80 L when a piston exerts a pressure of 1.5×10^5 Pa. If the external pressure on the piston is increased to 2.1×10^5 Pa, what will the new volume be?

Analysis

We can visualise the conditions by drawing a schematic diagram of the initial and final conditions (p = initial pressure, p_f = final pressure, V_i = initial volume, V_f = final volume).



Solution

Gas behaviour is involved, so the equation that applies is the ideal gas equation, $pV = nRT$. Rearranging the gas equation to solve for V will not help because we do not know n, the amount of He present, or T, the temperature of the gas. We do know, however, that n and T remain unchanged as the pressure increases.

To determine the final volume of the helium gas, apply the ideal gas equation to the initial and final conditions (shown with subscripts i and f, respectively).

$$p_i V_i = n_i R T_i \quad \text{and} \quad p_f V_f = n_f R T_f$$

In this problem, the quantity of He inside the cylinder and the temperature of the gas are constant:

$$n_i = n_f \quad \text{and} \quad T_i = T_f \quad \text{so} \quad n_i R T_i = n_f R T_f$$

Therefore:

$$p_i V_i = p_f V_f \quad \text{(constant } n \text{ and } T\text{)}$$

Notice that we can solve this for V_f without knowing the values of n and T.

Now we rearrange the above equation, substitute the appropriate values and calculate the final volume.

$$V_f = \frac{p_i V_i}{p_f} = \frac{(1.5 \times 10^5 \text{ Pa})(0.80 \times 10^{-3} \text{ m}^3)}{2.1 \times 10^5 \text{ Pa}} = 0.57 \times 10^{-3} \text{ m}^3$$
$$= 0.57 \text{ L}$$

Is our answer reasonable?

This answer is reasonable because an external pressure increase has caused a volume decrease.

PRACTICE EXERCISE 6.2

The piston in worked example 6.2 is withdrawn until the gas volume is 2.55 L. Calculate the final pressure of the gas.

In worked example 6.2, the quantities on the right-hand side of the ideal gas equation ($pV = nRT$) are fixed, whereas the quantities on the left are changing. A useful strategy for organising gas calculations is to rearrange the gas equation to place all variables that do not change on one side.

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6.3 Molecular View of Gases

To understand why all gases can be described by a single equation, we need to explore how gases behave at the molecular level. As gases are characterised by rapid motion of their constituent atoms or molecules, the most important energy component to consider is their kinetic energy, E_{kinetic}. The kinetic energy of an object is given by the equation:

$$E_{\text{kinetic}} = \frac{1}{2}mu^2$$

where m is the mass of the object (in this case an individual gas atom or molecule) and u is its speed. We can easily obtain the mass of a single atom or molecule from the molar mass of the gas, but in order to calculate E_{kinetic} we must measure the speed with which an atom or molecule is moving. As the atoms or molecules in any sample of gas are constantly undergoing collisions with other atoms or molecules and with the walls of the container, they might not necessarily all be moving at the same speed. On the following pages, we describe a method of measuring the speeds of gas atoms or molecules to give an overall distribution of speeds for a gas sample. This allows us to determine the kinetic energy distribution of the atoms or molecules in a sample of gas.

Molecular Speeds

The speeds of molecules in a gas can be measured using a molecular beam apparatus, which is shown schematically in figure 6.6. Gas molecules in an oven escape through a small hole into a chamber with very low molecular density: that is, high vacuum. A set of slits blocks the passage of all molecules except those moving in the forward direction. The result is a beam of molecules, all moving in the same direction. A rotating disc blocks the beam path except for a small slit that allows a packet of molecules to pass through. Each molecule moves down the beam axis at its own speed undergoing minimal collisions with other molecules in the packet. The faster a molecule moves, the less time it takes to travel the length of the chamber. A detector at the end of the chamber measures the number of molecules arriving as a function of time, giving a profile of speeds.

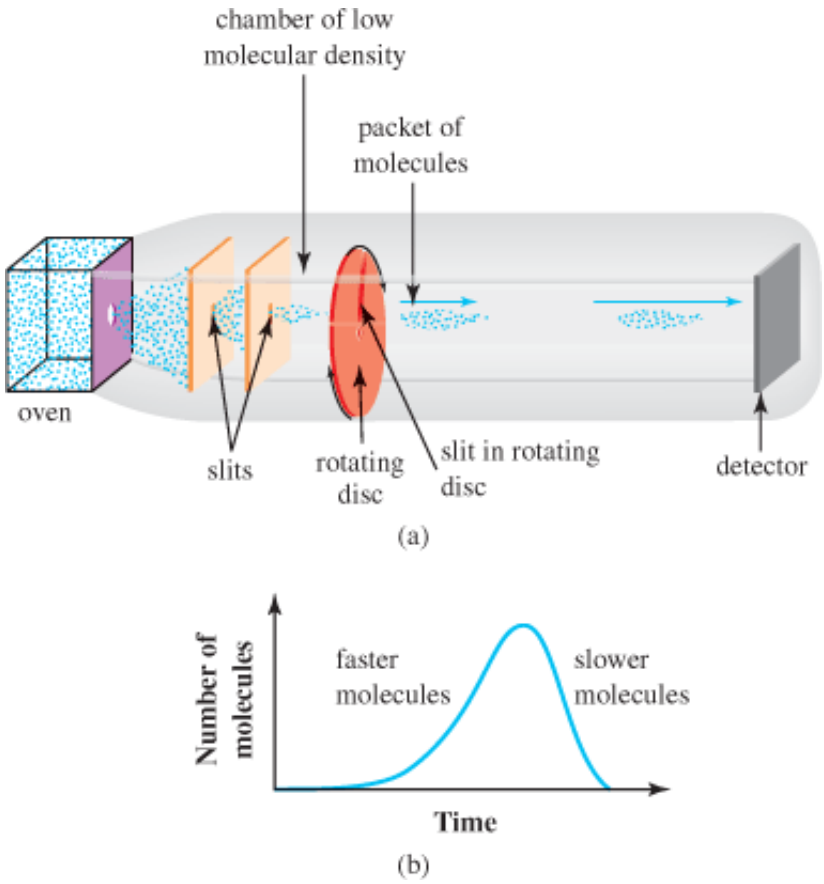


FIGURE 6.6

(a) Schematic diagram of a molecular beam apparatus designed to measure the speeds of gas molecules.

(b) Distribution of molecules observed by the detector as a function of the time after a packet of molecules reaches the slit in the disc.

When the speed profile of a gas is measured in this way, the results give a distribution like the one shown in figure 6.6b. If all the molecules travelled at the same speed, they would all reach the detector at the same time, in a single clump. Instead, faster molecules move ahead of the main packet, and slower molecules fall behind. This experiment shows that molecules in a gas have a distribution of speeds.

A pattern emerges when this molecular beam experiment is repeated for various gases at a common temperature; molecules with small masses move, on average, faster than those with large masses. Figure 6.7 shows this for H_2, CH_4 and CO_2. Of these molecules, H_2 has the smallest mass and CO_2 the largest. The vertical line drawn for each gas shows the speed at which there is the largest number of molecules. More molecules have this speed than any other, so this is the most probable speed for molecules of that gas. The most probable speed for a molecule of hydrogen at 300 K is 1.57×10^3 ms^{-1} or 5.65×10^3 km h^{-1}.

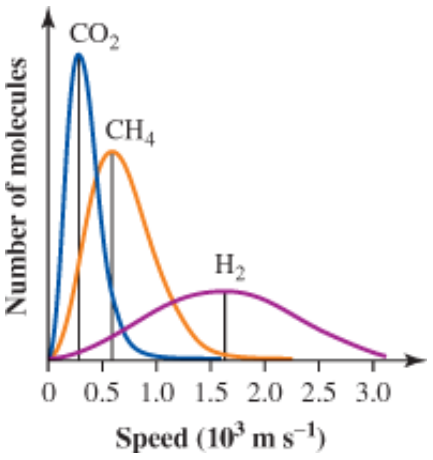
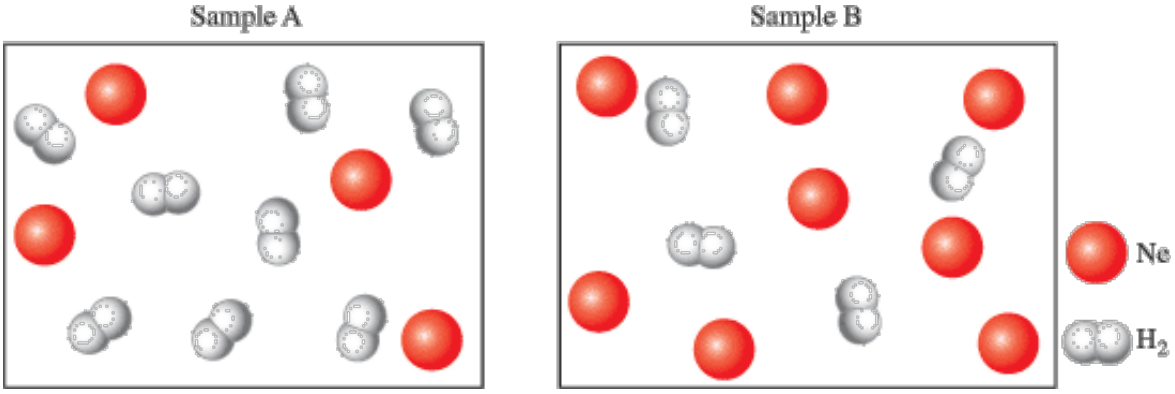


FIGURE 6.7 Graph showing molecular speed distributions for CO_2, CH_4 and H_2 at a temperature of 300 K.

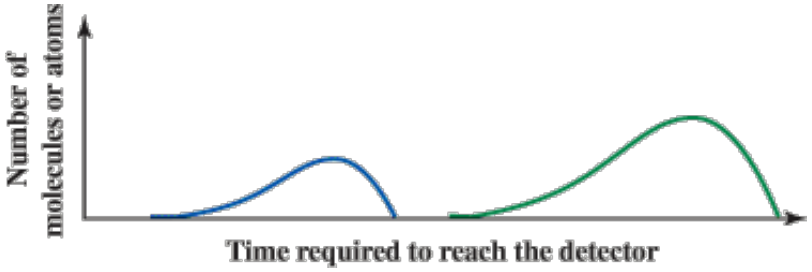
WORKED EXAMPLE 6.3

A Molecular Beam Experiment

The figures below represent mixtures of neon atoms and hydrogen molecules.



One of the gas mixtures was used in a molecular beam experiment. The result of the experiment is shown below. Which of the two gas samples, A or B, was used for this experiment?



Analysis

Examine the two samples, and then decide how each of them would behave in a beam experiment.

Solution

Sample A contains eight H_2 molecules and four Ne atoms, and sample B contains four H_2

molecules and eight Ne atoms. In a molecular beam experiment, both samples would give two peaks in relative areas of 2 : 1. Atoms or molecules with a small mass move faster than those with a large mass, so we expect H_2 (M = 2.02 g mol^{-1}) to reach the detector before Ne (M = 20.2 g mol^{-1}). The data show that the first substance to reach the detector is present in the smaller amount. Consequently, the sample used in the beam experiment is the one with the smaller amount of hydrogen molecules — sample B.

Is our answer reasonable?

H_2 moves faster than other, heavier substances, so it makes sense that the H_2 molecules, which are lighter than Ne atoms, get to the detector faster. H_2 molecules are present in a smaller amount than Ne atoms, and the experimental data are consistent with that.

PRACTICE EXERCISE 6.3

Suppose that, in worked example 6.3, sample A is used and that the second gas is helium instead of neon. Sketch a graph, similar to the one in worked example 6.3, showing the number of molecules/atoms versus time.

Chemical Connections

Metal-Organic Frameworks for Greenhouse Gas Separation and Hydrogen Storage Applications

Deanna M D'Alessandro, University of Sydney

The prospect of a worsening climatic situation due to global warming is one of the most pressing environmental concerns for our generation. The urgent need for strategies to reduce atmospheric concentrations of greenhouse gases has prompted action from many governments and industries, and a number of high-profile collaborative programs have been established to tackle the issue. Two of the central strategies in these initiatives include the capture and sequestration of carbon dioxide, the predominant greenhouse gas, from large stationary sources such as power plants, and the introduction of hydrogen as a cleanburning alternative to fossil fuels in mobile applications such as cars.

Among several candidate groups of materials for gas storage and separation, highly porous three-dimensional solids known as metal-organic frameworks (MOFs, which are also known as porous coordination polymers, figure 6.8) show exceptional promise. Believe it or not, one teaspoon of one of these materials can have a surface area that is equivalent to a football field! These microporous crystalline solids are composed of organic bridging ligands or ‘struts’ coordinated to metal-based nodes to form a three-dimensional extended network with uniform pore diameters typically in the range of 3 to 20 Å. The nodes generally consist of one or more metal ions (e.g. Al^{3+}, Cr^{3+}, Cu^{2+}, Zn^{2+}) to which the organic bridging ligands

coordinate via a specific functional group (e.g. carboxylate, pyridyl).

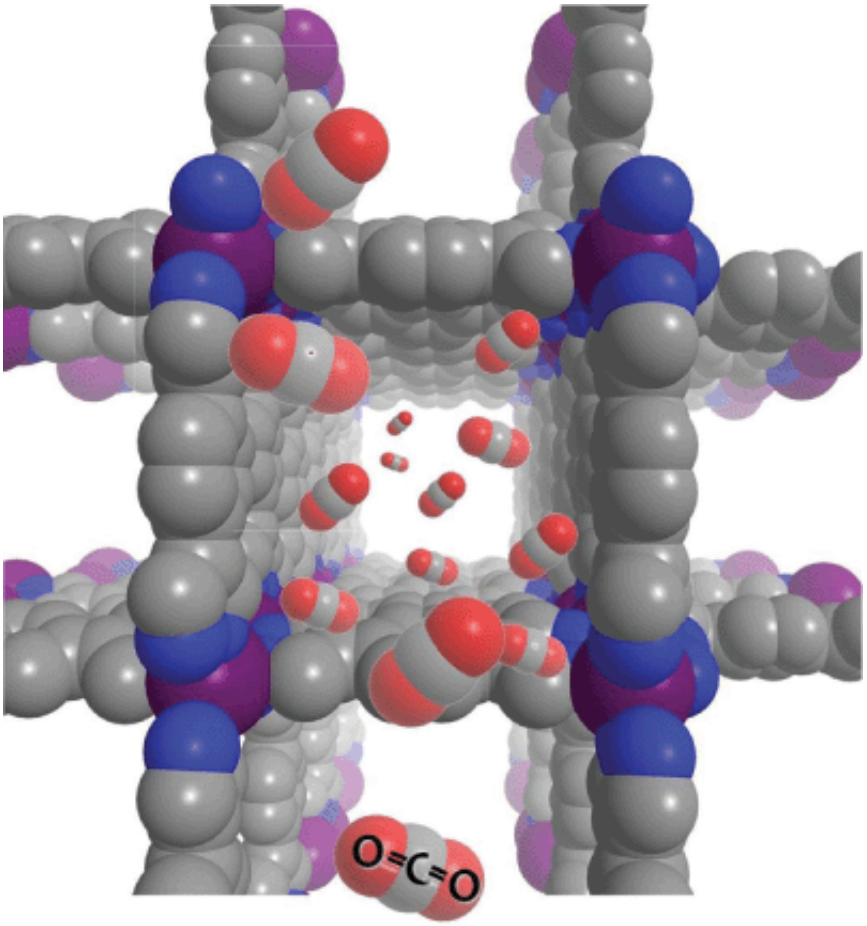


FIGURE 6.8 Representation of CO_2 diffusing through a microporous MOF structure.

The intense current research effort towards industrial applications of MOFs in gas storage, separation and catalysis is attributed to their unique structural properties, including: robustness, high thermal and chemical stabilities, unprecedented internal surface areas (up to 6000 $m^2\ g^{-1}$), high void volumes (55–90%) and low densities (from 0.21 to 1.00 $g\ cm^{-3}$), which can be maintained even upon evacuation of the guest molecules from the pores. The regular monodisperse nature of the crystalline array of micropores is a key feature that distinguishes MOFs from other porous materials (e.g. polymers, mesoporous silicas, activated carbon). In addition, the ability to systematically modulate the pore dimensions and surface chemistry within MOFs is a feature that was previously largely absent in zeolite materials.

The CO_2 capture problem: Gas streams from power station chimneys consist primarily of N_2, H_2O and CO_2 in a 13 : 2 : 2 ratio by mass. Using conventional technologies, the separation of CO_2 from this high volume of effluent gas, which is at approximately atmospheric pressure, would require approximately 25–35% of the energy generated by a power station. It is therefore obvious why so few large-scale power stations worldwide (and none in Australia or New Zealand) perform postcombustion carbon capture. Clearly, there is an urgent need for cheaper alter-natives to the conventional ‘wet scrubbing’ methods that are based on the absorption of CO_2 by aqueous amine solutions.

MOFs offer a potential solution to this gas separation problem as their pore volumes and surface functionalities can be tuned to preferentially separate one gas from another (figure 6.9). There are other applications where CO_2 capture using MOFs can also be envisaged; for example, the ‘sweetening’ of natural gas requires the separation of mixtures of N_2, CO_2 and

CH_4 from gas fields.

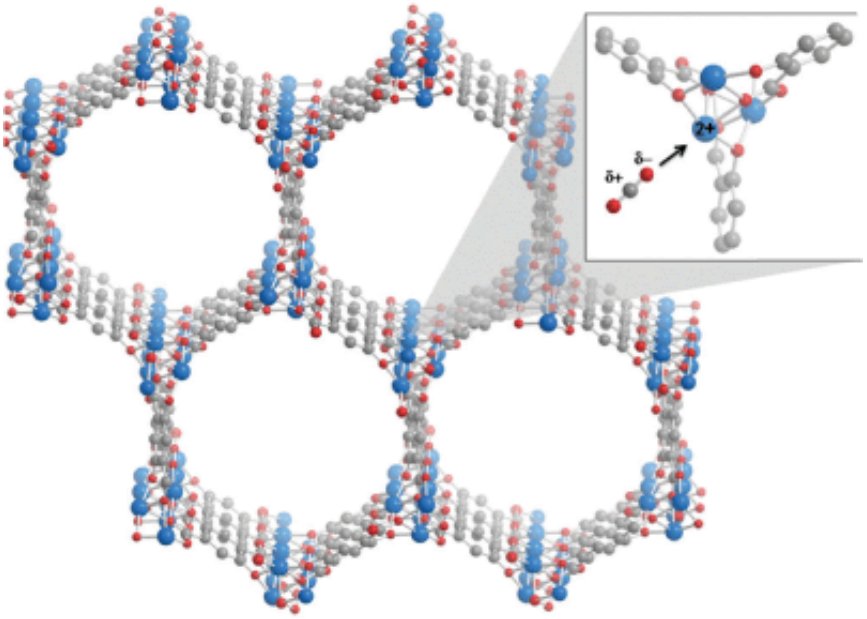


FIGURE 6.9 Representation of part of the crystal structure of a magnesium-based MOF along the one-dimensional channels. The inset shows the charge-induced interaction between one of the open Mg^{2+} coordination sites and a CO_2 molecule.

The H_2 storage problem: Hydrogen is an ideal energy carrier for transportation because it is lightweight, can be produced using renewable resources such as sunlight, and the only byproduct is water. Commercial application is problematic, though, as hydrogen is hard to store without taking up a very large amount of space. One solution to this storage issue is to use MOFs which, by virtue of their extraordinarily high surface areas, could one day store enough hydrogen at normal operating temperatures and pressures in fuel cells to drive more than 1000 kilometres.

Speed and Energy

The energy of a molecule is related to its speed. As we learned on p. 218, any moving object has kinetic energy (E_{kinetic}) with a magnitude given by:

$$E_{\text{kinetic}} = \frac{1}{2}mu^2$$

where m is the object's mass and u is its speed. The most probable speed of hydrogen molecules at 300 K is 1.57×10^3 m s^{-1}(see p. 219). We need the mass of one H_2 molecule to be able to calculate its most probable kinetic energy. The SI unit of energy is the joule (J), which equals 1 kg m^2 s^{-2}. Thus, we need the mass (m) in kilograms. The molar mass gives the mass of 1 mole of molecules, so dividing molar mass by the Avogadro constant (N_A) gives the mass of 1 molecule.

$$m = \frac{M}{N_A} = \frac{2.016\ \text{g mol}^{-1}}{6.022 \times 10^{23}\ \text{mol}^{-1}}$$

$$m = 3.348 \times 10^{-24}\ \text{g}$$

$$= 3.348 \times 10^{-27}\ \text{kg}$$

Now apply:

$$E_{\text{kinetic}} = \frac{1}{2}mu^2$$

$$E_{\text{kinetic (most probable)}} = \frac{1}{2}(3.348 \times 10^{-27}\ \text{kg})(1.57 \times 10^{3}\ \text{m s}^{-1})^2$$

$$= 4.13 \times 10^{-21}\ \text{kg m}^2\ \text{s}^{-2}$$

$$E_{\text{kinetic (most probable)}} = 4.13 \times 10^{-21}\ \text{J}$$

The most probable speeds of methane and carbon dioxide are slower than the most probable speed of hydrogen (see figure 6.7), but CH_4 and CO_2 molecules have larger masses than H_2. When kinetic energy calculations are repeated for these gases, they show that the most probable kinetic energy is the same for all three gases.

For a CH_4 molecule ($m = 2.664 \times 10^{-26}$ kg):

$$E_{\text{kinetic}} = \frac{1}{2} \times 2.664 \times 10^{-26}\ \text{kg} \times (5.57 \times 10^{2}\ \text{m s}^{-1})^2 = 4.13 \times 10^{-21}\ \text{J}$$

For a CO_2 molecule ($m = 7.308 \times 10^{-26}$ kg);

$$E_{\text{kinetic}} = \frac{1}{2} \times 7.308 \times 10^{-26}\ \text{kg} \times (3.36 \times 10^{2}\ \text{m s}^{-1})^2 = 4.13 \times 10^{21}\ \text{J}$$

Even though the speed distributions for these three gases peak at different values, the most probable kinetic energies are identical. We can also show that, *at a given temperature, all gases have the same molecular kinetic energy distribution*.

Molecular beam experiments show that molecules move faster as the temperature increases. Molecules escaping from the oven at 900 K take less time to reach the detector than molecules escaping at 300 K. As the molecular speed increases, so does the kinetic energy. Figure 6.10 shows the molecular kinetic energy distributions at 300 K and 900 K. By comparing this figure with figure 6.7, we see that the molecular energies show a wide distribution that is similar to the distribution in molecular speeds. Unlike speeds, however, the molecular energy distributions are the same for all gases at any particular temperature. The distributions shown in figure 6.10 apply to any gas.

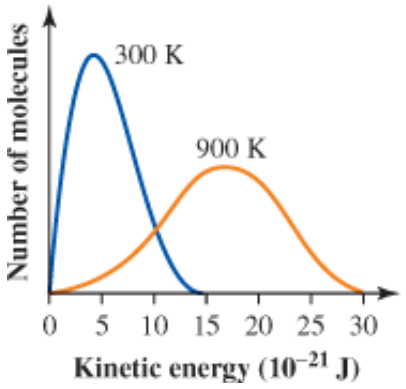


FIGURE 6.10 Graph of distribution of molecular energies for any gas at 300 K and 900 K.

Average Kinetic Energy and Temperature

The most probable kinetic energy is not the same as the average kinetic energy. To find the average kinetic energy per molecule ($\bar{E}_{\text{kinetic}}$, the bar over a variable indicates that it is an average value), we must add all the individual molecular energies and divide by the total number of molecules. The result describes how the average kinetic energy of gas molecules is related to the temperature of the gas.

$$\bar{E}_{\text{kinetic}} = \frac{3RT}{2\,N_{\text{A}}}$$

In this equation, T is the temperature in kelvin, N_{A} is the Avogadro constant and R is the gas constant (8.314 J mol^{-1} K^{-1}).

The average kinetic energy expressed by the equation is kinetic energy per molecule. We find the total kinetic energy of 1 mole ($E_{\text{kinetic, molar}}$) of gas molecules by multiplying by the Avogadro constant.

$$E_{\text{kinetic,molar}} = N_{\text{A}}\frac{3RT}{2N_A} = \frac{3}{2}RT$$

Thus, 1 mole of a gas has a total molecular kinetic energy of $\frac{3}{2}RT$ independent of the nature of that gas. While the equation is usually stated in this way, it is worthwhile to note that it is the temperature that is a measure of average kinetic energy.

WORKED EXAMPLE 6.4

Molecular Kinetic Energies

Determine the average molecular kinetic energy and molar kinetic energy of gaseous sulfur hexafluoride, SF_6, at 150 °C.

Analysis

The problem asks for a calculation of kinetic energies and provides a temperature. We have two equations for the kinetic energy of a gas.

$$\bar{E}_{\text{kinetic}} = \frac{3RT}{2N_{\text{A}}} \quad \text{and} \quad E_{\text{kinetic,molar}} = \frac{3}{2}RT$$

To carry out the calculations, we need to know the constants R (8.314 J mol^{-1} K^{-1}) and N_{A} (6.022×10^{23} mol^{-1}) as well as T in kelvin.

Solution

Convert the temperature from °C to K by adding 273.15.

$$T = 150\ ^{\circ}\text{C} + 273.15 = 423\ \text{K}$$

Now substitute this into the kinetic energy equation and calculate.

For a single molecule:

$$\bar{E}_{\text{kinetic}} = \frac{3(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(423\text{K})}{2(6.022 \times 10^{23}\ \text{mol}^{-1})} = 8.76 \times 10^{-21}\text{J}$$

For 1 mole of molecules:

$$E_{\text{kinetic,molar}} = \frac{3}{2}(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(423\ \text{K}) = 5.28 \times 10^{3}\text{J mol}^{-1}$$

Is our answer reasonable?

We have shown that the average kinetic energy is independent of the nature of the gas. Figure 6.10 shows the molecular energy distributions for a temperature of 300 K and 900 K. The temperature of 423 K is in between these and the molecular energy that we calculated is also between the values at 300 K and 900 K. This answer, therefore, seems reasonable.

PRACTICE EXERCISE 6.4

The atmospheric temperature at the altitudes where commercial jets fly is around -35 °C. Calculate the average molecular and molar kinetic energies of N_2 at this temperature.

Rates of Gas Movement

The average speed of the molecules in a gas determines its temperature. To state this dependence quantitatively, we start with:

$$\bar{E}_{\text{kinetic}} = \frac{1}{2}m\bar{u}^2$$

and:

$$\bar{E}_{\text{kinetic}} = \frac{3RT}{2N_A}$$

We set the two expressions for kinetic energy equal to each other.

$$\frac{1}{2}m\bar{u}^2 = \frac{3\,RT}{2N_A}$$

Now solve this equality for u, noting that the product mN_A N is equal to the molar mass of the gas in kg mol^{-1}.

$$\bar{u}^2 = \frac{3RT}{mN_A} = \frac{3\,RT}{M} \quad \text{so} \quad \bar{u}_{\text{RMS}} = \left(\frac{3RT}{M}\right)$$

This speed is called the **root-mean-square speed** because it is found by taking the square root of $\bar{u}^2$. The average speed of gas molecules is directly proportional to the square root of the temperature and is inversely proportional to the square root of the molar mass of the gas in kg mol^{-1}. This equation can be applied directly to the movement of molecules escaping from a container into a vacuum. This process is one example of **effusion** (more generally, effusion is the flow of molecules through an opening without collisions between molecules). Effusion is exemplified by the escape of molecules from the oven shown in figure 6.6a.

A second type of gas movement is **diffusion**, the movement of one type of molecule through molecules of the same or another type. Diffusion is exemplified by air escaping from a punctured tyre. The escaping molecules must diffuse among the molecules already present in the atmosphere. Diffusing molecules undergo frequent collisions, so their paths are similar to that shown in figure 6.1. Nevertheless, their average rate of movement depends on temperature and molar mass. Figure 6.11 shows a molecular-level comparison of effusion and diffusion.

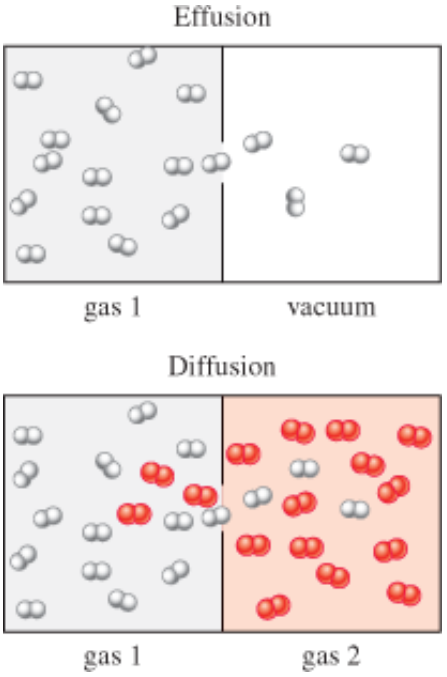


FIGURE 6.11 Effusion is the movement of a gas into a vacuum. Diffusion is the mixing of two or more gases.

An example of diffusion is shown in figure 6.12, in which concentrated aqueous solutions of hydrochloric acid, HCl, and ammonia, NH_3, are placed at opposite ends of a glass tube. Molecules of HCl gas and NH_3 gas escape from the solutions and diffuse through the air in the tube. When the two gases meet, they undergo a reaction that produces ammonium chloride, a white solid salt.

$$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$$

The lighter NH_3 molecules diffuse more rapidly than the heavier HCl molecules, so the white band of salt forms closer to the HCl end of the tube, as can be seen in figure 6.12.

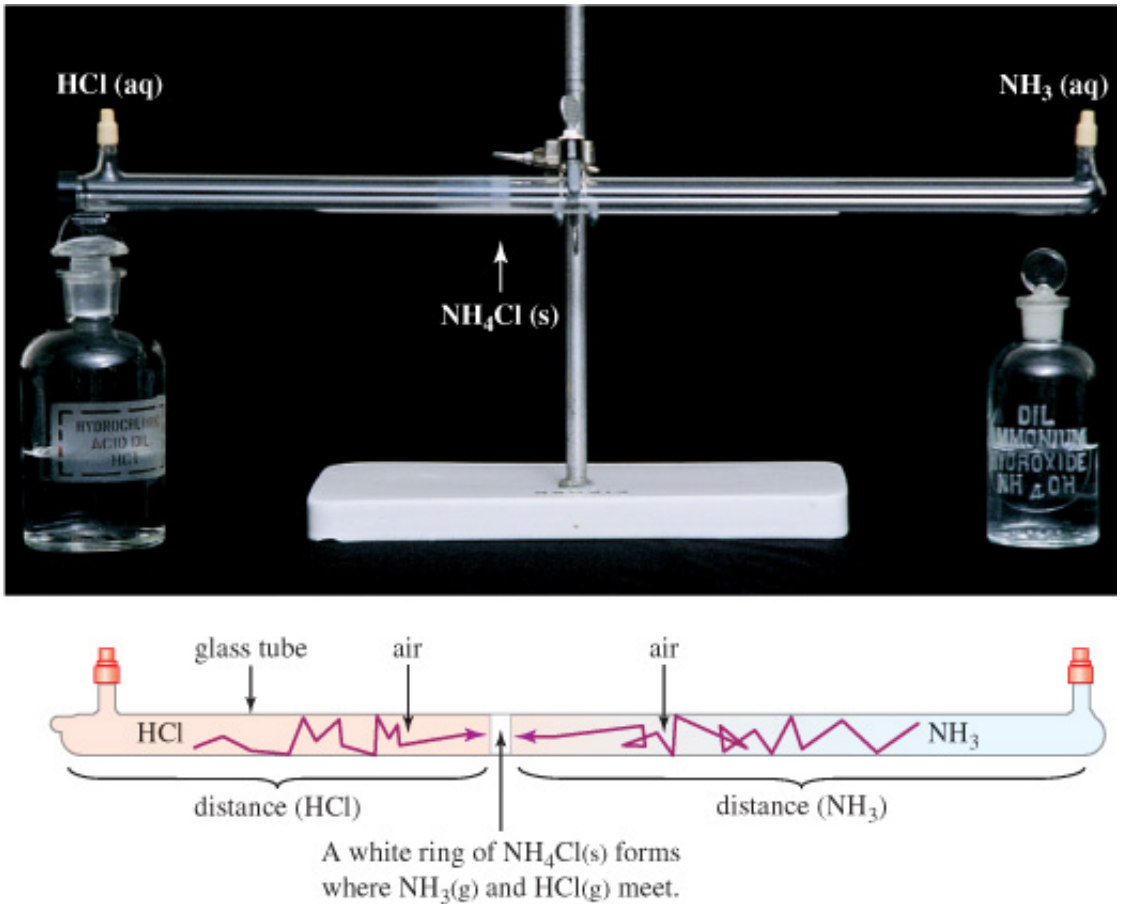


FIGURE 6.12 NH_3 diffuses through a glass tube faster than HCl. When the two gases meet, they form solid ammonium chloride, $NH_4Cl(s)$, which appears as a white band closer to the end of the tube that contains HCl.

From the discussion of root-mean-square speed on the previous page, it follows that the ratio of distances that HCl and NH_3 travel, respectively, is inversely related to the square root of the molar masses:

$$\frac{d_{NH_3}}{d_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$$

Rates of molecular motion are directly proportional to molecular speeds, so, for any gas, rates of effusion and diffusion increase with the square root of the temperature in kelvin. Also, at any particular temperature, ratios of effusion and diffusion are faster for molecules with small molar masses.

Ideal Gases

As we have seen in this chapter, gases can consist of either atoms or molecules. In what follows, we will use the term ‘molecules’ exclusively for brevity's sake, but you must remember that everything said about molecules in this section applies equally to atoms.

The behaviour of gases suggests that gas molecules have little effect on one another. Gases are easy to compress, showing that there is lots of empty space between molecules. Gases also escape easily through any opening, indicating that their molecules are not strongly attracted to one another. An ideal gas is defined as a gas for which both the volume of molecules and the forces between the molecules are so small that they have no effect on the behaviour of the gas. We can assume that this is the case when molecular sizes are negligible compared with the volume of the container, and the energies

generated by forces between molecules are negligible compared with molecular kinetic energies.

As we describe later in this chapter, small molecules usually have small attractive forces with respect to their kinetic energies, or with respect to *RT*, often called the *thermal energy*. Table 6.1 lists the substances that exist as gases under ambient conditions (note that a binary gas is one that contains molecules formed from two elements). These gases are mostly small molecules with molar masses less than 50 g mol^{-1}. There are some notable exceptions to this, however. Tungsten hexafluoride, WF_6 (M = 297.8 g mol^{-1}), and the element radon, Rn (M = 222 g mol^{-1}), are examples of gases having molar masses greater than 200 g mol^{-1}. Uranium hexafluoride, UF_6 (M = 334 g mol^{-1}), a solid compound used in the separation of the fissionable uranium isotope ^{235}U from the more abundant ^{238}U isotope (see chapter 27), sublimes (changes directly from a solid to a gas) at 56.5 °C to give $UF_6(g)$ at atmospheric pressure.

TABLE 6.1 Molar masses of some gaseous substances (at 298 K and 1.013 × 10^5 Pa)

Elemental gases			Binary gases		
Substance	**Formula**	***M*** **(g** mol^{-1}**)**	**Substance**	**Formula**	***M*****(g** mol^{-1}**)**
hydrogen	H_2	2.016	methane	CH4	16.04
helium	He	4.003	ammonia	NH_3	17.03
neon	Ne	20.18	carbon monoxide	CO	28.01
nitrogen	N_2	28.02	nitrogen oxide	NO	30.01
oxygen	O_2	32.00	ethane	C_2H_6	30.07
fluorine	F_2	38.00	hydrogen sulfide	H_2S	34.09
argon	Ar	39.95	hydrogen chloride	HCl	36.46
ozone	O3	48.00	carbon dioxide	CO_2	44.01
chlorine	Cl_2	70.90	nitrogen dioxide	NO_2	46.01

How does an ideal gas behave? We can answer this question by considering, for example, how changes in *V*, *T* or *n* affect the pressure, *p*. Each time a molecule strikes a wall, it exerts a force on the wall. During each second, many collisions exert many such forces. Pressure is the sum of all these forces per unit area and unit time. In an ideal gas, each molecule is independent of all others. This independence means that the total pressure is the sum of the pressure created by each individual molecule.

To see how pressure depends on *V*, *T* or *n*, we consider the effect of changing one property while holding the other properties constant. We analyse what happens to the molecular collisions as each property changes.

First, consider increasing the amount of gas while keeping the temperature and volume fixed. Doubling the amount of gas in a fixed volume (figure 6.13) doubles the number of collisions with the walls. Thus, as pressure is essentially a measure of the number of collisions of the molecules with the walls of the container, pressure is directly proportional to the amount of gas. This agrees with the ideal gas equation.

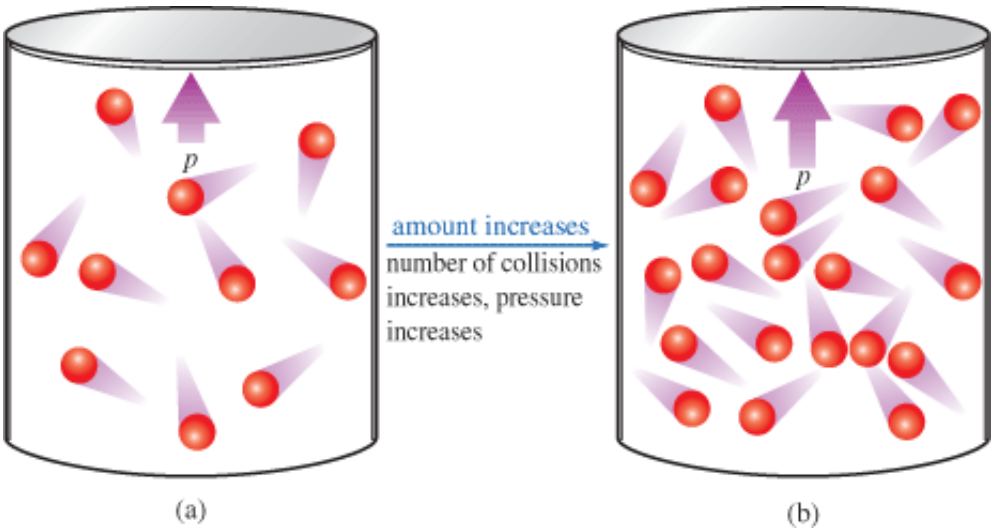


FIGURE 6.13 Schematic view of the effect of doubling the number of gas molecules in a fixed volume. The container in (b) has twice as many molecules as it does in

(a) Consequently, the molecular density is twice as large in

(b) with twice as many collisions per second with the walls.

Next, consider keeping the temperature and amount fixed and changing the volume of the gas. Figure 6.14 shows that compressing a gas into a smaller volume has the same effect as adding more molecules. The result is more collisions with the walls. If the molecules act independently, cutting the volume in half will double the pressure. In other words, pressure is inversely proportional to volume, again in agreement with the ideal gas equation.

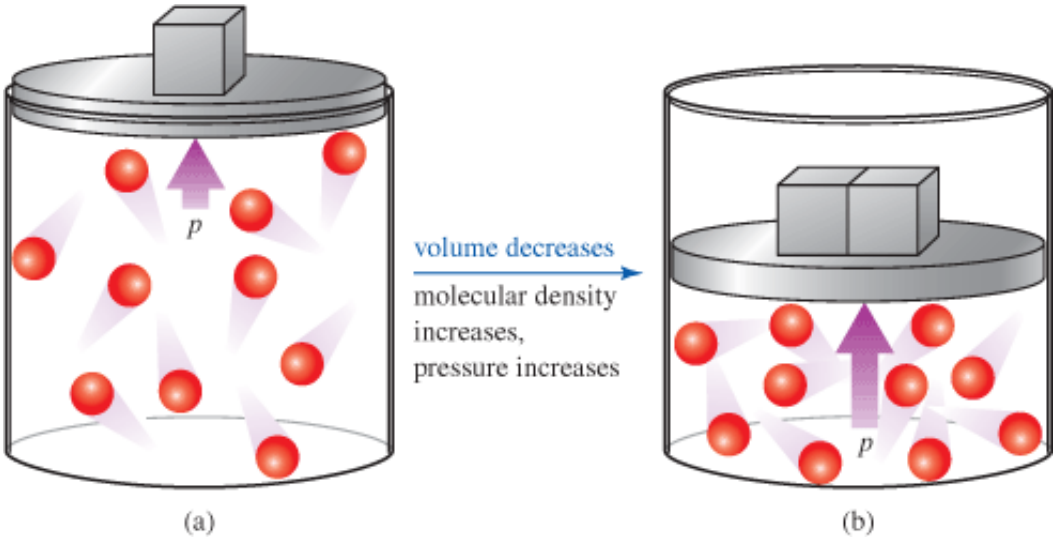


FIGURE 6.14 Schematic view of the effect of compressing a fixed quantity of gas into a smaller volume at constant *T*. Decreasing the volume increases the molecular density, which increases the number of collisions per second with the walls.

To complete our analysis, we must determine the effect of a change in temperature, keeping volume and amount fixed. Recall that kinetic energy is proportional to the square of the molecular speed (a microscopic variable), and temperature (a macroscopic variable) is a measure of average molecular kinetic energy. Thus, the square of the molecular speed is proportional to temperature. We can summarise these relationships by:

$$T \propto E_{\text{kinetic}} \quad \text{and} \quad E_{\text{kinetic}} = \frac{1}{2}mu^2 \quad \text{so} \quad T \propto u^2$$

Molecular speed affects pressure in two ways, which are illustrated in figure 6.15. First, faster moving

molecules hit the walls more often than slower moving molecules. The number of collisions each molecule makes with the wall is proportional to the molecule's speed. Second, the force exerted when a molecule strikes the wall also depends on the molecule's speed. A fast-moving molecule exerts a larger force than the same molecule moving more slowly. Force per collision and number of collisions increase with speed, so the total effect of a single molecule on the pressure of a gas is proportional to the square of its speed.

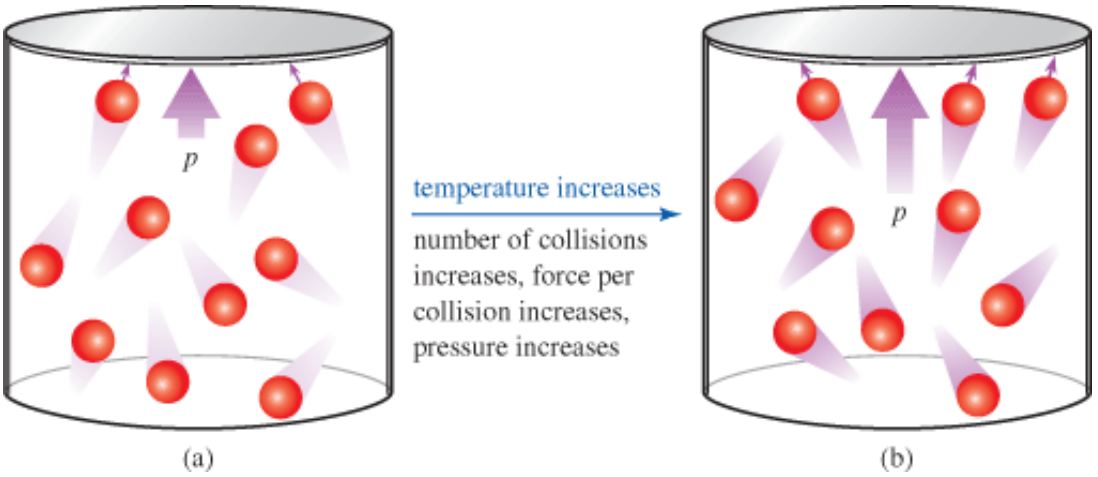


FIGURE 6.15 Schematic view of the effect of increasing molecular speeds (as measured by an increase in temperature), resulting in more wall collisions and more force per collision, and therefore an increase in pressure.

Pressure is proportional to molecular speed squared, which in turn is proportional to temperature. For an ideal gas, then, the pressure is directly proportional to temperature, and a plot of p versus T yields a straight line. Again, this agrees with the ideal gas equation.

A gas will obey the ideal gas equation if its molecular sizes are negligible compared with the volume of the container, and the energies generated by forces between molecules are negligible compared with molecular kinetic energies. The behaviour of any real gas departs somewhat from ideality because real molecules occupy volume and exert forces on one another. Nevertheless, departures from ideality are small enough to neglect under many circumstances, and real gases approximate ideal behaviour under conditions of low pressure and high temperature. We consider departures from ideal gas behaviour later in this chapter.

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6.4 Gas Mixtures

The atmosphere, which contains nitrogen, oxygen and various trace gases, is an obvious example of a gas mixture. Another example is the gas used by deep-sea divers, which contains a mixture of helium and oxygen (figure 6.16). The ideal gas model provides guidance as to how to describe mixtures of gases.



FIGURE 6.16 Deep-sea divers use mixtures of helium and molecular oxygen in their breathing tanks.

All constituents of an ideal gas, whether atoms or molecules, act independently. This notion applies to gas mixtures as well as to pure gases. Gas behaviour depends on the *number* of gas atoms or molecules but not on their *identity*. The ideal gas equation applies to each gas in the mixture, as well as to the entire collection of atoms or molecules.

Suppose we introduce 0.1 mol of helium into an evacuated 20 L flask. If we add another 0.1 mol of He, the container now contains 0.2 mol of gas. The pressure can be calculated using the ideal gas equation, with n = 0.1 mol + 0.1 mol = 0.2 mol. Suppose that we add 0.1 mol of molecular oxygen. Now the container holds a total of 0.3 mol of gas. According to the ideal gas model, it does not matter whether we add the same gas or a different gas because all atoms or molecules in a sample of an ideal gas behave independently. The pressure increases in proportion to the increase in the total amount of gas. Thus, we can calculate the total pressure from the ideal gas equation, using n = 0.2 mol + 0.1 mol = 0.3 mol.

How does a 1 : 2 mixture of O_2 and He appear on the molecular level? As O_2 is added to the container, its molecules move throughout the volume and become distributed uniformly. Dif-fusion causes gas mixtures to become homogeneous. Figure 6.17 illustrates this.

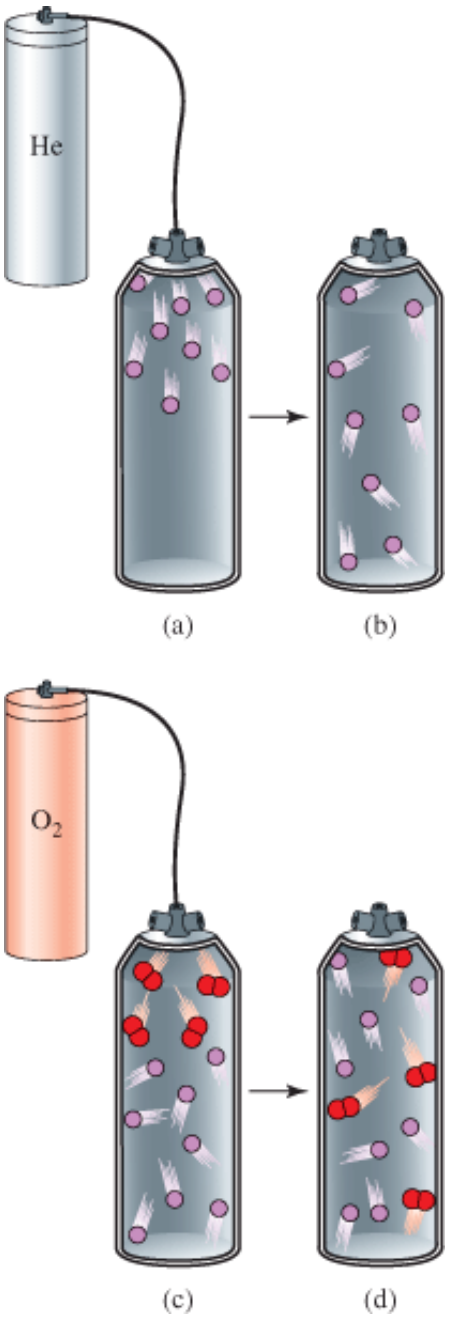


FIGURE 6.17

(a) 0.2 mol of He are added to a container.

(b) The atoms quickly become distributed uniformly throughout the container.

(c) 0.1 mol of O_2 are added to this container.

(d) The molecules move about independently of the He atoms, causing the gases to mix uniformly.

Dalton's Law of Partial Pressures

The pressure exerted by an ideal gas mixture is determined by the total amount (n_{total}) of gas.

$$p = \frac{n_{total}RT}{V}$$

We can express the total amount of gas as the sum of the amounts of the individual gases. For the He and O_2 mixture:

$$n_{total} = n_{He} + n_{O_2}$$

Substitution gives a two-term equation for the total pressure.

$$p = \frac{(n_{He} + n_{O_2})RT}{V} = \frac{n_{He}RT}{V} + \frac{n_{O_2}RT}{V}$$

Notice that each term on the right resembles the ideal gas equation rearranged to express pressure. Each term therefore represents the **partial pressure** of one of the gases. As figure 6.18 illustrates, partial pressure is the pressure that would be present in a gas container if one gas were present by itself.

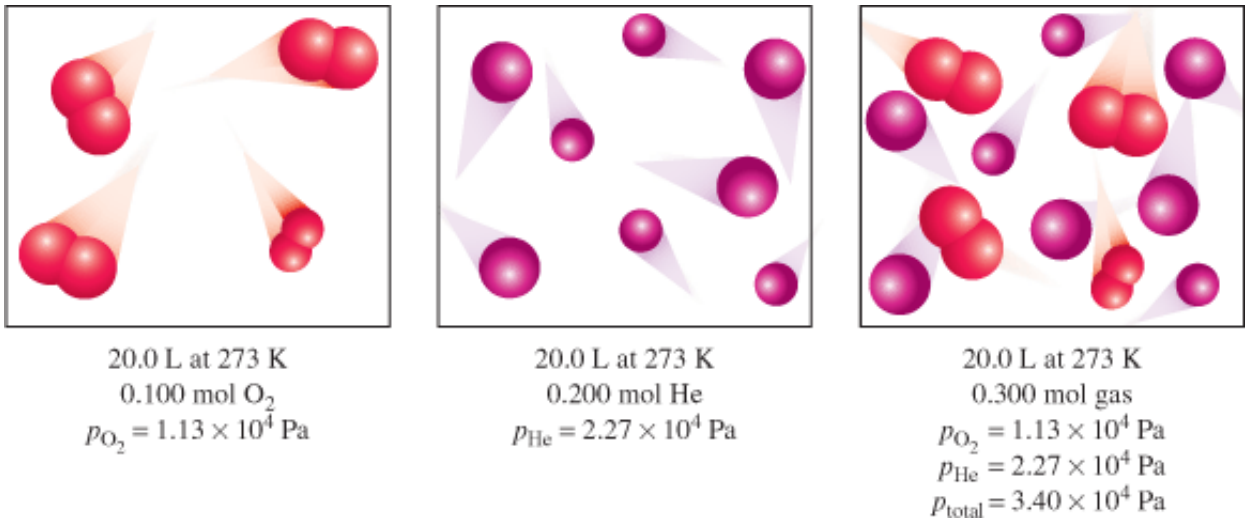


FIGURE 6.18 Schematic representation of a sample of O_2, a sample of He and a mixture of the two gases. Both components are distributed uniformly throughout the gas volume. Each gas exerts the same pressure, whether it is pure or part of a mixture.

$$p_{He} = \frac{n_{He}RT}{V} \quad \text{and} \quad p_{O_2} = \frac{n_{O_2}RT}{V}$$

The total pressure in the container is the sum of the partial pressures.

$$p_{total} = p_{He} + p_{O_2}$$

We have used He and O_2 to illustrate the behaviour of a mixture of ideal gases, but this relation-ship can be extended from a mixture of two ideal gases to mixtures with three or more substances behaving as ideal gases. *In a mixture of gases in which no chemical reaction occurs, each gas contributes to the total pressure the amount that it would exert if the gas were present in the container by itself.* This is **Dalton's law of partial pressures**. To obtain a total pressure, simply add the contributions from all gases present.

$$p_{total} = p_1 + p_2 + p_3 + \ldots + p_i$$

When doing calculations on a mixture of gases, we can apply the ideal gas equation to each component to find its partial pressure (p_i). Alternatively, we can treat the entire gas as a unit, using the total amount to determine the total pressure of the mixture (p).

Describing Gas Mixtures

There are several ways to describe the chemical composition of a mixture of gases. The simplest method is to list each component with its partial pressure or amount. Two other descriptions, mole fractions and parts per million, are also used frequently.

Chemists often express chemical composition in fractional terms, stating the amount of a substance as a fraction of the amount of all substances in the mixture. This way of stating composition is the **mole fraction (x)**.

$$\text{mole fraction of A} = x_A = \frac{n_A}{n_{total}}$$

Mole fractions provide a simple way to relate the partial pressure of one component to the total pressure of the gas mixture.

$$p_A = \frac{n_A RT}{V} \quad \text{and} \quad p_{total} = \frac{n_{total} RT}{V}$$

Dividing p_A by p_{total} gives:

$$\frac{p_A}{p_{total}} = \frac{\left(\frac{n_A RT}{V}\right)}{\left(\frac{n_{total} RT}{V}\right)} = \frac{n_A}{n_{total}} = x_A$$

or:

$$p_A = x_A p_{total}$$

The partial pressure of a component in a gas mixture is its mole fraction multiplied by the total pressure.

WORKED EXAMPLE 6.5

Gas Mixtures

Exactly 8.00 g of O_2 and 2.00 g of He was placed in a 5.00 L tank at 298 K. Determine the total pressure of the mixture, and find the partial pressures and mole fractions of the two gases.

Analysis

We have a mixture of two gases in a container with known volume and temperature. The problem asks for pressures and mole fractions. Assuming that molecular interactions are negligible, each gas can be described independently by the ideal gas equation. As usual, we need molar amounts for the calculations.

Solution

Begin with the data provided.

$$V = 5.00\ \text{L} = 5.00 \times 10^{-3}\ \text{m}^3 \quad T = 298\ \text{K} \quad m_{He} = 2.00\ \text{g} \quad m_{O_2} = 8.00\ \text{g}$$

Convert the mass of each gas into an amount in moles.

$$n = \frac{m}{M} \qquad n_{He} = 0.500\ \text{mol} \qquad n_{O_2} = 0.250\ \text{mol}$$

Next, use the ideal gas equation to calculate the partial pressure of each gas.

$$p_{He} = \frac{(0.500\ \text{mol})(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}{5.00 \times 10^{-3}\ \text{m}^3} = 2.48 \times 10^5\ \text{Pa}$$

The same calculation for O_2 gives $p_{O_2} = 1.24 \times 10^5$ Pa.

The total pressure is the sum of the partial pressures.

$$p_{total} = p_{He} + p_{O_2} = (2.48 \times 10^5\ Pa) + (1.24 \times 10^5\ Pa) = 3.72 \times 10^5\ Pa$$

Mole fractions can be calculated from amounts or partial pressures.

$$x_{He} = \frac{n_{He}}{n_{total}} = \frac{0.500\ mol}{0.750\ mol} = 0.667 \quad \text{and} \quad x_{O_2} = \frac{p_{O_2}}{p_{total}} = \frac{1.24 \times 10^5\ Pa}{3.72 \times 10^5\ Pa} = 0.333$$

Is our answer reasonable?

The mole fractions calculated from the partial pressures must sum to 1.00. They do in this case, suggesting that our answer is reasonable.

PRACTICE EXERCISE 6.5

A 5.00 L tank is charged with 7.50 g of O_2 and 2.50 g of He. Calculate the mole fractions and the partial pressures of the gases at 25 °C.

When referring to lower concentrations in a gas mixture, scientists typically use **parts per million (ppm)** or **parts per billion (ppb)**. Mole fractions, parts per million and parts per billion can all describe ratios of amount of a particular substance to total amount of a sample. Mole fraction is moles per amounts, ppm is moles per million moles and ppb is moles per billion moles. A concentration of 1 ppm is a mole fraction of 10^{-6}, and 1 ppb is a mole fraction of 10^{-9}.

WORKED EXAMPLE 6.6

Working With Parts Per Million (ppm)

The exhaust gas from an average car contains 206 ppm of the pollutant nitrogen oxide, NO. If a car emits 0.125 m^3 of exhaust gas at 1.00×10^5 Pa and exactly 350 K, what mass of NO has been added to the atmosphere?

Analysis

The question asks for the mass of NO. Information about concentration in ppm tells us the amount of NO present in 1 mole of exhaust gas. We can use the ideal gas equation to determine the total amount of gas emitted, then use the concentration information to find the amount of NO, and use the molar mass of NO to obtain the required mass.

Solution

$$[NO] = 206\ ppm \quad V = 0.125\ m^3 \quad p = 1.00 \times 10^5\ Pa \quad T = 350\ K$$

$$
\begin{aligned}
n_{\text{gas}} &= \frac{pV}{RT} = \frac{(1.00 \times 10^5\ \text{Pa})(0.125\ \text{m}^3)}{(8.314\ \text{J mol}^{-1}\text{K}^{-1})(350\ \text{K})} = 4.30\ \text{mol} \\
x_{\text{NO}} &= 206\ \text{ppm} = 206 \times 10^{-6} = 2.06 \times 10^{-4} \\
n_{\text{NO}} &= (x_{\text{No}})(n_{\text{gas}}) = (2.06 \times 10^{-4})(4.30\ \text{mol}) = 8.86 \times 10^{-4}\ \text{mol} \\
m &= nM = (8.86 \times 10^{-4}\ \text{mol})(30.0\ \text{mol}^{-1}) = 2.66 \times 10^{-2}\ \text{g}
\end{aligned}
$$

Is our answer reasonable?

The mass of NO is rather small, only 27 mg, but the mole fraction is also small, so this is a reasonable result.

PRACTICE EXERCISE 6.6

If the maximum NO emission allowed in worked example 6.6 is 762 ppm, what mass of NO is allowed per litre of exhaust emitted at a temperature of exactly 50 °C?

The description presented in this section applies to a gas mixture that is not undergoing chemical reactions. As long as reactions do not occur, the amount of each gas is determined by the amount of that substance initially present. When reactions occur, the amounts of reactants and products change as predicted by the principles of stoichiometry. Changes in composition must be taken into account before the properties of the gas mixture can be calculated. Gas stoichiometry is described in section 6.6.

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6.5 Applications of the Ideal Gas Equation

The ideal gas equation and the molecular view of gases lead to several useful applications. We have already described how to carry out calculations involving *p*–*V*–*n*–*T* relationships. In this section, we examine the use of the gas equation to determine molar masses and gas density.

Determination of Molar Mass

The ideal gas equation can be combined with the equation $n = \frac{m}{M}$ (from chapter 3) to find the molar mass of an unknown gas.

$$pV = nRT \quad \text{and} \quad n = \frac{m}{M}$$

If we know the pressure, volume and temperature of a gas sample, we can use this information to calculate the amount in moles of the unknown gas in the sample.

$$n = \frac{pV}{RT}$$

If we also know the mass of the gas sample, we can use that information to determine the molar mass of the gas.

$$M = \frac{m}{n}$$

WORKED EXAMPLE 6.7

Molar Mass Determination

Pure calcium carbide, CaC_2, is a hard, colourless solid that was used in caving lamps. It has a melting point of 2160 °C, and it reacts vigorously with water to produce a gas and a solution containing OH^- ions.

A 12.8 g sample of CaC_2 was treated with excess water and the resulting gas was collected in an evacuated 5.00 L glass bulb with a mass of 1254.49 g. The filled bulb had a mass of 1259.70 g and the pressure of the gas inside was 1.00×10^5 Pa when the temperature was 26.8 °C. Calculate the molar mass of the gas and determine its formula. (Assume that the product gas is insoluble in water and that the vapour pressure of water is negligible in relation to the pressure of the product gas.)

Analysis

We can use the ideal gas equation to calculate the molar mass. Then we can use the molar mass to identify the correct molecular formula from a group of possible candidates, as the products may contain only the same elements as the reactants. The problem involves a chemical reaction, so we must make a connection between the gas measurements and the chemistry that takes place. Because the reactants and one product are known, we can write a partial equation that describes the chemical reaction.

$$CaC_2(s) + H_2O(l) \rightarrow OH^-(aq) + \ ?\ (?)$$

In any chemical reaction, atoms must be conserved, so the gas molecules can contain only H, O, C and/or Ca atoms. To determine the chemical formula of the gas, we must find the combination of these elements that gives the observed molar mass.

Solution

Use the data to determine the molar mass. The problem gives the following data about the unknown gas.

$$V_{\text{bulb}} = V_{\text{gas}} = 5.00\ \text{L} = 5.00 \times 10^{-3}\ \text{m}^3 \qquad T = 26.8\ ^{\circ}\text{C} = 300.0\ \text{K} \qquad p = 1.00 \times 10^5\ \text{pa}$$

$$m_{\text{bulb+gas}} = 1259.70\ \text{g} \qquad m_{\text{bulb}} = 1254.49\ \text{g} \qquad m_{\text{gas}} = m_{\text{bulb+ gas}} - m_{\text{bulb}} = 5.21\ \text{g}$$

We use *V*, *T*, *p* and the ideal gas equation to find the amount of gas in moles. Then, with the mass of the gas sample, we can determine the molar mass.

$$n_{\text{gas}} = \frac{pV}{RT} = \frac{m_{\text{gas}}}{M}$$

We could rearrange this expression and solve the equality for *M* directly, but, in problems like this, it is often better to carry out each step explicitly. Therefore, we will first determine *n* and then solve for *M*.

$$n_{\text{gas}} = \frac{pV}{RT} = \frac{(1.00 \times 10^5\ \text{Pa})(5.00 \times 10^{-3}\ \text{m}^3)}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(3000.0\ \text{K})} = 2.00 \times 10^{-1}\ \text{mol}$$

$$M = \frac{m_{\text{gas}}}{n_{\text{gas}}} = \frac{5.21\ \text{g}}{2.00 \times 10^{-1}\ \text{mol}} = 26.0\ \text{g mol}^{-1}$$

To identify the gas, we examine the formulae and molar masses of known compounds that contain only H, O, C or Ca.

Formula	*M*	Comment
Ca	40	A gas with *M* = 26.0 g mol^{-1} cannot contain Ca.
CO	28	This is close but too high.
O_2	32	This is also too high.
H_2O	18	This is too low, and H_2O is a reactant not a product.
CH_4	16	This is too low.
C_2H_2	26	This substance has the observed molar mass.

Consideration of these possibilities leads to the molecular formula C_2H_2, ethyne (commonly known as acetylene).

Is our answer reasonable?

Knowing the formula of the gaseous product and that OH is another product, we can write a balanced equation for the generation of ethyne.

$$CaC_2(s) + 2H_2O(1) \rightarrow Ca^{2+}(aq) + 2OH^-(aq) + C_2H_2(g)$$

The balanced equation suggests that the result is reasonable. A systematic evaluation of all possible gases from the reagents that involve only one or two atoms other than hydrogen shows that there are no other possibilities for molar mass 26 g mol^{-1}.

PRACTICE EXERCISE 6.7

The glass bulb in worked example 6.7 is filled with an unknown gas until the pressure is 1.03 × 10^5 Pa at a temperature of 24.5 °C. The mass of the bulb plus contents is 1260.33 g.
Determine the molar mass of the unknown gas.

Determination of Gas Density

One characteristic of gases is that the density of a gas varies significantly with the conditions. To see this, we combine the ideal gas equation and $n = \frac{m}{M}$ and rearrange to obtain an equation for density $\left(\rho = \frac{m}{v}\right)$.

$$n = \frac{pV}{RT} \quad \text{and} \quad n = \frac{m}{M}$$

Set the two expressions for *n* equal to each other.

$$\frac{m}{M} = \frac{pV}{RT}$$

Now, multiply both sides of the equality by *M* and divide both sides by *V*.

$$p_{\text{gas}} = \frac{m}{V} = \frac{pM}{RT}$$

This equation reveals three features of gas density:

1. The density of an ideal gas increases linearly with increasing pressure at fixed temperature. The reason is that increasing the pressure compresses the gas into a smaller volume without changing its mass.
$$p_{\text{gas}} \propto p$$
2. The density of an ideal gas decreases linearly with increasing temperature at fixed pressure. The reason is that increasing the temperature causes the gas to expand without changing its mass.
$$p_{\text{gas}} \propto \frac{1}{T}$$
3. The density of ideal gases increases linearly with increasing molar mass at a given temperature and pressure. The reason is that equal amounts of different gases occupy equal volumes at a given temperature and pressure.
$$p_{\text{gas}} \propto M$$

There are practical applications of all these features:

- SCUBA divers use high-pressure cylinders, where the high density of the gas gives them more dive time per volume (figure 6.19).



FIGURE 6.19 The high density of air inside a SCUBA tank increases the time that a diver can remain under water.

- Balloons inflated with helium rise in the atmosphere because the molar mass of helium is substantially lower than the average molar mass of air (figure 6.20). Consequently, the density of a helium-filled balloon is less than the density of air, and the balloon rises, just as a cork released under water rises to the surface.



FIGURE 6.20 A helium-filled balloon floats because helium is less dense than air.

- When the air within a hot-air balloon is heated, its density decreases below that of the outside air. With sufficient heating, the balloon rises and floats (figure 6.21). In contrast, cold air is denser than warm air, so cold air sinks. For this reason, valleys often are colder than the surrounding hillsides.



FIGURE 6.21 A hot-air balloon rises because the air inside is heated to reduce its density, so that it is less dense than the outside air.

When a gas is released into the atmosphere, whether it rises or sinks depends on its molar mass. If the molar mass of the gas is greater than the average molar mass of air, the gas remains near the ground. Carbon dioxide fire extinguishers are effective for certain fires because of this feature. The molar mass of CO_2 (44.0 g mol^{-1}) is greater than that of N_2 (28.0 g mol^{-1}) or O_2 (32.0 g mol^{-1}), and so a CO_2 fire extinguisher lays down a blanket of this gas that excludes oxygen from the fire.

WORKED EXAMPLE 6.8

Gas Density

A certain hot-air balloon will rise when the density of its air is 15.0% lower than that of the surrounding atmospheric air. Calculate the density of air at 295 K and 1.00×10^5 Pa (assume that dry air is 78.0% N_2 and 22.0% O_2), and determine the minimum temperature of air inside the balloon that will cause the balloon to rise.

Analysis

The problem has two parts. First, we must calculate the density of atmospheric air. To do this, we need to determine the molar mass of dry air, which is the weighted average of the molar masses of its components. Then we must calculate the temperature needed to reduce the density by 15.0%. For both calculations, we use the ideal gas equation as rearranged to give gas density.

$$p_{\text{gas}} = \frac{pM}{RT}$$

Solution

Begin by calculating the molar mass of dry air. Multiply the fraction of each component by its molar mass.

$$M_{\text{air}} = \left(\frac{0.78}{1.00}\right)(28.02\ \text{g mol}^{-1}) + \left(\frac{0.22}{1.00}\right)(32.00\ \text{g mol}^{-1}) = 28.9\ \text{g mol}^{-1}$$

The other conditions are stated in the problem.

$$T = 295\ \text{K} \quad p = 1.00 \times 10^5\ \text{Pa}$$

Recall that, because the unit Pa is defined in terms of N m^{-2}, and that 1 N = 1 kg m s^{-2}, we must use a molar mass in kg mol^{-1} in this equation. Substituting these into the equation for gas density gives:

$$\rho_{\text{gas}} = \frac{pM}{RT} = \frac{(1.00 \times 10^5\ \text{Pa})(28.9 \times 10^{-3}\ \text{kg mol}^{-1})}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(295\ \text{K})} = 1.18\ \text{kg m}^{-3}$$

The balloon will rise when the density of its contents is 15% less than the density of the surrounding air.

$$\rho_{\text{gas}} = 1.18\ \text{kg m}^{-3} - \left(\frac{0.15}{1.00}\right)(1.18\ \text{kg m}^{-3}) = 1.00\ \text{kg m}^{-3}$$

Rearrange the density equation to solve for temperature, then substitute and calculate.

$$\rho_{\text{gas}} = \frac{pM}{RT} \quad \text{so} \quad T = \frac{pM}{R\rho}$$

$$T = \frac{\left(1.00 \times 10^5\text{Pa}\right)\left(28.9 \times 10^{-3}\text{kgmol}^{-1}\right)}{\left(8.314\,\text{Jmol}^{-1}K^{-1}\right)\left(1.00\,\text{kgm}^{-3}\right)} = 348\text{K}$$

Is our answer reasonable?

A temperature of 348 K or 75 °C is a reasonable result as it is higher than the temperature of the surrounding air. Notice that the molar mass and gas constant appear in both calculations, so we can also find the temperature requirement by simple proportions (comparing the air inside and outside the balloon).

$$T_{\text{inside}} = T_{\text{outside}}\left(\frac{\rho_{\text{outside}}}{\rho_{\text{inside}}}\right) = \frac{(295\ \text{K})(1.18\ \text{kg m}^{-3})}{1.00\ \text{kg m}^{-3}} = 348\ \text{K, which rounds to } 350\ \text{K}.$$

PRACTICE EXERCISE 6.8

Helium is used for lighter-than-air blimps, whereas argon is used to exclude air from flasks in which air-sensitive syntheses are performed. Calculate the densities of these two group 18 gases at 295 K and 1.00 × 10^5 Pa, and explain why the two gases have different uses.

Gas density has a significant effect on the interactions between molecules of a gas. As molecules move about, they collide regularly with one another and with the walls of their container. Figure 6.22 shows that the frequency of collisions depends on the density of the gas. At low density, a molecule may move a significant distance before it encounters another molecule. At high density, a molecule travels only a short distance before it collides with another molecule.

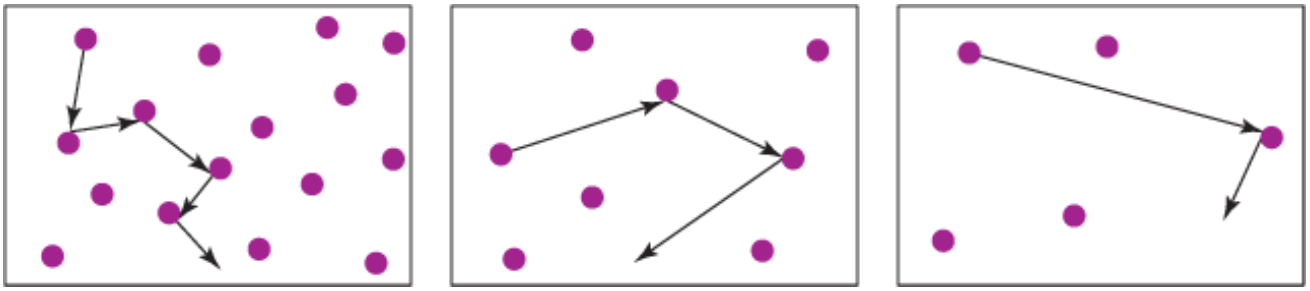


FIGURE 6.22 As the molecular density decreases, the average distance travelled between molecular collisions increases.

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6.6 Gas Stoichiometry

The principles of stoichiometry apply equally to solids, liquids and gases. No matter what phase substances are in, their chemical behaviour can be described in molecular terms, and their transformations must be visualised and balanced using molecules and moles.

The ideal gas equation relates the amount of gas to the physical properties of that gas. When a chemical reaction involves a gas, the ideal gas equation provides the link between *p*–*V*–*T* data and molar amounts.

$$n_i = \frac{p_i V}{RT}$$

Stoichiometric calculations always require amounts and, for gases, these are usually calculated from the ideal gas equation.

WORKED EXAMPLE 6.9

Gas Stoichiometry

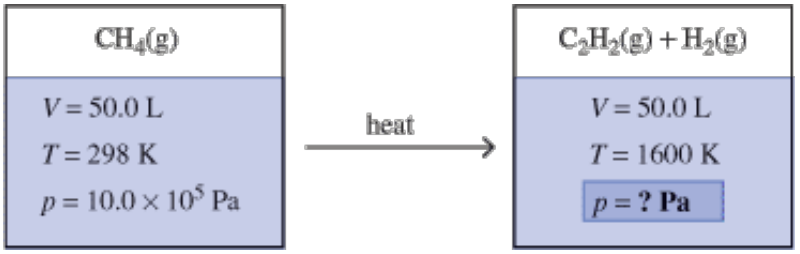
Worked example 6.7 described the formation of ethyne, C_2H_2, from calcium carbide, CaC_2. Modern industrial production of ethyne is based on a reaction of methane, CH_4, under carefully controlled conditions. At temperatures greater than 1600 K, two methane molecules rearrange to give three molecules of hydrogen and one molecule of ethyne.

$$2CH_4(g) \xrightarrow{1600\ K} C_2H_2(g) + 3H_2(g)$$

A 50.0 L steel vessel, filled with CH_4 to a pressure of 10.0×10^5 Pa at 298 K, is heated to exactly 1600 K to convert CH_4 into C_2H_2. What is the maximum possible mass of C_2H_2 that can be produced? What pressure does the reactor reach at 1600 K? Assume that both CH_4 and C_2H_2 behave as ideal gases under the conditions of the reaction.

Analysis

This is a stoichiometry problem involving gases. The mass of a product and the final pressure must be calculated. We can draw a diagram showing the process and listing the data.



Solution

In any stoichiometry problem, we work with amounts. This problem involves gases, so we use the ideal gas equation to obtain amounts in moles from the *p*–*V*–*T* information. Use the ideal gas equation to calculate the amount of CH_4 present initially.

$$n = \frac{p_i V}{RT_i} = \frac{(10.0 \times 10^5\ \text{Pa})(0.0500\ \text{m}^3)}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}$$
$$= 20.18\ \text{mol}\ CH_4$$

From the stoichiometry of the balanced chemical equation, we can determine that complete conversion of 20.18 mol of CH_4 into C_2H_2 and H_2 will give $(\frac{1}{2} \times 20.18) = 10.09$ mol C_2H_2 and $(\frac{3}{2} \times 20.18) = 30.27$ mol H_2.

Now we determine the mass of ethyne formed.

$$m = nM = (10.09\ \text{mol})(26.04\ \text{g mol}^{-1})$$
$$= 263\ \text{g}\ C_2H_2$$

Using the ideal gas equation and the total amount present at the end of the reaction, and assuming all the CH_4 has reacted, we can calculate the final pressure.

$$n_{\text{total}} = 10.09 + 30.27 = 40.36\ \text{mol}$$
$$pV = nRT, \text{ and so } p = \frac{nRT}{V}$$
$$P = \frac{(40.36\ \text{mol})(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(1600\ \text{K})}{0.0500\ \text{m}^3} = 1.07 \times 10^7\ \text{Pa}$$

Is our answer reasonable?

From the initial amount of methane, we can calculate the initial mass of methane, which is 323 g. The mass of ethyne, 263 g, is less than this, a reasonable result given that H_2 is also produced. The final pressure, 1.07×10^7 Pa, seems high, but the temperature of the reactor has increased substantially and the amount of products is twice the amount of reactants, so a large pressure increase is to be expected.

PRACTICE EXERCISE 6.9

Calculate the volume of hydrogen gas generated when 1.52 g of Mg reacts with an excess of aqueous HCl, if the gas is collected at 1.00×10^5 Pa and 22.5 °C. The balanced chemical equation for the reaction is:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Any of the types of problems discussed in chapter 3 can involve gases. The strategy for doing stoichiometric calculations is the same whether the species involved are solids, liquids or gases. In this chapter, we add the ideal gas equation to our equations for relating measured quantities to amounts.

WORKED EXAMPLE 6.10

Limiting Reagents in a Gas Mixture

Margarine can be made from natural oils such as coconut oil by hydrogenation.

$$\underset{\text{oli}}{C_{57}H_{104}O_6(l)} + 3H_2(g) \xrightarrow{200\ ^\circ C,\ 7 \times 10^5\ Pa,\ \text{Ni catalyst}} \underset{\text{margarine}}{C_{57}H_{10}O_6(s)}$$

A hydrogenator (figure 6.23) with a volume of 2.50×10^2 L is charged with 12.0 kg of oil. The remaining volume is then filled with 7.00×10^5 Pa of hydrogen, H_2, at 473 K. The reaction produces the maximum amount of margarine. What is the final pressure of H_2, and what mass of margarine will be produced? Assume that H_2 does not dissolve in coconut oil or margarine, that it behaves as an ideal gas under the reaction conditions and that the coconut oil and margarine occupy a negligible volume in the hydrogenator.



FIGURE 6.23 A hydrogenator available commercially for small-scale use, e.g. in a research laboratory.

Analysis

We have data from which we can calculate the amounts of both starting materials. Given the chemical equation, the first step in a stoichiometry problem is to determine the initial amount of each starting material. Next, calculate ratios of amounts to coefficients to identify the limiting reagent. After that, use the ideal gas equation and the stoichiometric principles we learned in chapter 3 to obtain the final answers.

Solution

The ideal gas equation is used for the gaseous starting material.

$$n_{H_2} = \frac{pV}{RT} = \frac{(7.00 \times 10^5\ \text{Pa})(2.50 \times 10^{-1}\ \text{m}^3)}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(473\ \text{K})} = 44.50\ \text{mol}$$

We obtain the amount of oil from the mass and the molar mass.

$$n_{\text{oil}} = \frac{m}{M} = \frac{1.20 \times 10^4\ \text{g}}{885.4\ \text{g mol}^{-1}} = 13.55\ \text{mol}$$

Now we divide each amount by the stoichiometric coefficient to identify the limiting reagent.

$$\text{For } H_2, \frac{44.50\ \text{mol}}{3\ \text{mol}} = 14.83$$

$$\text{For oil, } \frac{13.55\ \text{mol}}{1\ \text{mol}} = 13.55$$

The reactant with the smaller ratio, oil, is limiting. (Excess hydrogen is easily recovered from a gas-phase reactor, so margarine manufacturers make the oil the limiting reagent to ensure complete conversion of oil into margarine. The excess H_2 gas is recovered and reused.)

From the balanced chemical equation, 13.55 mol of oil will react with 40.65 mol (3 × 13.55) of H_2 to give 13.55 mol of margarine. Therefore, the amount of unreacted H_2 will be (44.50 - 40.65) = 3.85 mol. Note that we have carried an extra figure through the calculation. We therefore need to round to the correct number of significant figures at this point, so 13.6 mol of margarine will be produced and 3.9 mol of H_2 will remain unreacted.

Using the ideal gas equation, we calculate the pressure of hydrogen at the end of the reaction.

$$p = \frac{nRT}{V} = \frac{(3.9\ \text{mol})(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(473\ \text{K})}{2.50 \times 10^{-1}\ \text{m}^3}$$

$$= 0.61 \times 10^5\ \text{Pa}$$

Now we calculate the mass of margarine.

$$m = nM = (13.6\ \text{mol})(891.5\ \text{g mol}^{-1})$$

$$= 1.21 \times 10^4\ \text{g} = 12.1\ \text{kg}$$

Is our answer reasonable?

In this example, oil is the limiting reagent and not all the H_2 will react. Therefore, some H_2 will be left, but we expect the pressure of H_2 at the end of the reaction to be lower than at the start, which it is. Notice that the mass of margarine produced (12.1 kg) is only slightly greater than the mass of oil we started with (12.0 kg). This is to be expected, as the molar masses of coconut oil and margarine are very similar.

PRACTICE EXERCISE 6.10

In the industrial production of nitric acid, one step is the oxidation of nitrogen oxide: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$. A reaction chamber is charged with 5.00×10^5 Pa each of NO and O_2. If the reaction gives the maximum possible amount of $NO_2(g)$ without a change in temperature or volume,

calculate the final pressures of each reagent.

Summary of Mole Conversions

On the microscopic level, moles are the currency of chemistry; therefore, all stoichiometric calculations require amounts. On the macroscopic level, we measure mass, volume, temperature and pressure. Table 6.2 lists three equations that can be used to convert between the microscopic and macroscopic levels. Each of these equations applies to a particular category of chemical substances. You should have a working knowledge of these three equations, along with the category of substances to which they apply.

TABLE 6.2 Summary of stoichiometric relationships

Substance	Relationship	Equation
pure solid, liquid or gas	$\text{amount(mol)} = \dfrac{\text{mass(g)}}{\text{molar mass(g mol}^{-1}\text{)}}$	$n = \dfrac{m}{M}$
solution	$\text{amount(mol)} = \text{concentration(mol L}^{-1}\text{)} \times \text{volume(L)}$	$n = cV$
gas	$\text{amount(mol)} = \dfrac{\text{pressure(Pa)} \times \text{volume (m}^3\text{)}}{\text{constant (J mol}^{-1}\text{ K}^{-1}\text{)} \times \text{temperature (K)}}$	$n = \dfrac{pV}{RT}$

Worked example 6.11 uses all three relationships. Viewed as a whole, the example may seem complicated. However, as the solution illustrates, breaking the problem into separate parts allows each part to be solved using simple chemical and stoichiometric principles. Complicated problems are often simplified considerably by looking at them one piece at a time.

WORKED EXAMPLE 6.11

General Stoichiometry

Reaction of magnesium metal with acid (figure 6.24) generates hydrogen gas and an aqueous solution of ions. Suppose that 3.50 g of magnesium metal is dropped into 0.150 L of 6.00 M HCl in a 5.00 L cylinder at 25.0 °C. The initial gas pressure of the cylinder is 1.00×10^5 Pa, and it is immediately sealed. Find the final partial pressure of hydrogen, the total pressure in the container and the concentration of Mg^{2+} in solution.



FIGURE 6.24 Magnesium reacting with aqueous HCl.

Analysis

Data are given for all reactants. We must first write a balanced chemical equation and then use the equations in table 6.2, along with the stoichiometry of the reaction, to calculate the required pressures and concentrations.

Solution

We begin by writing the balanced chemical equation, which we have seen previously in practice exercise 6.9.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

The problem asks for pressures and ion concentrations. The final pressure can be deter-mined from *p*–*V*–*T* data and n_{H2}. The amount of hydrogen can be found from the mass of magnesium and the stoichiometric ratio. Here is a summary of the data.

$$V_{\text{container}} = 5.00\,\text{L} = 5.00 \times 10^{-3}\text{m}^3 \qquad T = 298\,\text{K} \qquad m_{Mg} = 3.50\text{g}$$

$$V_{\text{solution}} = 0.150 \times 10^{-3}\text{m}^3 \qquad P_{\text{air}} = 1.00 \times 10^5\,\text{Pa} \qquad [HCl] = 6.00\,\text{M}$$

Now we analyse the stoichiometry of the reaction. The starting mass of Mg and the volume and concentration of HCl are given, and we can use these data to find the limiting reactant.

$$n_{Mg} = \frac{m}{M} = \frac{3.50\ \text{g}}{24.31\ \text{g mol}^{-1}} = 0.144\ \text{mol}$$

$$n_{HCl} = cV = (6.00\ \text{mol L}^{-1})(0.150\ \text{L}) = 0.900\ \text{mol}$$

We divide by the stoichiometric coefficients to show that magnesium is the limiting reagent.

$$\text{For Mg, } \frac{0.144\ \text{mol}}{1\ \text{mol}} = 0.144 \qquad \text{For HCl, } \frac{0.900\ \text{mol}}{2\ \text{mol}} = 0.450$$

From the stoichiometry of the balanced chemical equation, we can show that 0.144 mol of Mg will form 0.144 mol H_2. We therefore use this amount to calculate the pressure of H_2. However, before doing this, we must visualise the reaction vessel. The container's total volume is 5.00×10^{-3} m^3, but 0.150×10^{-3} m^3 is occupied by the aqueous solution. This

leaves 4.85×10^{-3} m^3 for the gas mixture. The partial pressure of hydrogen is calculated using the ideal gas equation and assuming that no H_2 remains in solution; this is a good assumption because hydrogen gas is not very soluble in water.

$$p_{H_2} = \frac{nRT}{V} = \frac{(0.144\ \text{mol})(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}{4.85 \times 10^{-3}\ \text{m}^3} = 0.736 \times 10^5\ \text{Pa}$$

Assuming that the amount of air originally present does not change in the reaction, the pressure exerted by the air remains constant at 1.00×10^5 Pa. The final total pressure is the sum of the partial pressures.

$$\begin{aligned} p_{\text{total}} = p_{H_2} + p_{\text{initial}} &= 0.736 \times 10^5\ \text{Pa} + 1.00 \times 10^5\ \text{Pa} \\ &= 1.74 \times 10^5\ \text{Pa} \end{aligned}$$

We can calculate the final concentration of Mg^{2+} using the initial amount of Mg and the volume of the solution.

$$[Mg^{2+}] = \frac{0.144\ \text{mol}}{0.150\ \text{L}} = 0.960\ \text{M}$$

PRACTICE EXERCISE 6.11

Repeat the calculations from worked example 6.11 with all conditions the same except that 14.0 g of Mg is added to the HCl solution.

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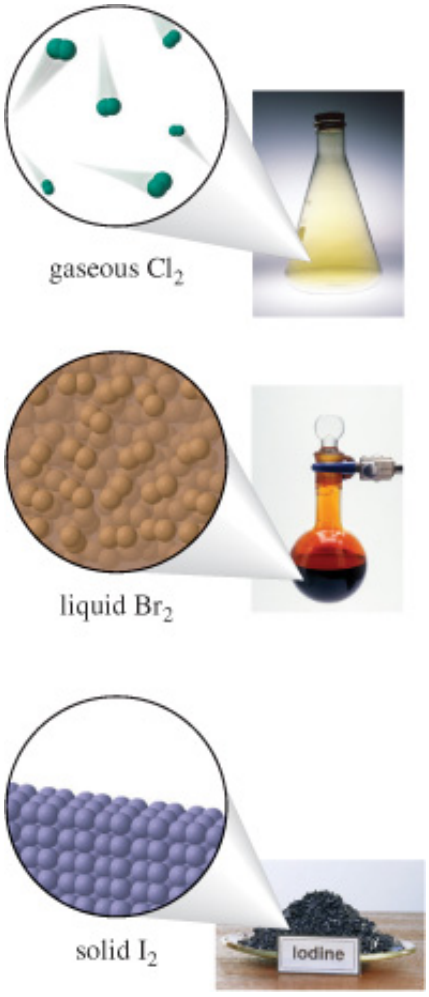
6.7 Real Gases

In chapter 5 we looked at what holds atoms and ions together, and we listed three types of bonding forces: ionic, covalent and metallic. In addition to these relatively strong bonding forces, there are much weaker forces that exist between atoms, ions and molecules. In the previous sections of this chapter we looked at ideal gases, assuming that there are no attractive forces between either atoms or molecules. However, weak attractive forces do occur in real gases, and much stronger forces are present in liquids and solids. In the absence of these **intermolecular forces**, all molecules would move independently, and all molecular substances would be gases. These intermolecular forces are essentially due to attractions between polarised molecules, but they also include polar interactions between ions and molecules as well as atoms. The name, intermolecular forces, is therefore somewhat inaccurate, but it can be justified by the fact that an overwhelming number of all chemical compounds are molecules.

The Halogens

The halogens, the elements from group 17 of the periodic table, provide an introduction to inter-molecular forces. These elements exist as diatomic molecules: F_2, Cl_2, Br_2 and I_2. Each molecule contains two atoms held together by a single covalent bond that can be described by end-on overlap of valence *p* orbitals.

Although they have similar covalent bonding, bromine and iodine differ from chlorine and fluorine in their macroscopic physical appearance and in their molecular behaviour. As figure 6.25 shows, at room temperature and pressure, chlorine (like fluorine) is a gas, bromine is a liquid and iodine is a solid.



Under normal conditions, chlorine is a pale yellow-green gas, bromine is a dark red liquid, and

FIGURE 6.25 iodine is a dark crystalline solid.

Gases and condensed phases (a term used to collectively describe liquids and solids) look very different at the molecular level. Molecules of F_2 or Cl_2 move freely throughout their gaseous volume, travelling many molecular diameters before colliding with one another or with the walls of their container. Because much of the volume of a gas is empty space, samples of gaseous F_2 and Cl_2 readily expand or contract in response to changes in pressure. This freedom of motion exists because the intermolecular forces between these molecules are small with respect to their kinetic energy.

Molecules of liquid bromine also move about relatively freely, but there is not much empty space between molecules. A liquid cannot be compressed significantly by increasing the pressure, because its molecules are already in close contact with one another. Neither does a liquid expand significantly if the pressure is reduced, because the intermolecular forces in a liquid are strong enough to prevent the molecules from breaking away from one another.

Solid iodine, like liquid bromine, has little empty space between molecules. Like liquids, solids have sufficiently strong intermolecular forces that they neither expand nor contract significantly when the pressure changes. In solids, the intermolecular forces are strong enough to prevent molecules from moving freely past one another. Instead, the I_2 molecules in the solid phase are arranged in ordered arrays. Each molecule vibrates back and forth around a single most stable position, but it cannot slide easily past its neighbours.

The balance between molecular kinetic energies and intermolecular attractive forces accounts for these striking differences (figure 6.26). Recall from section 6.2 that molecules are always moving. Intermolecular attractive forces tend to hold molecules together in a condensed phase, but molecules that are moving fast enough can overcome these forces and move freely in the gas phase. When the average kinetic energy is large enough, molecules remain separated from one another, and the substance is a gas. Conversely, when intermol ecular attractive forces are large enough, molecules remain close to one another, and the substance is a liquid or solid.

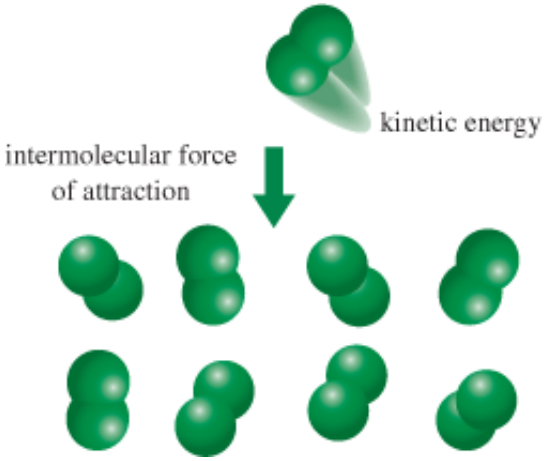


FIGURE 6.26 A substance exists in a condensed phase when its molecules have too little average kinetic energy to overcome intermolecular forces of attraction.

The bars in figure 6.27 compare the attractive energies arising from intermolecular forces acting on the halogens. The figure also shows the average molecular kinetic energy at room temperature. For fluorine and chlorine, the attractive energy generated by intermolecular forces is smaller than the average molecular kinetic energy at room temperature. Thus, these elements are gases under these conditions. In contrast, bromine molecules have enough kinetic energy to move freely about, but their energy is insufficient to overcome the intermolecular forces of the liquid phase. Finally, attractive forces in iodine are strong enough to lock the I_2 molecules in position in the solid state.

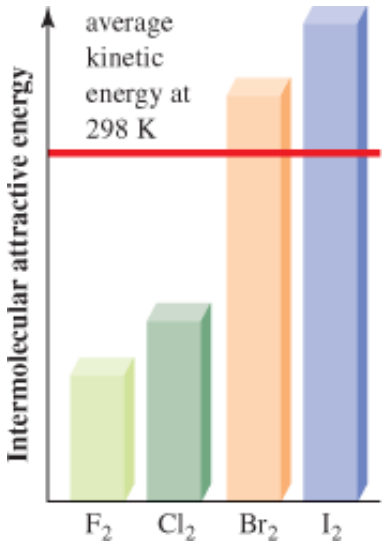


FIGURE 6.27 The balance of average kinetic energy (red line) and intermolecular energies of attraction favours the gas phase for F_2 and Cl_2, and the condensed phases for Br_2 and I_2.

Properties of Real Gases

As we described in section 6.3, the ideal gas model makes two assumptions: a gas has negligible forces between its constituent atoms or molecules, and gas atoms or molecules have negligible volumes. Neither of these assumptions is true for a real gas. At sufficiently high pressures and sufficiently low temperatures, all gases can be liquefied.

How close do real gases come to ideal behaviour? To answer this question, we rearrange the ideal gas equation to examine the ratio $\frac{pV}{nRT}$. Figure 6.28 shows how the $\frac{pV}{nRT}$ ratio varies with pressure for chlorine gas at room temperature. If chlorine were an ideal gas, the $\frac{pV}{nRT}$ ratio would always be 1, as shown by the red line on the graph. Instead, chlorine shows deviations from 1 as the pressure increases.

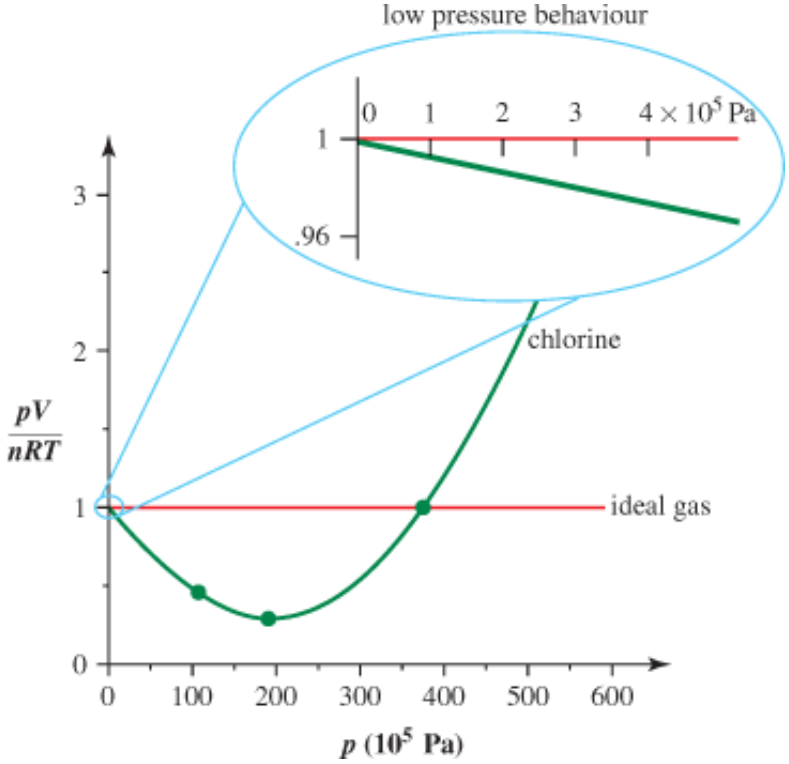


FIGURE 6.28 The variation in $\frac{pV}{nRT}$ with pressure shows that chlorine is not an ideal gas.

Notice in the inset of figure 6.28 that chlorine is nearly ideal at pressures around 1×10^5 Pa. In fact, $\frac{pV}{nRT}$ deviates from 1.0 by less than 4% at pressures below 4×10^5 Pa. As the pressure increases, however, the deviations become increasingly significant. With increasing pressure, the $\frac{pV}{nRT}$ ratio for chlorine drops below 1. This is because the chlorine molecules are close enough together for attractive forces to play a significant role. These intermolecular attractions hold molecules together and reduce the forces exerted when the molecules strike the walls of the container. Intermolecular attractions tend to make the pressure of a real gas lower than the ideal value.

Figure 6.28 also shows that at pressures greater than 375×10^5 Pa, $\frac{pV}{nRT}$ becomes *larger* than 1. This is due to the effect of molecular size.At high enough pressure, the molecules are packed so close together that the total volume of the molecules is no longer negligible compared with the overall volume of the container. The result is that the container volume is effectively decreased by the molecules' volume and the pressure of the real gas tends to be greater than that of the ideal gas.

Every gas shows deviations from ideal behaviour at high pressure. Figure 6.29 shows $\frac{pV}{nRT}$ for He, F_2, CH_4 and N_2, all of which are gases at room temperature. Notice that $\frac{pV}{nRT}$ for helium increases steadily as pressure increases. Interatomic forces for helium are too small to reduce the ratio below 1, but the finite size of the helium atom generates deviations from ideal behaviour that become significant at pressures above 100×10^5 Pa.

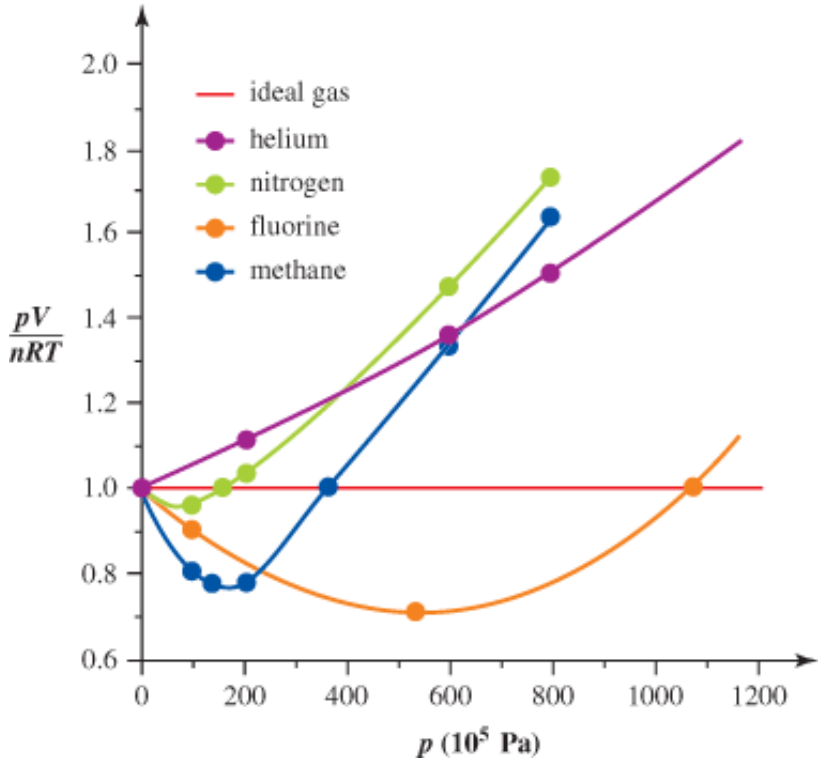


FIGURE 6.29 Variations in $\frac{PV}{nRT}$ for He, N_2, F_2 and CH_4 at 300 K.

Given that every gas deviates from ideal behaviour to some degree, can we use the ideal gas model to discuss the properties of real gases? The answer is yes, as long as conditions do not become too extreme. The gases with which chemists often work, such as chlorine, helium and nitrogen, are nearly

ideal at room temperature at pressures below about 10×10^5 Pa, but, at very high pressures or near the condensation points of substances, deviations from the ideal gas equation become large.

The Van Der Waals Equation

It would be useful to have an equation that describes the relationship between pressure and volume for a real gas, just as $\frac{pV}{nRT}$ describes an ideal gas. One way to approach real gas behaviour is to modify the ideal gas equation to account for attractive forces and molecular volumes. The result is the **van der Waals equation**, named after the scientist who first proposed it in 1873, Johannes van der Waals (1837–1923, Nobel Prize in physics, 1910).

$$(p + \frac{n^2 a}{V^2})(V - nb) = nRT$$

The van der Waals equation adds two correction terms to the ideal gas equation. Each correction term includes a constant that has a specific value for every gas. The first correction term, $\frac{n^2 a}{V^2}$, adjusts for attractive intermolecular forces. The van der Waals constant *a* reflects the strength of intermolecular forces for the gas; the stronger the forces, the larger the value of *a*. The second correction term, *nb*, adjusts for molecular sizes. The van der Waals constant *b* reflects the size of gas atoms or molecules; the larger they are, the larger the value of *b*.

The van der Waals constants for a number of gases appear in table 6.3, and the magnitude of van der Waals corrections is explored in worked example 6.12.

TABLE 6.3 Values of van der Waals constants for a variety of gases

	a	*b*
Substance	(m^6 Pa mol^{-2})	(m^3 mol^{-1})
He	3.457×10^{-3}	2.37×10^{-5}
Ne	2.135×10^{-2}	1.709×10^{-5}
Ar	1.363×10^{-1}	3.219×10^{-5}
H_2	2.476×10^{-2}	2.661×10^{-5}
N_2	1.408×10^{-1}	3.913×10^{-5}
O_2	1.378×10^{-1}	3.183×10^{-5}
CO	1.505×10^{-1}	3.985×10^{-5}
F_2	1.156×10^{-1}	2.90×10^{-5}
Cl_2	6.579×10^{-1}	5.622×10^{-5}
CO_2	3.640×10^{-1}	4.267×10^{-5}
H_2O	5.536×10^{-1}	3.049×10^{-5}
NH_3	4.225×10^{-1}	3.707×10^{-5}

CH_4	2.283×10^{-1}	4.278×10^{-5}
C_2H_6	5.562×10^{-1}	6.38×0^{-5}
C_6H_6	1.824×10^{-1}	1.154×10^{-5}

WORKED EXAMPLE 6.12

Magnitudes of Van Der Waals Corrections

Gases such as methane are sold and shipped in compressed gas cylinders (figure 6.30). A typical cylinder has a volume of 15.0 L and, when full, contains 62.0 mol of CH_4. After prolonged use, 0.620 mol of CH_4 remains in the cylinder.



FIGURE 6.30 Gases such as methane, butane and propane are sold in compressed gas cylinders.

Use the van der Waals equation to calculate the pressures in the cylinder when full and after use, and compare the values with those obtained from the ideal gas equation. Assume a constant temperature of 25 °C.

Analysis

We are asked to calculate and compare the pressures of methane gas using the van der Waals equation and the ideal gas equation. Van der Waals constants *a* and *b* must be looked up in a data table such as table 6.3. To calculate pressures, we rearrange the van der Waals equation and the ideal gas equation.

$$p_{\text{real}} = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \quad \text{and} \quad p_{\text{ideal}} = \frac{nRT}{V}$$

Solution

The van der Waals constants for CH_4 are:

$$a = 2.283 \times 10^{-1}\ \text{m}^6\ \text{Pa mol}^{-2} \qquad b = 4.278 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$$
$$V = 15.0 \times 10^{-3}\ \text{m}^3 \qquad T = (25 + 273.15)\text{K} = 298\ \text{K}$$

When the tank is full, n = 62.0 mol.

$$p_{\text{real}} = \frac{(62.0\ \text{mol})(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}{15.0 \times 10^{-3}\text{m}^3 - (62.0\ \text{mol})(4.278 \times 10^{-5}\text{m}^3\ \text{mol}^{-1})} - \frac{(62.0\ \text{mol})^2(2.283 \times 10^{-1}\text{m}^6\ \text{Pa mol}^{-2})}{(15.0 \times 10^{-3}\text{m}^3)^2}$$

$$p_{\text{real}} = \frac{1.537 \times 10^5\ \text{J}}{1.24 \times 10^{-2}\text{m}^3} - 3.900 \times 10^6\ \text{Pa} = 85.48 \times 10^5\ \text{Pa} (\text{recall that 1 Pa} = 1\ \text{J m}^{-3})$$

$$p_{\text{ideal}} = \frac{nRT}{V} = \frac{(62.0\ \text{mol})(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}{15.0 \times 10^{-3}\text{m}^3} = 102 \times 10^5\ \text{Pa}$$

After use, n = 0.620 mol.

$$p_{\text{real}} = \frac{(0.620\ \text{mol})(8.314\ \text{mol}^{-1}\text{K}^{-1})(298\text{K})}{15.0 \times 10^{-3}\ \text{m}^3 - (0.620\ \text{mol})(4.278 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1})} - \frac{(0.620\ \text{mol})^2(2.283 \times 10^{-1}\ \text{m}^6\ \text{Pa mol}^{-2})}{(15.0 \times 10^{-3}\ \text{m}^3)^2}$$

$$p_{\text{real}} = \frac{1.537 \times 10^3}{1.50 \times 10^{-2}\ \text{m}^3} - 3.90 \times 10^2\ \text{Pa} = 1.023 \times 10^5\ \text{Pa}$$

$$p_{\text{ideal}} = \frac{nRT}{V} = \frac{(0.620\ \text{mol})(8.314\text{J mol}^{-1}\text{K}^{-1})(298\text{K})}{15.0 \times 10^{-3}\ \text{m}^3} = 1.02 \times 10^5\ \text{Pa}$$

Organise the results to make a comparison.

$$p_{\text{full, real}} = 85.5 \times 10^5\ \text{Pa} \quad \text{and} \quad p_{\text{full, ideal}} = 102 \times 10^5\ \text{Pa}$$
$$p_{\text{used, real}} = 1.02 \times 10^5\ \text{Pa} \quad \text{and} \quad p_{\text{used, ideal}} = 1.02 \times 10^5\ \text{Pa}$$

Notice that the van der Waals correction is appreciable (15.4%) at high pressure, but is negligible at atmospheric pressure (1.013×10^5 Pa).

Is our answer reasonable?

We know that methane is normally a gas at 298 K and atmospheric pressure, so it makes sense that the gas behaves ideally under these conditions. A pressure above 100×10^5 Pa is substantially higher than normal conditions, so we expect to see deviations from ideal behaviour.

PRACTICE EXERCISE 6.12

Methane boils at -164 °C. Use the ideal gas equation to calculate the molar volume of

methane gas at this temperature at 1.013×10^5 Pa pressure. Then use the van der Waals equation to calculate the pressure exerted by 1.00 mole of the gas if it occupies this volume at -164 °C.

Melting and Boiling Points

Melting points and boiling points can be used as indicators of the strengths of intermolecular forces. Remember that the temperature increases with the average kinetic energy of molecular motion. The boiling point of a substance is the temperature at which the average kinetic energy of molecular motion balances the attractive energy of intermolecular attractions. When the pressure is 1.013×10^5 Pa, that temperature is the **normal boiling point**. For example, the normal boiling point of bromine is 332 K (59 °C). Above this temperature, the average kinetic energy exceeds the attractive energies created by intermolecular forces of attraction, and bromine exists as vapour. Under atmospheric pressure, bromine is a liquid at temperatures below 332 K. Note that, because boiling points are determined primarily by intermolecular attractive forces, factors other than the molar mass of the molecule may be important. For example, carbon tetrachloride, CCl_4, (M = 153.81 g mol^{-1}) has a lower boiling point (77 °C) than the lighter molecule phenol, C_6H_5OH, (M = 94.12 g mol^{-1}, bp = 182 °C) because of the much stronger intermolecular forces in phenol.

The conversion of a liquid into a gas is called **vaporisation**. A liquid vaporises when molecules leave the liquid phase faster than they are captured from the gas. **Condensation** is the reverse process. A gas condenses when molecules leave the gas phase more rapidly than they escape from the liquid. We explore these processes in more detail in chapter 7.

The molecules in a liquid are able to move about freely. When a liquid is cooled, however, the kinetic energies decrease. At temperatures below the freezing point, the molecules become locked in place and the liquid solidifies. When the pressure is 1.013×10^5 Pa, that temperature is the **normal freezing point**. A liquid freezes when liquid molecules have too little kinetic energy to slide past one another. Conversely, a solid melts when its molecules have enough kinetic energy to move freely past one another. Just as intermolecular forces determine the normal boiling point, these forces also determine the freezing point. The stronger the intermolecular forces, the higher the freezing point; fluorine freezes at 53.5 K, chlorine at 172 K and bromine at 266 K.

Boiling points and melting points depend on the strengths of intermolecular forces. This is because the rates of escape and capture from a phase depend on the balance between molecular kinetic energies and intermolecular forces of attraction. A substance with large intermolecular forces must be raised to a high temperature before its molecules have sufficient kinetic energies to overcome those forces. A substance with small intermolecular forces must be cooled to a low temperature before its molecules have small enough kinetic energies to coalesce into a condensed phase. Table 6.4 lists the boiling and melting points of some elemental substances.

TABLE 6.4 Normal melting and boiling points of selected elements

Substance	mp (K)	bp (K)
He	0.95[(a)]	4.2
H_2	14.0	20.3

N_2	63.3	77.4
F_2	53.5	85.0
Ar	83.8	87.3
O_2	54.8	90.2
Cl_2	172	239
Br_2	266	332
I_2	387	458
P_4	317	553
Na	371	1156
Mg	922	1363
Si	1683	2628
Fe	1808	3023

(a) Under high pressure, as helium cannot be solidified at atmospheric pressure.

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6.8 Intermolecular Forces

In chapter 5 we encountered ionic, covalent and metallic bonding that hold atoms and ions together. In addition, so-called intermolecular forces exist between all molecules (hence the name), but they also include attractive forces between atoms, ions and molecules other than bonding forces. Intermolecular forces are typically much weaker than bonding forces and generally influence physical properties of compounds (e.g. whether they are gaseous, liquid or solid at ambient conditions) rather than their chemical properties. As stated earlier in this chapter, intermolecular forces are caused by differences in polarity (permanent or temporary) between entities (see below). In this section, we will talk only about molecules, but the discussion also encompasses ions and atoms.

Different intermolecular forces can be thought of as points along a bonding continuum; all of them rely on the attraction between positively and negatively charged parts of neighbouring molecules (i.e. electron clouds and nuclei), and the distinction between them is in some cases rather fluid. Forces in order of increasing strength are:

- instantaneous dipole-induced dipole forces (also called dispersion forces)
- dipole-induced dipole forces
- dipole–dipole forces (including hydrogen bonds, which are typically relatively strong dipole–dipole interactions). These are also called dipolar forces.

Analogous forces also exist between ions and both dipoles and induced dipoles. Ion–dipole forces and ion-induced dipole forces are stronger than the intermolecular forces above.

Dispersion forces are the attractions between the negatively charged electron cloud of one molecule and the positively charged nuclei of neighbouring molecules. All substances display dispersion forces. They are caused by the usually symmetrical electron distribution around a molecule not being symmetrical at every instant of time. This creates an instantaneous dipole, which in turn can induce a dipole in a neighbouring molecule.

Dipole-induced dipole forces are somewhat stronger than dispersion forces; the difference is that, in this case, a molecule with a permanent dipole induces a dipole in a neighbouring molecule.

Dipole–dipole forces are the attractions between the negatively charged end of a polar molecule and the positively charged ends of neighbouring polar molecules. Dipole–dipole forces exist only for compounds that possess permanent dipole moments (see section 5.5).

If these dipole–dipole forces involve a hydrogen atom, they are called **hydrogen bonds**. They occur mainly between a lone pair of electrons on a small, highly electronegative atom (usually N, O or F) and a hydrogen atom bonded to a highly electronegative atom. Strong hydrogen bonds occur primarily with molecules that contain O —H, N—H and F—H covalent bonds.

Dispersion forces, dipole–dipole forces and hydrogen bonds are all much weaker than intramolecular covalent bonds. For example, the average C—C bond energy is 345 kJ mol^{-1}, whereas dispersion forces are just 0.1 to 5 kJ mol^{-1} for small alkanes such as propane. Dipole–dipole forces between polar molecules such as acetone range between 5 and 20 kJ mol^{-1}, and hydrogen bonds range between 5 and 50 kJ mol^{-1}. This generalisation, however, needs to be treated with care. In a large molecule, the sum of all the weak dispersion forces may be much stronger than a dipole–dipole interaction in a different molecule, leading to a higher melting or boiling point.

Dispersion Forces

Dispersion forces exist because the electron clouds of molecules can be distorted. For example, consider what happens when two halogen molecules approach each other. Each molecule contains positive nuclei surrounded by a cloud of negative electrons. As two molecules approach, the nucleus of one molecule attracts the electron cloud of the other. Electrons are highly mobile, so the electron clouds change shape in response to this attraction. At the same time, the two electron clouds repel each other, which leads to further distortion to mini-mise electron– electron repulsion. As figure 6.31 indicates, this distortion of the electron cloud creates a charge imbalance, giving the molecule a slight positive charge at one end and a slight negative charge at the other. Dispersion forces are the net attractive forces between molecules generated by all these induced charge imbalances.

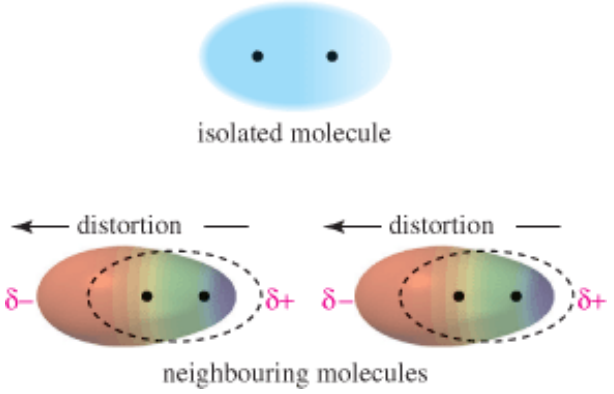


FIGURE 6.31 Exaggerated view of how dispersion forces arise.

The magnitude of dispersion forces depends on how easy it is to distort the electron cloud of a molecule. This ease of distortion is called the **polarisability** because distortion of an electron cloud generates a temporary polarity, called an instantaneous dipole, within the molecule. We can explore how polarisability varies by examining boiling points of the halogens, as shown in figure 6.32. The data reveal that boiling points increase with the total number of electrons. Fluorine, with 18 total electrons, has the lowest boiling point (85 K). Iodine, with 106 electrons, has the highest boiling point (458 K). The large electron cloud of I_2 distorts more readily than the small electron cloud of F_2. Figure 6.33 shows schematically how a large electron cloud distorts more than a small one, generating larger dispersion forces and leading to a higher boiling point.

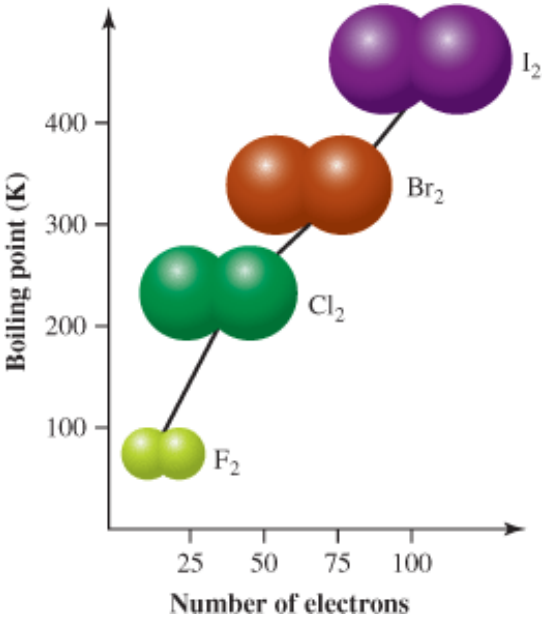


FIGURE 6.32 Boiling points of the halogens increase with the number of electrons.

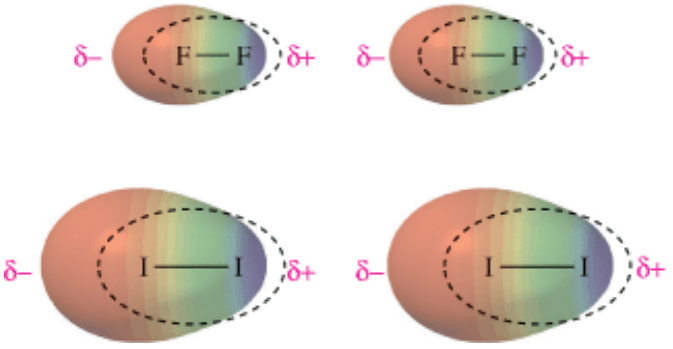


FIGURE 6.33 With many more electrons, the electron cloud of iodine is much larger and more polarisable than that of fluorine.

Molecular size increases with the number as well as with the size of individual atoms. Figure 6.34 shows how the boiling points of alkanes increase as the carbon chain gets longer. As alkanes get longer, their electron clouds become larger and more polarisable, making dispersion forces larger and raising the boiling point. As examples, methane (CH_4, 10 electrons) is a gas at 298 K, pentane (C_5H_{12}, 42 electrons) is a low-boiling-point liquid, decane ($C_{10}H_{22}$, 82 electrons) is a high-boiling-point liquid and icosane ($C_{20}H_{42}$, 162 electrons) is a waxy solid. The boiling point increases progressively as molecules become larger and more polarisable.

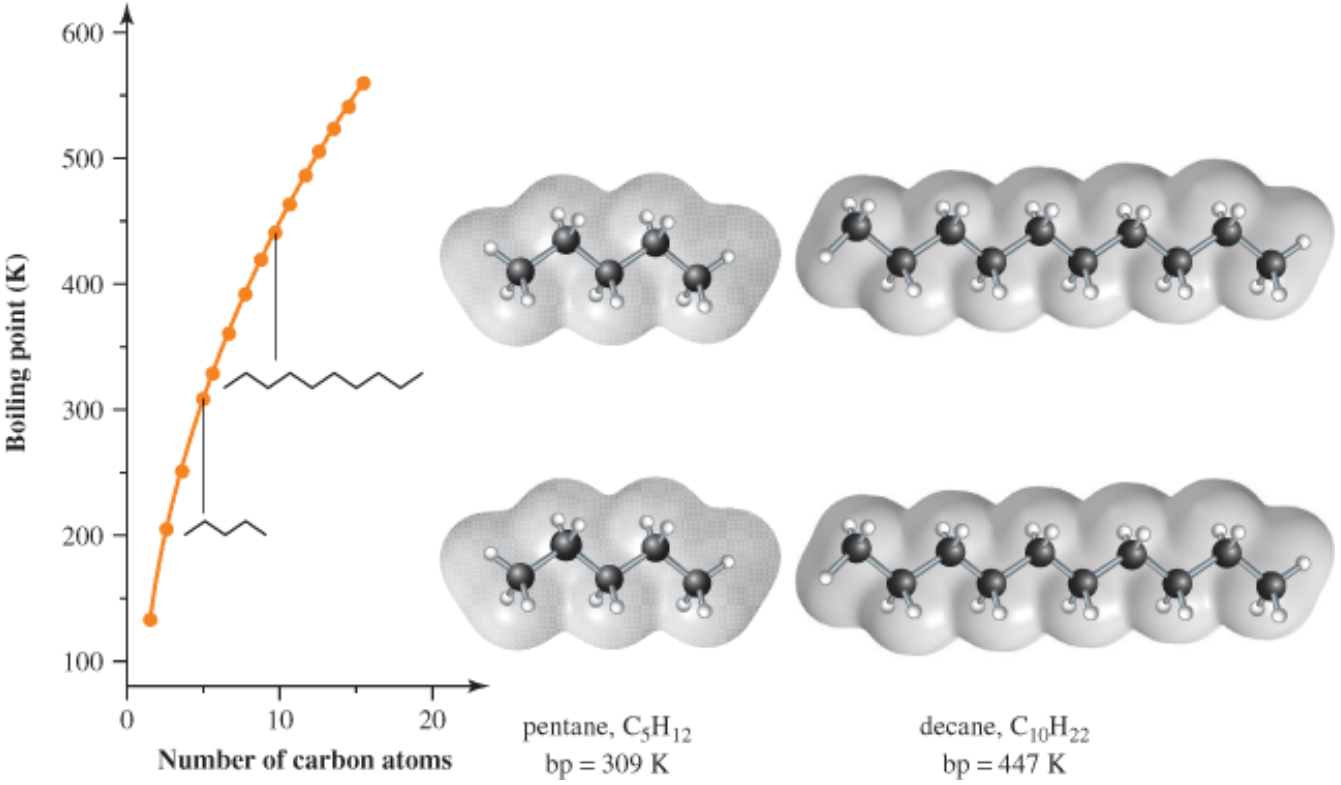


FIGURE 6.34 The boiling points of alkanes increase with the length of the carbon chain, because a large electron cloud is more polarisable than a small one.

Dispersion forces increase in strength with the number of electrons because larger electron clouds are more polarisable than smaller electron clouds. For molecules with comparable numbers of electrons, the shape of the molecule makes an important secondary contribution to the magnitude of dispersion forces. For example, figure 6.35 shows the shapes of pentane and 2,2-dimethylpropane. Both of these molecules have the formula C_5H_{12}, with 72 total electrons. Notice that 2,2-dimethylpropane has a more compact structure than pentane. This compactness results in a less polarisable electron cloud and smaller dispersion forces. Accordingly, pentane has a boiling point of 309 K, while 2,2-dimethylpropane boils at 283 K.

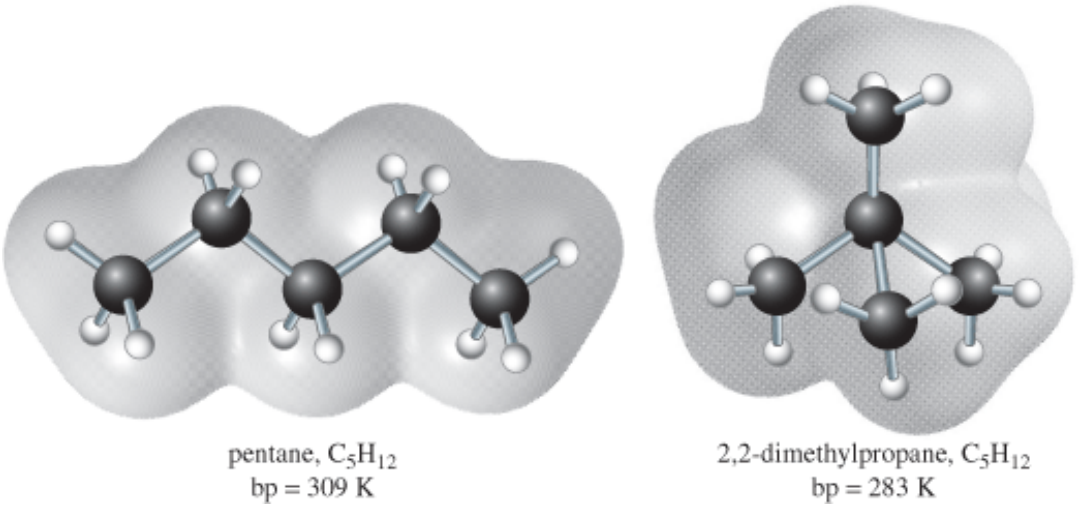


FIGURE 6.35 The boiling point of pentane is higher than the boiling point of 2,2-dimethylpropane because an extended electron cloud is more polarisable than a compact one.

Dipolar Forces

Dispersion forces exist between all molecules, but some substances remain liquid at much higher temperatures than can be accounted for by dispersion forces alone. Consider 2-methylpropane and propanone (acetone), whose structures are shown in figure 6.36. These molecules have similar shapes and nearly the same number of electrons (34 versus 32). They are so similar that we might expect the two to have nearly equal boiling points, but acetone is a liquid at room temperature, whereas 2-methylpropane is a gas.

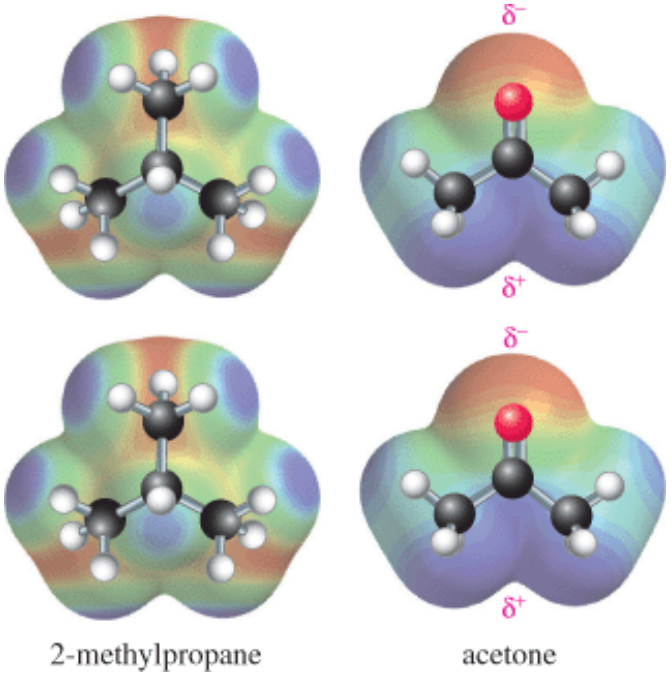


FIGURE 6.36 Acetone and 2-methylpropane have similar molecular shapes, but acetone has a large dipole moment resulting from its polar C═O bond.

Why does acetone remain a liquid at temperatures well above the boiling point of 2-methylpropane? The reason is that acetone has a large dipole moment. Remember from chapter 5 that chemical bonds are polarised toward the more electronegative atom. Thus, the C═O bond of acetone is highly polarised, with a partial negative charge on the O atom (χ = 3.5) and a partial positive charge on the C atom (χ = 2.5). The C—H bonds in these molecules, in contrast, are only very slightly polar, because the electronegativity of

hydrogen ($\chi = 2.1$) is only slightly smaller than that of carbon.

When two polar acetone molecules approach each other, they align so that the δ+ end of one molecule is close to the δ- end of the other (figure 6.36). In a liquid array, this repeating pattern of head-to-tail alignment creates significant net attractive dipolar forces between the molecules.

These dipolar forces in addition to dispersion forces, which are nearly the same in acetone and 2-methylpropane, make the total amount of intermolecular attraction between acetone molecules substantially greater than between molecules of 2-methylpropane. Consequently, acetone boils at a considerably higher temperature than 2-methylpropane.

WORKED EXAMPLE 6.13

Boiling Points and Structure

The line structures of butane, methoxyethane and acetone are shown below. Explain the trend in boiling points: butane (273 K), methoxyethane (281 K) and acetone (329 K).



Analysis

These boiling points can be explained in terms of dispersion and dipolar forces. First, assess the magnitudes of dispersion forces, which are present in all substances, and then look for polarity within the molecules.

Solution

A table helps to organise the available information.

Substance	Boiling point	Total electrons
butane	273 K	34
methoxyethane	281 K	34
acetone	329 K	32

The table shows that dispersion forces alone cannot account for the range in boiling temperatures. Methoxyethane and butane have the same number of electrons and similar shapes; yet their boiling points are different. Acetone, which has fewer electrons than the other compounds, has slightly smaller dispersion forces, yet it boils at a higher temperature. The order of boiling points indicates that acetone is a more polar molecule than methoxyethane, which in turn is more polar than butane.

We expect butane to be nonpolar because of the small electronegativity difference between carbon and hydrogen. Acetone and methoxyethane, on the other hand, both contain polar carbon–oxygen bonds. Molecular geometry reveals why acetone is more polar than methoxy ethane. The full structures of these molecules show that the oxygen atom in the ether has four sets of electron pairs and a bent geometry. The two C—O bond dipoles in methoxyethane partially cancel each other, leaving a relatively small molecular dipole moment. On the other

hand, the polar C═O bond in acetone is unopposed, so acetone has a larger dipole moment and is more polar than methoxyethane.

Is our answer reasonable?

For the molecules in this example, we would expect those containing electronegative oxygen atoms to have higher boiling points than butane because of the presence of significant permanent dipoles. An O atom bonded to only one atom results in a large dipole moment for the molecule as explained previously, and therefore we expect acetone to have a higher boiling point than methoxyethane. Experimental values for the dipole moments are: butane, 0 C m; methoxyethane, 3.74×10^{-30} C m; and acetone, 9.62×10^{-30} C m.

PRACTICE EXERCISE 6.13

Acetaldehyde, CH_3CHO, has a structure similar to acetone but with a CH_3 group replaced by H. This substance boils at 294 K. Explain its boiling point relative to the three compounds described in worked example 6.13.

Although not strictly classed as an intermolecular force, the interaction between an ion and the permanent dipole of a molecule can be significant. Such interactions are called ion– dipole interactions, and these can be viewed as lying between dipole–dipole interactions and pure ionic interactions. In addition, ions polarise neighbouring molecules, leading to induced dipole interactions, which are much weaker than ion–dipole interactions.

Hydrogen Bonds

Methoxyethane is a gas at room temperature (boiling point = 281 K), but propan-1-ol, shown in figure 6.37, is a liquid (boiling point = 370 K). The compounds have the same molecular formula, C_3H_8O, and each has a chain of four inner atoms, C—O —C—C and O—C —C —C. Consequently, the electron clouds of these two molecules are about the same size, and their dispersion forces are comparable. Each molecule has an sp^3-hybridised oxygen atom with two polar single bonds, so their dipolar forces should be similar. The very different boiling points of propan-1-ol and methoxyethane make it clear that dispersion and dipolar forces do not reveal the entire story of intermolecular attractions.

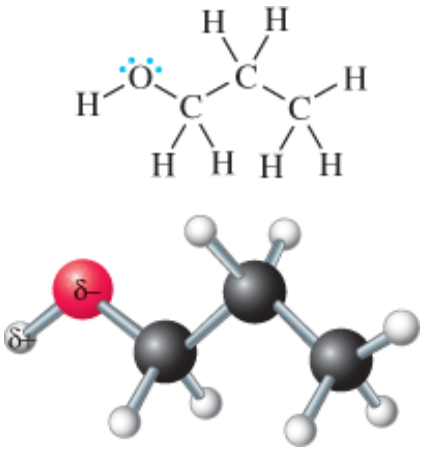


FIGURE 6.37 The structural formula and a ball-and-stick model of propan-1-ol.

The forces of attraction between propan-1-ol molecules are stronger than those between methoxyethane molecules because of an intermolecular interaction called a hydrogen bond. A hydrogen bond occurs between a small, highly electronegative atom with a lone pair of electrons and a positively polarised hydrogen atom. These interactions can be considered a special example of dipole–dipole interactions, and their strengths generally lie between those of dispersion forces and covalent bonds.

There are two requirements for hydrogen bond formation. First, there must be an electron-deficient hydrogen atom that can be attracted to an electron pair. Hydrogen atoms in O—H, F—H and N—H bonds meet this requirement. Second, there must be a small, highly electronegative atom with an electron pair that can interact with the electron-deficient hydrogen atom. Three second-row elements, O, N and F, meet this requirement, and there is evidence that S and Cl atoms can also form hydrogen bonds, but these are much weaker than those involving F, O and N atoms. Figure 6.38 shows representative examples of hydrogen bonding. The hydrogen bonds are shown as dotted lines to indicate the weak bonding nature of these interactions.

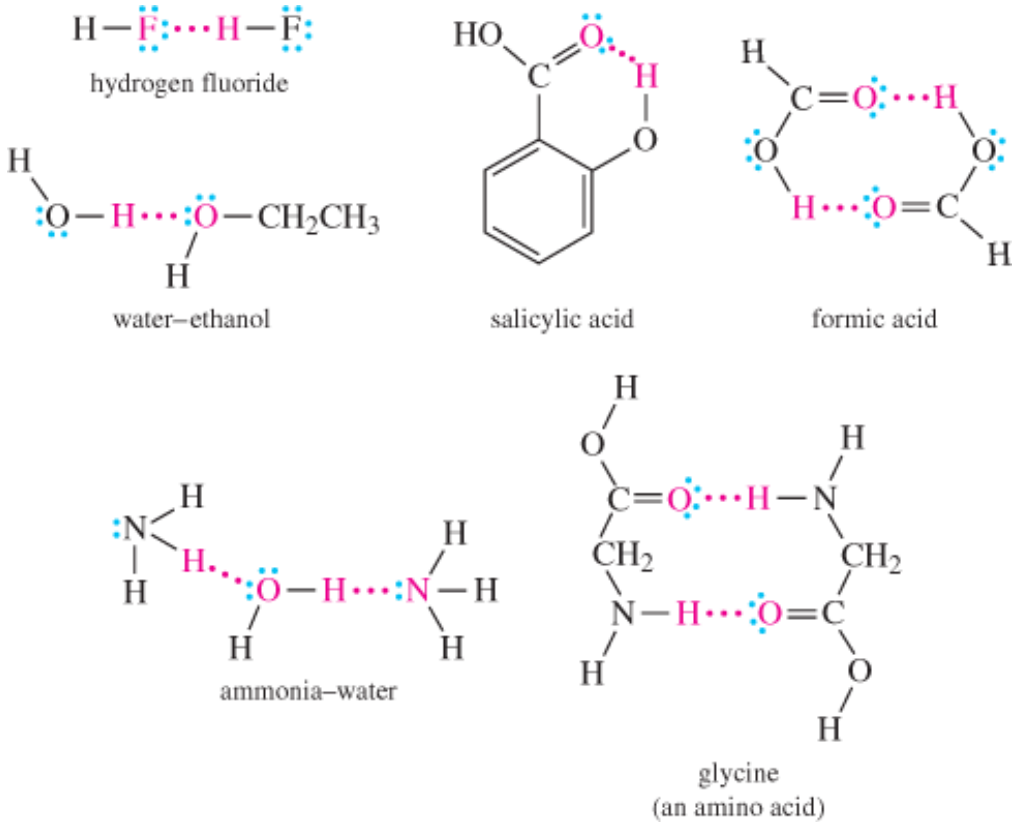


FIGURE 6.38 Examples of hydrogen bonding.

Notice from the examples shown in figure 6.38 that hydrogen bonds can form between different molecules

(for example, $H_3N\cdots H_2O$) or between identical molecules (for example, HF…HF). Also notice that molecules can form more than one hydrogen bond (glycine, for example) and that hydrogen bonds can form between molecules as well as within a molecule (salicylic acid, for example).

WORKED EXAMPLE 6.14

Formation of Hydrogen Bonds

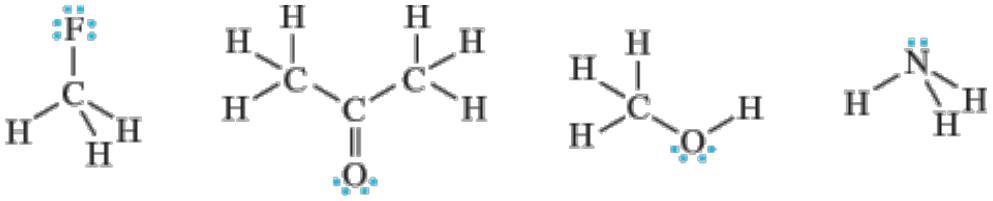
In which of the following systems will hydrogen bonding play an important role: CH_3F, $(CH_3)_2CO$ (acetone), CH_3OH, and NH_3 dissolved in $(CH_3)_2CO$?

Analysis

Hydrogen bonds require electron-deficient hydrogen atoms in polar H—X bonds and small, highly electronegative atoms with nonbonding pairs of electrons. Use line structures to determine whether these requirements are met.

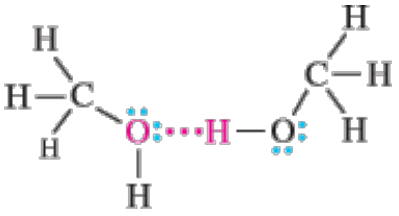
Solution

Here are the structural formulae of the four molecules with nonbonding electron pairs indicated.

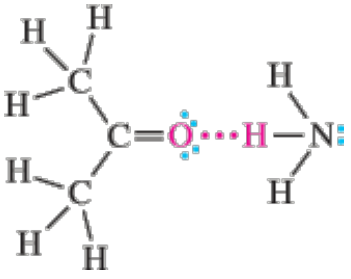


Acetone and CH_3F contain electronegative atoms with nonbonding pairs, but neither has any highly polar H—X bonds. Thus, the magnitude of any hydrogen bonding between molecules of these substances will be small.

The O—H bond in CH_3OH meets both of the requirements for hydrogen bonding. The O—H hydrogen atom on one molecule interacts with the oxygen atom of a neighbouring molecule.



For a solution of ammonia in acetone, we must examine both components. Acetone has an electronegative oxygen atom with nonbonding pairs, whereas NH_3 has a polar N—H bond. Consequently, a mixture of these two compounds displays hydrogen bonding between the hydrogen atoms of ammonia and oxygen atoms of acetone, and, depending on the concentration, there will also be hydrogen bonds between ammonia molecules.



Is our answer reasonable?

Methanol has a considerably higher boiling point than the alkanes, methane and ethane, consistent with significant intermolecular forces. Ammonia dissolves readily in acetone, also consistent with significant intermolecular forces.

PRACTICE EXERCISE 6.14

Draw a picture that shows the hydrogen-bonding interactions of an acetone molecule dissolved in water.

Hydrogen bonding is particularly important in biochemical systems, because biomolecules contain many oxygen and nitrogen atoms that participate in hydrogen bonding. The most important example of biological hydrogen bonding is seen in DNA, where hydrogen bonds hold the two strands of DNA together in a double helix geometry. Likewise, the amino acids from which proteins are made contain—NH_2 (amino) and —CO_2H (carboxylic acid) groups, and four different types of hydrogen bonds exist in these systems: O…H—N, N…H—O, O…H—O and N…H—N. When biological molecules contain S atoms, S…H—O and S…H—N hydrogen bonds can also form. Figure 6.38 includes a view of hydrogen bonding between molecules of the amino acid glycine. More details of hydrogen bonding in biomolecules are examined in chapters 24 and 25.

chemical Connections

Methane Hydrates

You are all probably aware of the potential danger that carbon dioxide poses as a greenhouse gas in the Earth's atmosphere. However, you might be less familiar with the fact that methane, CH_4, is, on a mass basis, a much more potent greenhouse gas than carbon dioxide, and large-scale emissions of this gas could have a significant warming effect. The New Zealand government was one of the first in the world to attempt to take action to limit methane emissions from farm animals; however, their so-called ‘fart’ tax, which would have levied a tax on every New Zealand farm animal, was never implemented, owing to substantial public opposition.

While farm animals do indeed emit significant quantities of methane, the Earth's oceans, somewhat surprisingly, provide a far larger and potentially devastating store of methane in the form of an unusual chemical species called methane hydrate. When methane dissolved in water is subjected to the high pressures and (relatively) low temperatures found at the sea bottom, it forms methane hydrate, a solid species that looks like ice, and contains both methane and water. There are large deposits of methane hydrate on the sea floor in many parts of the world, and one such deposit lies off the east coast of the North Island of New Zealand.

Methane hydrate is an example of a chemical species called a clathrate, in which gas molecules are ‘trapped’ inside an array of water molecules that are held together in a highly symmetrical arrangement by hydrogen bonds. Figure 6.39 shows a model of such a hydrate, with the methane

molecule represented in the central cavity (the C atom is grey, O atoms are red and hydrogen atoms white). Methane is not alone in forming such clathrates — group 18 gases in particular are known to form similar species.

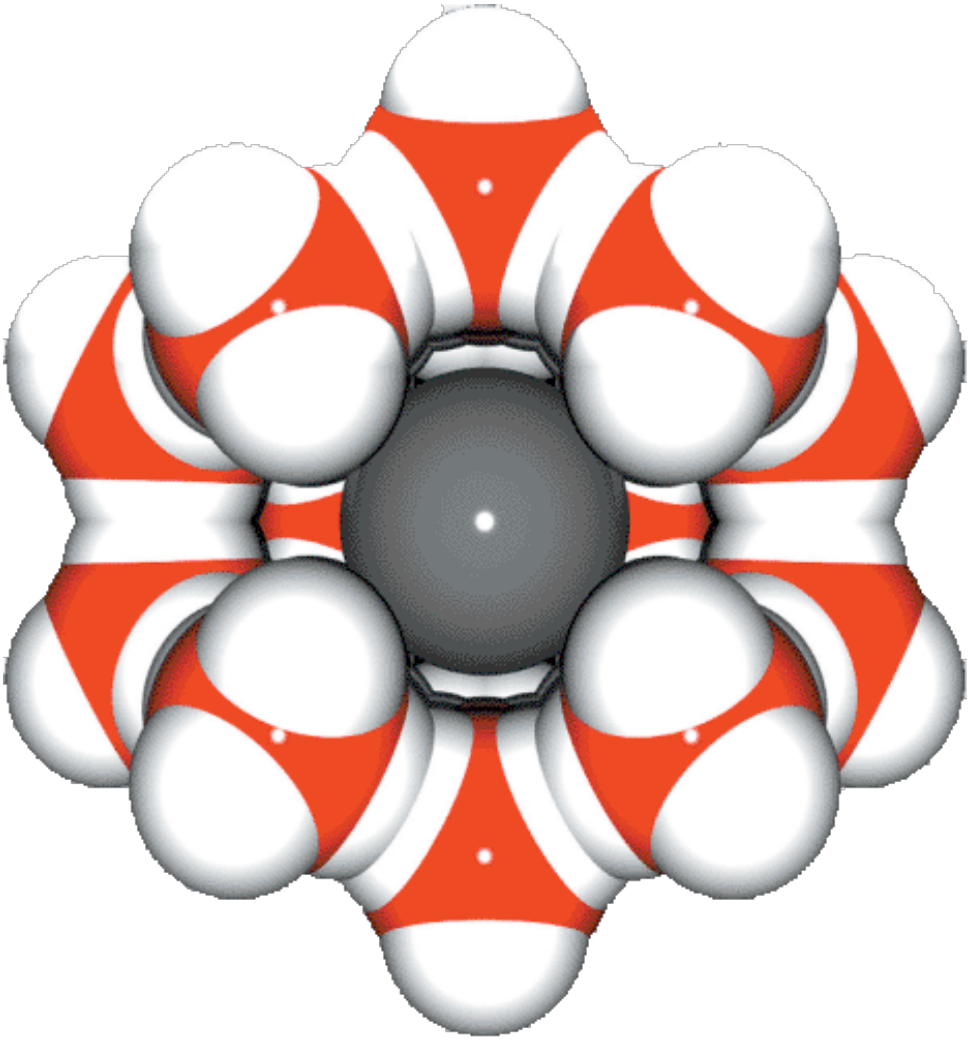


FIGURE 6.39 Representation of the structure of methane hydrate.

The formation of methane hydrate requires particular conditions of temperature and pressure. It is stable at depths greater than 300 m, where the water temperature is around 2 °C. However, a rise in the temperature of the Earth's oceans by only a few degrees could lead to conditions under which methane hydrate is no longer stable. In this case, it would decompose to liquid water and gaseous methane, leading to the release of a vast amount of gaseous methane (some estimates put the figure at around 10^{16} kg of carbon) into the atmosphere. This would almost certainly result in significant warming of the atmosphere, and, indeed, such a scenario has been postulated as the cause of previous warming events on planet Earth.

The mining of methane hydrate as a potential fuel for power stations has been proposed, and, if it was released into the atmosphere, the CO_2 formed from burning the evolved methane would have less of an effect as a greenhouse gas than would the gaseous methane itself.

Binary Hydrogen Compounds

Boiling points of binary hydrogen compounds illustrate the interplay between different types of intermolecular forces. Figure 6.40 shows that there are periodic trends in the boiling points of these

compounds. In general, the boiling points of the binary hydrogen compounds increase from top to bottom of each column of the periodic table. This trend is due to increasing dispersion forces; the more electrons the molecule has, the stronger are the dispersion forces and the higher is the boiling point. In group 16, for example, H_2S (18 electrons) boils at 213 K, H_2Se (36 electrons) at 232 K and H_2Te (54 electrons) at 269 K.

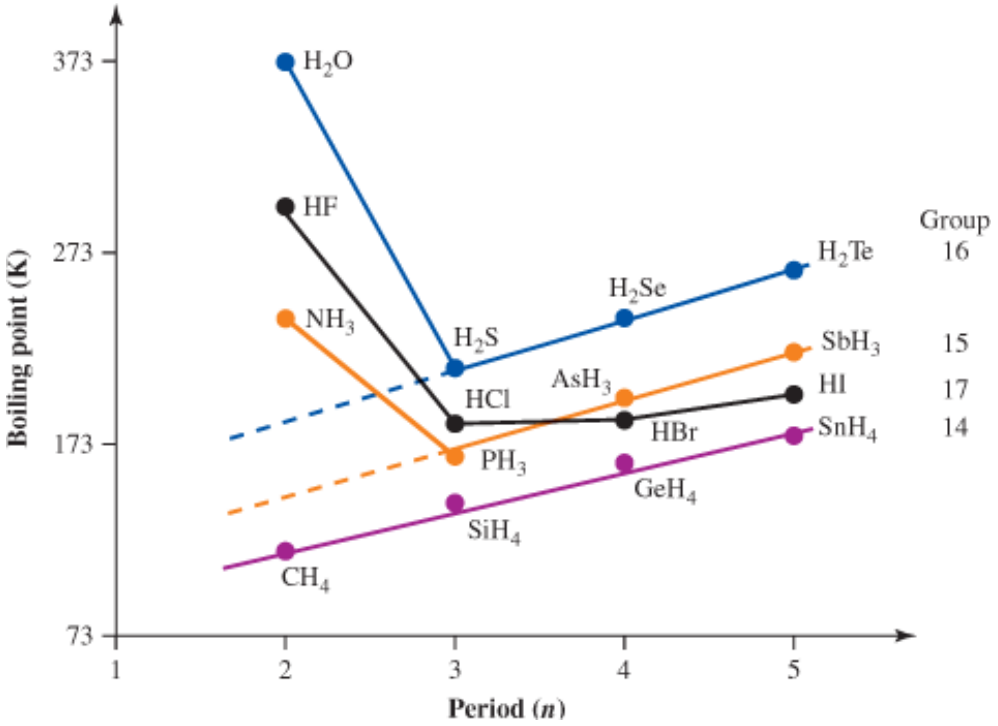


FIGURE 6.40 Periodic trends in the boiling points of binary hydrogen compounds. Notice that H_2O, HF and NH_3 are exceptions to the trends.

As figure 6.40 shows, ammonia, water and hydrogen fluoride depart dramatically from the periodic behaviour. This is because their molecules experience particularly large intermolecular forces resulting from hydrogen bonding. In hydrogen fluoride, for instance, hydrogen bonds form between the highly electronegative fluorine atom of one HF molecule and the electron-deficient hydrogen atom of another HF molecule. Similar interactions among many HF molecules result in chains of hydrogen-bonded HF molecules leading to a boiling point much higher than those of HCl, HBr and HI. Note, however, that even the boiling point of HCl is higher than if it were on a trendline parallel to those for groups 15 and 16, indicating that weak hydrogen bonds may be formed.

Fluorine has the highest electronegativity of any element, so the strongest *individual* hydrogen bonds are those in HF. Every hydrogen atom in liquid HF is involved in a hydrogen bond, but there is only one polar hydrogen atom per molecule. Thus, each HF molecule may participate in two hydrogen bonds with two other HF partners. There is one hydrogen bond involving the partially positive hydrogen atom and a second involving the partially negative fluorine atom, leading to the formation of HF chains.

Water has a substantially higher boiling point than hydrogen fluoride, which indicates that the *overall* hydrogen bonding in H_2O is stronger than that in HF, even though the individual hydrogen bonds in HF are stronger. The higher boiling point of water reflects the fact that it forms more hydrogen bonds of significant strength per molecule than hydrogen fluoride. A water molecule has two hydrogen atoms that can form hydrogen bonds and two nonbonding electron pairs on each oxygen atom. This permits every water molecule to be involved in four hydrogen bonds to four other H_2O partners, as shown in figure 6.41a.

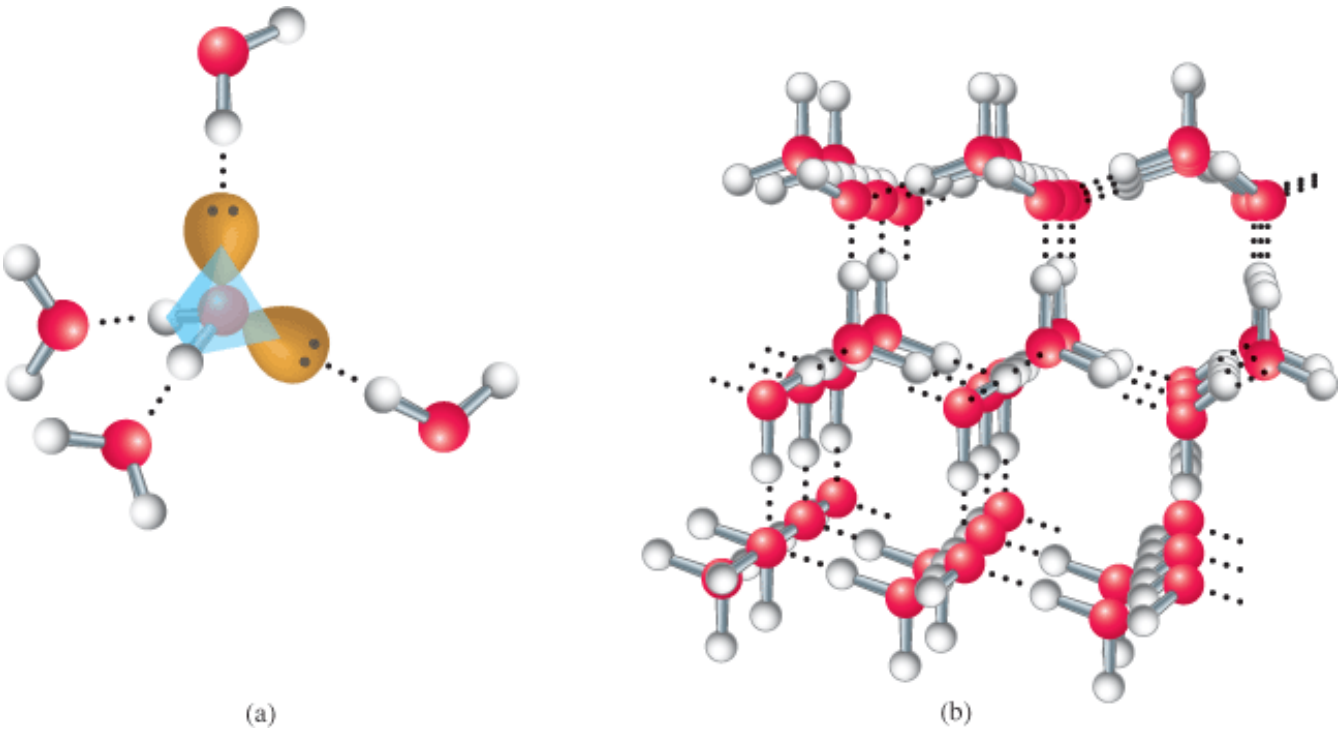


FIGURE 6.41 Two representations of structure of ice.

(a) Each oxygen atom is at the centre of a distorted tetrahedron of hydrogen atoms. The tetrahedron is composed of two short covalent O—H bonds and two long H…O hydrogen bonds.

(b) Water molecules in ice are held in a network of these tetrahedra.

Hydrogen bonding in ice creates a three-dimensional network (figure 6.41) that puts each oxygen atom at the centre of a distorted tetrahedron. Two arms of the tetrahedron are regular covalent O—H bonds, whereas the other two arms of the tetrahedron are hydrogen bonds to two different water molecules.

Therefore, both the strength *and* number of hydrogen bonds that a binary hydrogen compound *d* can form determine its boiling point. We will discuss the role of hydrogen bonding in solids in the next chapter.

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SUMMARY

The States of Matter

The three most important states of matter are solid, liquid and gas. Most substances can exist in any of these states, and the state adopted by a particular substance under defined conditions is determined by the magnitude of the forces between individual atoms, molecules or ions in the substance.

Describing Gases

Gases occupy all of the space in which they are contained. The pressure exerted by a gas is due to the collisions of rapidly moving gas atoms or molecules with the walls of the container. The SI unit of pressure is the pascal (Pa). Atmospheric pressure is measured with a barometer in which a pressure of 1 standard atmosphere (1 atm) will support a column of mercury 760 mm high. This is a pressure of 760 torr. By definition, 1 atm = 1.013 25 × 10^5 pascals (Pa), and standard pressure $(p^{\ominus}) = 1 \times 10^5\ \text{Pa}$. Manometers are used to measure the pressure of trapped gases. Boyle's Law, Charles' Law and Avogadro's Law describe the relationships between volume and pressure, volume and temperature, and volume and amount of a gas, respectively. The combination of these three laws gives the ideal gas equation:

$$pV = nRT$$

where p = pressure (Pa), V = volume (m^3), n = amount (mol), R = the gas constant (8.314 J mol^{-1} K^{-1}) and T is temperature (K).

Molecular View of Gases

In order to determine the kinetic energy of a gas molecule, it is necessary to measure the speed with which it is moving. This can be done using a molecular beam apparatus. This shows that all molecules within a particular gas sample do not move with the same speed and that small molecules move, on average, faster than large molecules. However, the most probable kinetic energy of a gas molecule is the same, regardless of its mass, and all gases have an identical molecular kinetic energy distribution. The average kinetic energy of a mole of any gas is related to the temperature in kelvin through the equation:

$$E_{\text{kinetic,molar}} = \frac{3}{2}RT$$

An ideal gas is one for which the volume of the molecules and the forces between the molecules are so small as to be insignificant. An ideal gas obeys the ideal gas equation exactly. Real gases approximate ideal behaviour under conditions of low pressure and high temperature.

The root-mean-square speed of a gas $(\bar{u}_{\text{RMS}})$ can be found from the equation:

$$\bar{u}_{\text{RMS}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

The movement of gas molecules can be described as either effusion (the movement of molecules into a vacuum) or diffusion (the movement of one type of molecule through molecules of the same or another type).

Gas Mixtures

Each gaseous component in a mixture of ideal gases exerts a partial pressure. The sum of partial pressures of all gases in a mixture equals the total pressure. This is a statement of Dalton's law of partial pressures, which can also be expressed as:

$$p_{\text{total}} = p_1 + p_2 + p_3 + \ldots + p_i$$

The mole fraction (x_A) of a substance A equals the ratio of the amount of A(n_A), to the total amount (n_{total}) of all the components of a mixture, i.e. $x_A = \frac{n_A}{n_{total}}$. In terms of mole fractions, $p_A = x_A p_{total}$. The composition of a gas mixture can also be expressed in terms of parts per million or parts per billion.

Applications of the Ideal Gas Equation

Combination of the ideal gas equation with the stoichiometric equation, $n = \frac{m}{M}$, allows determination of the molar mass and density of an unknown gas.

Gas Stoichiometry

The ideal gas equation can be used to determine amounts, through rearrangement into the form $n_i = \frac{p_i V}{RT}$, and can therefore be used in stoichiometric calculations involving pure gases and gas mixtures.

Real Gases

Intermolecular forces are partially responsible for the fact that real gases do not exactly obey the ideal gas laws. The variation from ideal behaviour can be shown by plotting $\frac{pV}{nRT}$ versus pressure; for an ideal gas, $\frac{pV}{nRT}$ should always equal 1. Values less than 1 are a result of significant intermolecular interactions between individual gas molecules, while values greater than 1 arise from the nonzero volume of the gas molecules. Every gas shows deviation from ideal behaviour at high pressures and at temperatures near the condensation point. The van der Waals equation for a real gas:

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

makes corrections for the volume of the gas molecules and for the attractive force between them. The van der Waals constant a reflects the attractive forces between molecules, whereas the constant b reflects the relative size of the gas molecules. Melting points and, especially, boiling points give good indications of the strengths of intermolecular forces. The normal boiling point is the temperature at which the average kinetic energy of molecular motion balances the attractive energy of intermolecular attractions at a pressure of 1.013×10^5 Pa. Under these conditions, the substance is converted from a liquid to a gas in a process called vaporisation. The reverse process is called condensation. The normal freezing point is the temperature at which a liquid solidifies at a pressure of 1.013×10^5 Pa.

Intermolecular Forces

There are three general types of intermolecular forces: dispersion forces, dipole-induced dipole forces and hydrogen bonds. These range in strength from 0.1–5 kJ mol^{-1}, 5–20 kJ mol^{-1} and 5–50 kJ mol^{-1} respectively.

Dispersion forces result from the asymmetrical distribution of a molecule's electrons at any instant of time, leading to the formation of instantaneous dipoles within the molecule. The ease of distortion of an electron cloud is called the polarisability of the molecule; molecules with large electron clouds have high polarisabilities and consequently display large dispersion forces. Dispersion forces occur in all molecules.

Polar molecules attract each other by dipolar forces, which arise because the positive end of a permanent dipole attracts the negative end of a dipole in a neighbouring molecule.

Hydrogen bonding, a special case of dipole–dipole attractions, occurs between molecules in which hydrogen is covalently bonded to a small, very electronegative atom — principally, nitrogen, oxygen or fluorine — and molecules containing atoms that have lone pairs of electrons (again mainly nitrogen, oxygen or fluorine). Hydrogen bonding is much stronger than the other types of inter-molecular attractions and is the reason for the anomalous behaviour of water, ammonia and hydrogen fluoride when compared with other binary hydrogen compounds.

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KEY CONCEPTS AND EQUATIONS

Ideal gas equation *(section 6.2)*

This can be used when any three of the four variables p, V, T or n, are known and we wish to calculate the value of the fourth.

$$pV = nRT$$

Dalton's law of partial pressures *(section 6.4)*

We use this law to calculate the partial pressure of one gas in a mixture of gases. This requires the total pressure and either the partial pressures of the other gases or their mole fractions. If the partial pressures are known, their sum is the total pressure.

$$p_{\text{total}} = p_1 + p_2 + p_3 + \ldots + p_i$$

Mole fractions *(section 6.4)*

Given the composition of a gas mixture, we can calculate the mole fraction of a component. The mole fraction can then be used to find the partial pressure of the component given the total pressure. If the total pressure and partial pressure of a component are known, we can calculate the mole fraction of the component.

$$p_A = x_A p_{\text{total}}$$

Relationship between intermolecular forces and molecular structure *(section 6.8)*

From the molecular structure, we can determine whether a molecule is polar and whether it has N—H or O—H bonds. This lets us predict and compare the strengths of intermolecular attractions. You should be able to identify when dispersion forces, dipolar forces or hydrogen bonding occur.

van der Waals equation *(section 6.8)*

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Boiling points of substances *(section 6.8)*

These allow us to compare the strengths of intermolecular forces in substances based on their boiling points.

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REVIEW QUESTIONS

Describing Gases

6.1 Describe what would happen to the barometer in figure 6.2 if the tube holding the mercury had a pinhole at its top.

6.2 Describe how the difference between an inflated and a flat car tyre shows that a gas exerts pressure.

6.3 Express the following in units of pascal:

(a) 455 torr

(b) 2.45 atm

(c) 0.46 torr

(d) 1.33×10^{-3} atm.

6.4 A sample of air was compressed to a volume of 20.0 L. The temperature was 298 K and the pressure was 5.00×10^5 Pa. What amount of gas was in the sample? If the sample was collected from air at a pressure of 1.00×10^5 Pa with a temperature of 298 K, what was the original volume of the gas?

6.5 Rearrange the ideal gas equation to give the following expressions.

(a) An equation that relates p_i, T_i, p_f and T_f when n and V are constant

(b) V = ?

(c) An equation that relates p_i, V_i, p_f and V_f when n and T are constant

6.6 It requires 0.255 L of air to fill a metal foil balloon to 1.000×10^5 Pa pressure at 25 °C. The balloon is tied off and placed in a freezer at -15 °C. What is the new volume of air in the balloon?

6.7 Under which of the following conditions could you use the equation $p_fV_f = p_iV_i$?

(a) A gas is compressed at constant T.

(b) A gas-phase chemical reaction occurs.

(c) A container of gas is heated.

(d) A container of liquid is compressed at constant T.

Molecular View of Gases

6.8 Redraw figure 6.6b to show the distribution of molecules if the temperature of the oven is doubled.

6.9 Draw a single graph that shows the speed distributions of N_2 at 200 K, N_2 at 300 K and He at 300 K.

6.10 Calculate the root-mean-square speed and average kinetic energy per mole for each of the following.

(a) He at 627 °C

(b) O_2 at 27 °C

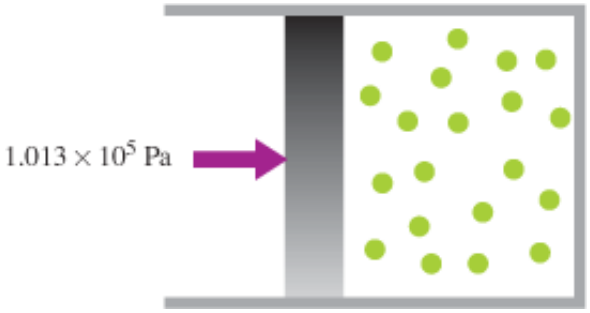
(c) SF_6 at 627 °C

6.11 Explain in molecular terms why each of the following statements is true.

(a) At very high pressure, no gas behaves ideally.

(b) At very low temperature, no gas behaves ideally.

6.12 The figure below represents an ideal gas in a container with a movable friction-free piston.



(a) The external pressure on the piston exerted by the atmosphere is 1.013×10^5 Pa. If the piston is not moving, what is the pressure inside the container? Explain in terms of molecular collisions.

(b) Redraw the sketch to show what would happen if the temperature of the gas in the container is doubled. Explain in terms of molecular collisions.

6.13 Describe the molecular changes that account for the result in question 6.6

6.14 Determine the root-mean-square speed of SF_6 molecules at 1.01×10^5 Pa and 27 °C.

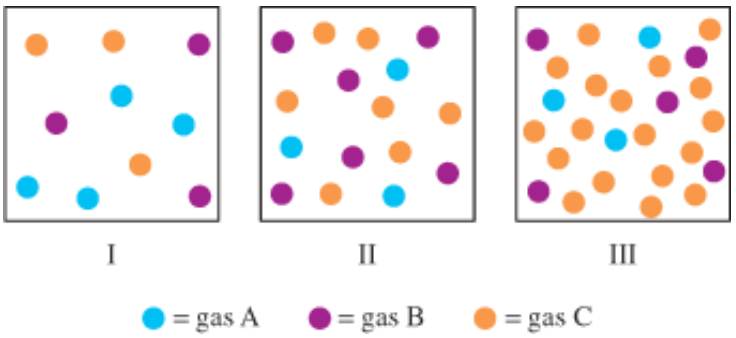
6.15 A student proposes to separate CO from N_2 by an effusion process. Is this likely to work? Why or why not?

Gas Mixtures

6.16 The concentration of NO_2 in a smoggy atmosphere was measured as 0.78 ppm. The barometric pressure was 1.011×10^5 Pa. Calculate the partial pressure of NO_2 in Pa.

6.17 In dry atmospheric air, the four most abundant components are N_2, $x = 0.7808$; O_2, $x = 0.2095$; Ar, $x = 9.34 \times 10^{-3}$; and CO_2, $x = 3.25 \times 10^{-4}$. Calculate the partial pressures of these four gases, in Pa, under standard atmospheric conditions.

6.18 The figures shown below represent very small portions of three gas mixtures, all at the same volume and temperature.



(a) Which sample has the highest partial pressure of gas A?

(b) Which sample has the highest mole fraction of gas B?

(c) In sample III, what is the concentration of gas A in ppm?

6.19 A sample of car exhaust is analysed. The gas contains 487.4 ppm CO_2, 10.3 ppb NO and 4.2 ppb CO. Calculate the partial pressures of these gases if the exhaust is emitted at 113.1 kPa pressure.

Applications of the Ideal Gas Equation

6.20 What is the density (g L^{-1}) of SF_6 gas at 1.01×10^5 Pa and 27 °C?

Gas Stoichiometry

6.21 Humans consume glucose to produce energy. The products of glucose consumption are CO_2 and

H_2O.

$$C_6H_{12}O_6(s) + O_2(g) \rightarrow CO_2\,(g) + H_2O(1) \quad \text{(unbalanced)}$$

What volume of CO_2 is produced under body conditions (37 °C, 1.013×10^5 Pa) during the consumption of 4.65 g of glucose?

6.22 Sodium metal reacts with molecular chlorine gas to form sodium chloride. A closed container of volume 3.00×10^3 mL contains chlorine gas at 27 °C and 1.67×10^5 Pa. Then 6.90 g of solid sodium is introduced, and the reaction goes to completion. What is the final pressure if the temperature rises to 47 °C?

6.23 Ammonia is produced industrially by reacting N_2 with H_2 at elevated pressure and temperature in the presence of a catalyst.

$$N_2(g) + H_2(g) \rightarrow NH_3(g) \quad \text{(unbalanced)}$$

Assuming 100% yield, what mass of ammonia would be produced from a 1 : 1 mole ratio mixture in a reactor that has a volume of 8.75×10^3 L, under a total pressure of 275×10^5 Pa at 455 °C?

6.24 In practice, the reaction of question 6.23 gives a yield of only 13%. Repeat the calculation taking this into account.

Real Gases

6.25 Predict whether the effects of molecular volume and intermolecular attractions become more or less significant when the following changes are imposed.

(a) A gas expands into a larger volume at constant temperature.

(b) More gas is introduced into a container of constant volume at constant temperature.

(c) The temperature of a gas increases at constant pressure.

6.26 From the following experimental data, calculate the percentage deviation from ideal behaviour: 1.00 mol CO_2 in a 1.20 L container at 40.0 °C exerts 19.7×10^5 Pa pressure.

6.27 Chlorine gas is commercially produced by electrolysis of sea water and is stored under pressure in metal tanks. A typical tank has a volume of 15.0 L and contains 1.25 kg of Cl_2. Use the van der Waals equation to calculate the pressure in this tank if the temperature is 295 K, and compare the result with the ideal gas value.

Intermolecular Forces

6.28 Arrange the following in order of ease of liquefaction: CCl_4, CH_4 and CF_4. Explain your ranking.

6.29 Arrange the following in order of increasing boiling point: Ar, He, Ne and Xe. Explain your ranking.

6.30 List ethanol, CH_3CH_2OH, propane, $CH_3CH_2CH_3$, and pentane, $CH_3CH_2CH_2CH_2CH_3$, in order of increasing boiling point, and explain what features determine this order.

6.31 Which of the following will form hydrogen bonds with another molecule of the same substance? Draw molecular pictures illustrating these hydrogen bonds.

(a) CH_2Cl_2

(b) H_2SO_4

(c) H_3COCH_3

(d) H_2NCH_2COOH

6.32 Which of the following molecules form hydrogen bonds with water? Draw molecular pictures

illustrating these hydrogen bonds.

(a) CH_4

(b) I_2

(c) HF

(d) H_3COCH_3

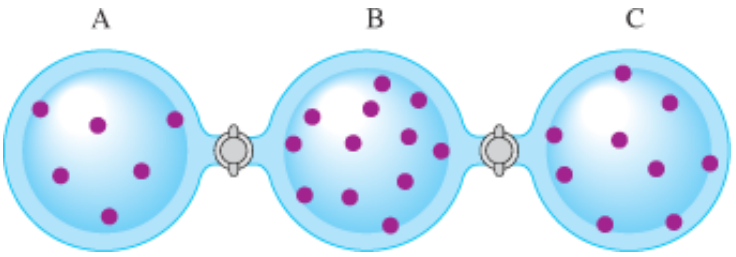
(e) $(CH_3)_3COH$

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REVIEW PROBLEMS

6.33 Nitrogen gas is available commercially in pressurised 9.50 L steel cylinders. If a tank has a pressure of 145×10^5 Pa at 298 K, what amount of N_2 is in the tank? What is the mass of N_2 in the tank?

6.34 The figure below shows three chambers with equal volumes, all at the same temperature, connected by closed valves. Each chamber contains helium gas, with amounts proportional to the number of atoms shown.



Answer each of the following questions, briefly stating your reasoning.

(a) Which of the three has the highest pressure?

(b) If the pressure in B is 1.0×10^5 Pa, what is the pressure in A?

(c) If the pressure in A starts at 1.0×10^5 Pa, and then all of the atoms from B and C are transferred to A, what will be the new pressure?

(d) If the pressure in B is 0.50×10^5 Pa, what will the pressure be after the valves are opened?

6.35 At an altitude of 40 km above the Earth's surface, the temperature is about –25 °C, and the pressure is about 4.0×10^2 Pa. Calculate the average molecular speed of ozone, O_3, at this altitude.

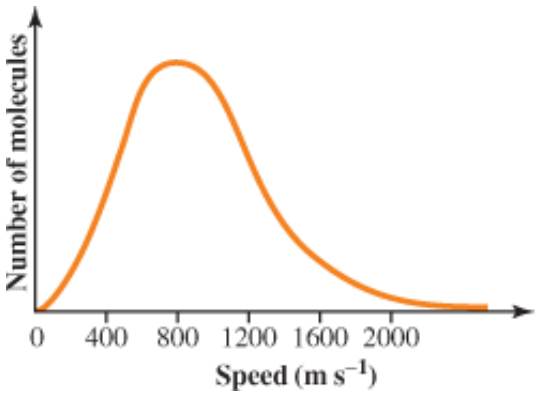
6.36 Molecular clouds composed mostly of hydrogen molecules have been detected in interstellar space. The molecular density in these clouds is about 10^{10} molecules per m^3, and their temperature is around 25 K. What is the pressure in such a cloud?

6.37 Describe a gas experiment that would show that the element oxygen exists naturally as diatomic molecules.

6.38 A mixture of cyclopropane gas, C_3H_6, and oxygen, O_2, in a 1.00 : 4.00 mole ratio is used as an anaesthetic. What mass of each of these gases is present in a 2.00 L bulb at 23.5 °C if the total pressure is 1.00×10^5 Pa?

6.39 Consider two gas bulbs of equal volume, one filled with H_2 gas at 0 °C and 2×10^5 Pa, the other containing O_2 gas at 25 °C and 1×10^5 Pa. Which bulb has (a) more molecules (b) a greater mass (c) a higher average kinetic energy of molecules and (d) a higher average molecular speed?

6.40 Molecular beam experiments on ammonia at 425 K give the speed distribution shown in the figure below.



(a) What is the most probable speed?

(b) What is the most probable kinetic energy?

6.41 A sample of gas is found to exert a pressure of 7.00×10^4 Pa when it is in a 3.00 L flask at 0.00 °C. Calculate:

(a) the new volume if p becomes 1.01×10^5 Pa and T is unchanged

(b) the new pressure if V becomes 2.00 L and T is unchanged

(c) the new pressure if the temperature is raised to 50.0 °C and V is unchanged.

6.42 Determine whether each of the following statements is true or false. If false, rewrite the statement so that it is true.

(a) At constant T and V, p is inversely proportional to the amount of gas.

(b) At constant V, the pressure of a fixed amount of gas is directly proportional to T.

(c) At fixed n and V, the product of p and T is constant.

6.43 A 3.00 g sample of an ideal gas at 22 °C and 0.969×10^5 Pa occupies 0.963 L. What is its volume at 15 °C and 1.00×10^5 Pa?

6.44 Recently, carbon dioxide levels at the South Pole reached 374.6 parts per million by volume. (The 1958 reading was 314.6 ppm by volume.) Convert this reading to a partial pressure in Pa. At this level, how many CO_2 molecules are there in 1.0 L of dry air at –45 °C?

6.45 List the different kinds of forces that must be overcome to convert each of the following from a liquid to a gas.

(a) NH_3

(b) $CHCl_3$

(c) CCl_4

(d) CO_2

6.46 For each of the following pairs, identify which has the higher boiling point, and identify the type of force that is responsible.

(a) H_3COCH_3 and CH_3OH

(b) SO_2 and SiO_2

(c) HF and HCl

(d) Br_2 and I_2

6.47 Which gas deviates more from ideal $\frac{pV}{nRT}$ behaviour, F_2 or Cl_2?

Explain your choice.

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6.48 Two chambers are connected by a valve. One chamber has a volume of 15 L and contains N_2 gas at a pressure of 2.0×10^5 Pa. The other has a volume of 1.5 L and contains O_2 gas at 3.0×10^5 Pa. The valve is opened, and the two gases are allowed to mix thoroughly. The temperature is constant at 300 K throughout this process.

(a) What amount of each of N_2 and O_2 is present?

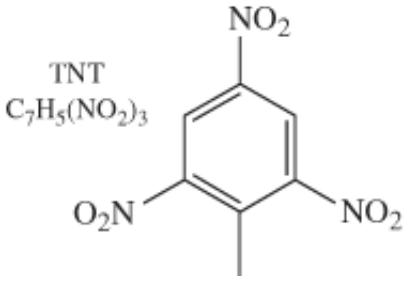
(b) What are the final pressures of N_2 and O_2, and what is the total pressure?

(c) What fraction of the O_2 is in the smaller chamber after mixing?

6.49 Liquid oxygen, used in some large rockets, is produced by cooling dry air to -183 °C. How many litres of dry air at 25 °C and 1.00×10^5 Pa have to be processed to produce 150 L of liquid oxygen (density = 1.14 g mL^{-1})? Assume that air is 21% O_2 by volume.

6.50 In an explosion, a compound that is a solid or a liquid decomposes very rapidly, producing large volumes of gas. The force of the explosion results from the rapid expansion of the hot gases. For example, TNT (trinitrotoluene) explodes according to the following balanced equation.

$$2C_7H_5(NO_2)_3(s) \rightarrow 12CO(g) + 2C(s) + 5H_2(g) + 3N_2(g)$$

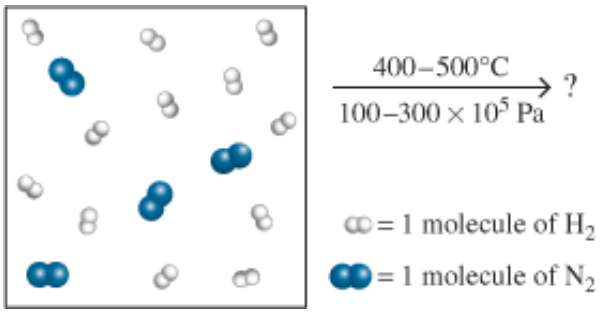


(a) What amount of gas is produced in the explosion of 1.0 kg of TNT?

(b) What volume will these gases occupy if they expand to a total pressure of 1.0×10^5 Pa at 25 °C?

(c) Calculate the partial pressure of each gas at 1.0×10^5 Pa total pressure.

6.51 The Haber synthesis of ammonia occurs in the gas phase at high temperature (400 to 500 °C) and pressure (100 to 300×10^5 Pa). The starting materials for the Haber synthesis are placed inside a container, in proportions shown in the figure below.

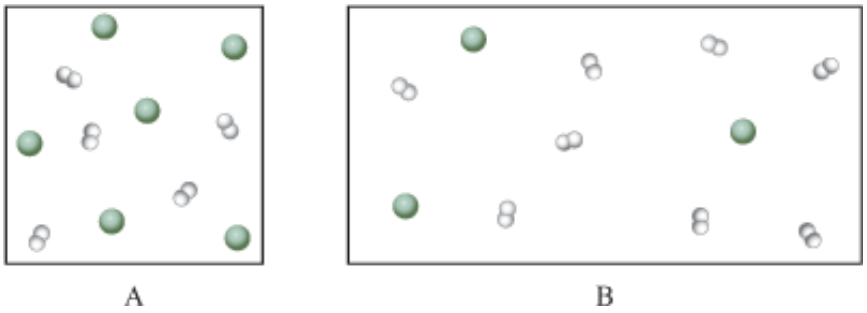


Assuming 100% yield, sketch the system at the end of the reaction.

6.52 People often remark that 'the air is thin' at higher elevation. Explain this comment in molecular terms using the fact that the atmospheric pressure at the top of Mount Everest is about 3.33×10^4 Pa.

6.53 The figures shown below represent mixtures of argon atoms and hydrogen molecules. The volume

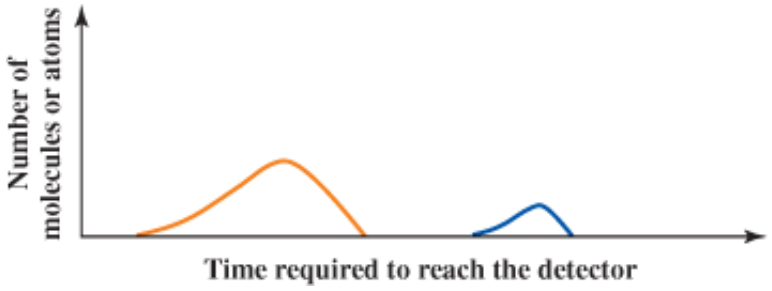
of container B is twice the volume of container A.



(a) Which container has a higher total gas pressure? Explain.

(b) Which container has a higher partial pressure of molecular hydrogen? Explain.

(c) One of the two gas mixtures (A or B) was used in a pulsed molecular beam experiment. The result of the experiment is shown below. Which of the two gas samples, A or B, was used for this experiment? Explain.



6.54 A 0.1054 g mixture of $KClO_3$ and a catalyst was placed in a quartz tube and heated vigorously to drive off all the oxygen as O_2. The O_2 was collected at 25.17 °C and a pressure of 1.012×10^5 Pa. The volume of gas collected was 22.96 mL.

(a) What amount of O_2 was produced?

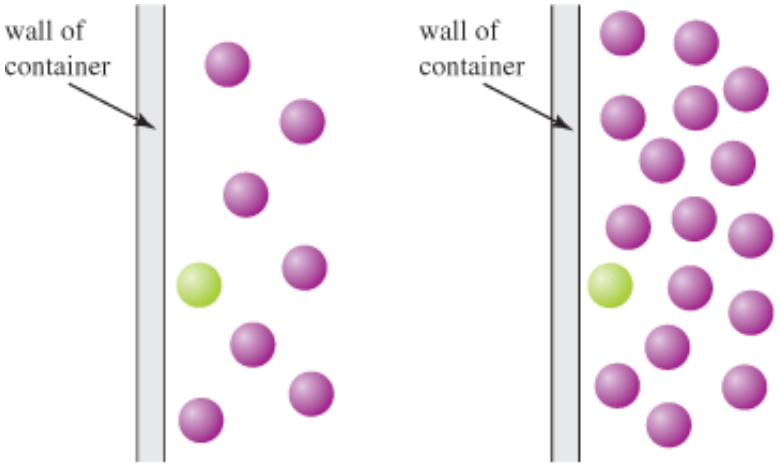
(b) What amount of $KClO_3$ was in the original mixture?

(c) What was the mass percent of $KClO_3$ in the original mixture?

6.55 Does the boiling point of HCl (see figure 6.40) suggest that it may form hydrogen bonds? Explain your answer and draw a molecular picture that shows the possible hydrogen bonds between HCl molecules.

6.56 Molecular hydrogen and atomic helium both have two electrons, but He boils at 4.2 K, whereas H_2 boils at 20 K. Neon boils at 27.1 K, whereas methane, which has the same number of electrons, boils at 114 K. Explain why molecular substances boil at a higher temperature than atomic substances with the same number of electrons.

6.57 In the two figures shown below, the green molecule is about to strike the wall of its container. Assuming all other conditions are identical, which collision will exert greater pressure on the wall? Explain in terms of intermolecular interactions.



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KEY TERMS

barometer
condensation
Dalton's law of partial pressures
diffusion
dipole-induced dipole force
dipole–dipole force
dispersion force
effusion
gas constant
hydrogen bonding
ideal gas
ideal gas equation
intermolecular forces
manometer
mole fraction (x)
normal boiling point
normal freezing point
partial pressure
parts per billion (ppb)
parts per million (ppm)
pascal (Pa)
polarisability
pressure
root-mean-square speed
van der Waals equation
vaporisation

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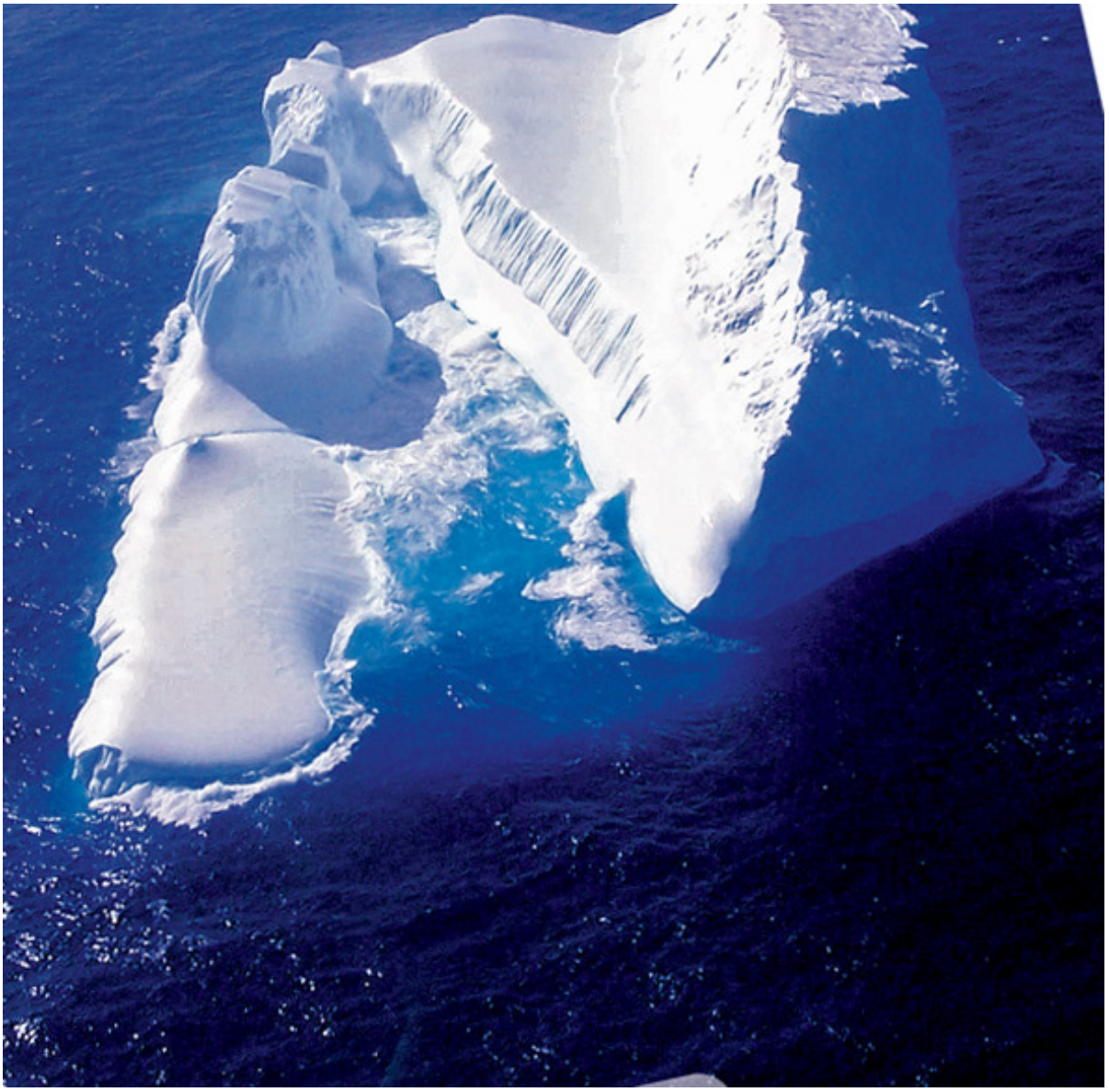
CHAPTER

7 Condensed Phases: Liquids and Solids

In the previous chapter, we learned about gases, one of the three common states of matter. The icebergs shown on this page, pictured off Dunedin in 2006, exemplify the other two common states of matter, liquid and solid. Ice is extremely unusual because it is *less* dense than its liquid phase and, therefore, floats on the surface of water. This has wide-ranging consequences for life on Earth; it means that ice will accumulate at the surface of a body of water, rather than at the bottom, ensuring that aquatic life can survive even in cold winters. It also means that a full bottle of drink that you put into the freezer might crack because water expands when it changes phase from liquid to solid.

In this chapter we will investigate liquids and solids, the two condensed phases of matter. We will also look at what happens when substances change phase between solid, liquid and gas, and how these phase changes depend on both temperature and pressure. Finally we will examine order in solids and some applications of modern materials.





KEY TOPICS

7.1 Liquids
7.2 Solids
7.3 Phase changes
7.4 Order in solids
7.5 X-ray diffraction
7.6 Amorphous solids
7.7 Crystal imperfections
7.8 Modern ceramics

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7.1 Liquids

In the previous chapter, we saw that, although many gases behave like an ideal gas under ambient conditions, all of them have intermolecular forces which may cause deviations from ideal behaviour. One consequence of these intermolecular forces in gases is that a gas condenses to a liquid if it is cooled sufficiently. Condensation occurs when the average kinetic energy of the molecules falls below the value needed for them to move about indepen dently. In a liquid, intermolecular forces are strong enough to confine the molecules to a specific volume, but not strong enough to keep molecules from moving freely within the liquid. As a consequence, like gases, liquids are fluid, and most flow easily from place to place. Unlike gases, however, liquids are compact, so they cannot expand or contract much.

Properties of Liquids

Intermolecular forces in liquids lead to three important properties: surface tension, capillary action and viscosity.

Surface tension is a measure of the resistance of a liquid to an increase in its surface area. This property is caused by attractive intermolecular forces between the molecules in a liquid. These attractive forces are known as cohesive forces.

Figure 7.1 illustrates at the molecular level why liquids exhibit surface tension. A molecule in the interior of a liquid is completely surrounded by other molecules. A molecule at a liquid surface, on the other hand, has other molecules beside it and beneath it, but very few above it in the gas phase. This difference means that there is a net attractive force on molecules at the surface that pulls them towards the interior of the liquid, resulting in as few particles as possible at the surface. A liquid will therefore adopt a shape with the minimum possible surface area. Small amounts of a liquid will adopt a spherical shape because spheres have less surface area per unit volume than any other shape. For example, water drips from a tap in nearly spherical liquid droplets. Large drops are distorted from ideal spheres by the force of gravity.

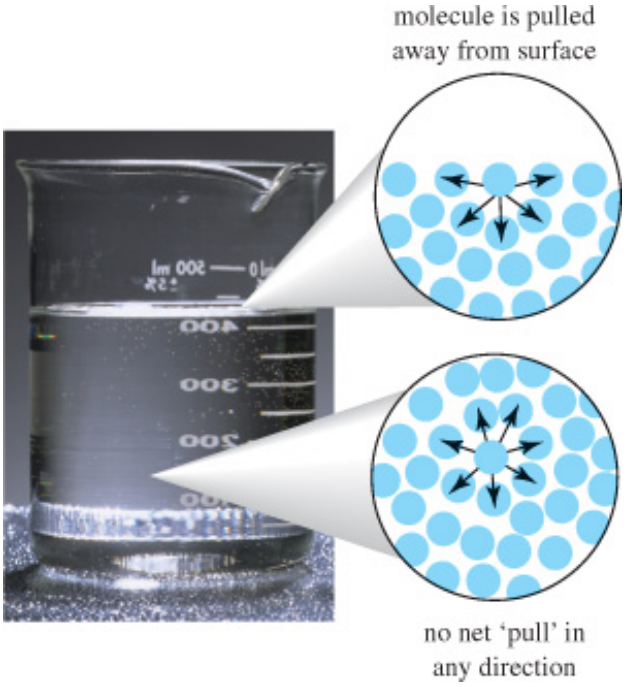


FIGURE 7.1 In the interior of a liquid (*bottom*), each molecule experiences equal forces in all directions (represented by the arrows). A molecule at the surface of a liquid (*top*) is pulled back into the liquid by intermolecular forces.

Molecules in contact with the surface of their container experience two sets of intermolecular forces.

Cohesive forces attract molecules in the liquid to one another. *Adhesive forces* attract molecules in the liquid to the walls of the container.

One result of adhesive forces is the curved surface of a liquid, called a **meniscus**. Water in a glass tube forms a concave meniscus that increases the number of water molecules in contact with the walls of the tube. This is because the adhesive forces between water and glass are stronger than the cohesive forces between water molecules.

Figure 7.2 shows another result of adhesive forces. In a tube of small enough diameter, water actually climbs the walls because the adhesive forces between water and glass are stronger than the force of gravity. This upward movement of water against the downward force of gravity is called **capillary action** and is due to attractions between polar water molecules and oxygen atoms in SiO_2 (glass). Similarly, capillary action involving sap and the cellulose walls of wood fibre plays a role in how trees transport sap from their roots to their highest branches.

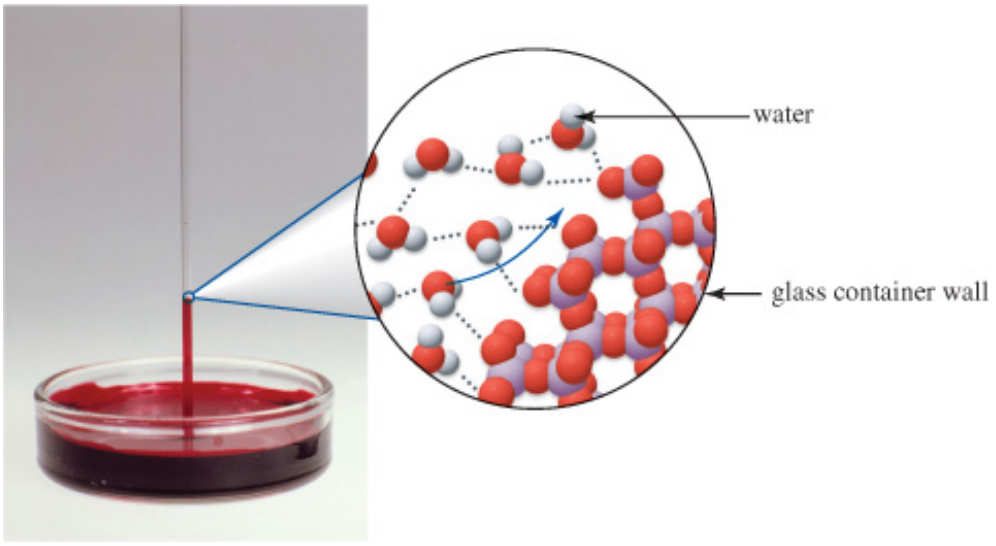


FIGURE 7.2 Water rises inside a small-diameter tube because of capillary action. The water in this photo has been coloured to show the effect of capillary action more clearly.

Water can be poured very quickly from one container to another, while oil pours more slowly, and honey sometimes seems to take forever. A liquid's resistance to flow is called its **viscosity**; the greater the viscosity, the more difficult the liquid is to pour. Viscosity is a measure of how easily molecules slide by one another. Viscosity is, therefore, affected by a combination of molecular shape and the strength of the intermolecular forces. The greater the contact area of each molecule in a liquid, the higher the viscosity of the liquid. The molecules in liquids such as water, acetone and benzene are small and compact; they have small contact areas and thus low viscosity. In contrast, molecules with a large surface area, such as the sugars in honey and the hydrocarbons found in oils, have large areas of contact and thus high viscosity.

Viscosity is affected by temperature. This dependence is quite noticeable for highly viscous substances such as honey and syrup, which are much easier to pour when hot than when cold. At higher temperature, the average kinetic energy of the molecules in the liquid is higher, which allows them to overcome the intermolecular forces more easily. Thus, viscosity decreases as temperature increases.

Vapour Pressure

Our senses tell us that molecules escape from a liquid. For example, both the smell of petrol around an open tank and the evaporation of a rain puddle in the sunshine suggest that molecules escape from the liquid into the vapour phase. The red vapour phase that can be observed above liquid bromine suggests that bromine molecules are present in both phases.

Recall from section 6.3 that any collection of molecules has a distribution of kinetic energies. In a liquid, the distribution of kinetic energies is such that molecules can move about within the liquid, but on average they do not have sufficient kinetic energy to escape into the gas phase. Nevertheless, the distribution of molecular energies guarantees that some of the molecules in any liquid have enough kinetic energy to overcome the intermolecular forces that confine the liquid. These molecules escape into the vapour phase whenever they are at the surface of the liquid. If the surface of a liquid is in contact with a gas phase, some of its molecules will escape into the gas phase.

The number of molecules of a liquid that have enough energy to escape into the vapour phase depends both on the strength of intermolecular forces within the liquid and the temperature. As figure 7.3 shows, at a particular temperature more molecules can escape from liquid bromine than from liquid water. This is because the intermolecular forces between water molecules are stronger than those between bromine molecules. A water molecule needs more kinetic energy to escape the liquid phase. Figure 7.3b illustrates that, when the temperature rises, the fraction of molecules having enough energy to escape increases.

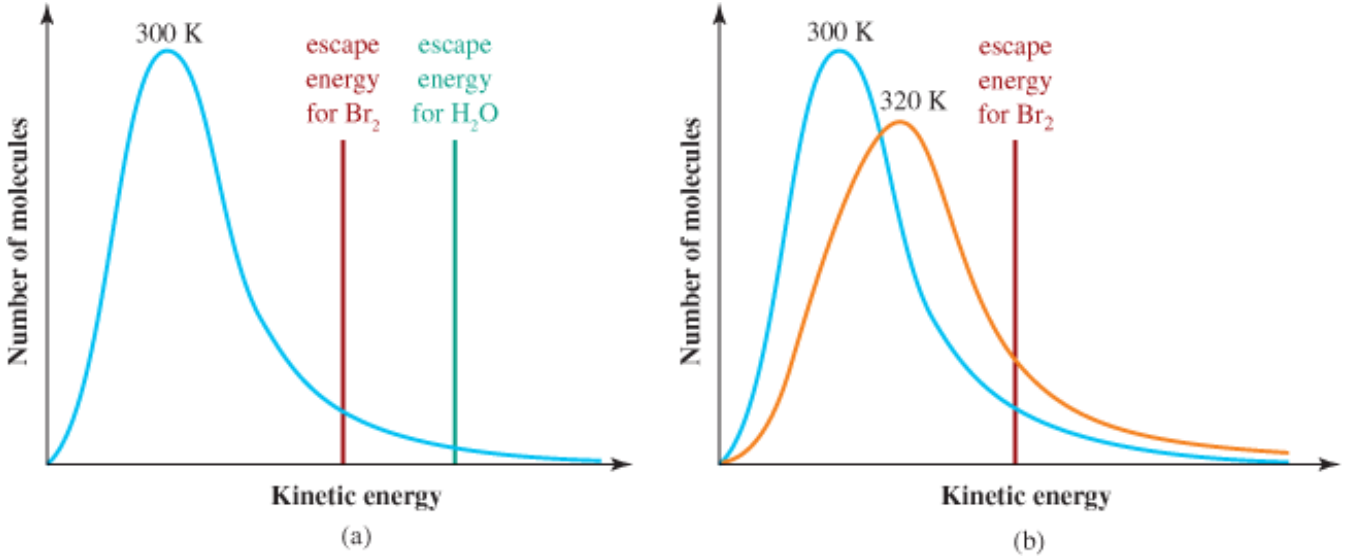


FIGURE 7.3 The fraction of molecules with enough kinetic energy to escape a liquid depends on the strength of intermolecular forces and temperature.

(a) At 300 K, more bromine molecules can escape than water molecules because bromine has weaker intermolecular forces than water.

(b) More bromine molecules can escape at 320 K (area under orange curve to the right of escape energy) than at 300 K (area under the blue curve to the right of escape energy) because there are more molecules with at least the escape energy.

A liquid in an open container continually loses molecules until eventually it has evaporated completely. However, in a closed container such as the one shown in figure 7.4, the partial pressure of the vapour increases as more and more molecules enter the gas phase. As this partial pressure builds, increasing numbers of molecules from the vapour strike the liquid surface and return to the liquid. Eventually, as figure 7.4 illustrates, the number of molecules escaping from the liquid exactly matches the number of molecules being captured by the liquid. There is no net change in the total number of molecules in the gas and the liquid, and we call this a dynamic equilibrium. The pressure at which this equilibrium exists is the **vapour pressure** of the liquid. The vapour pressure of any liquid rises with increasing temperature because more molecules have sufficient kinetic energy to escape the liquid phase into the gas phase.

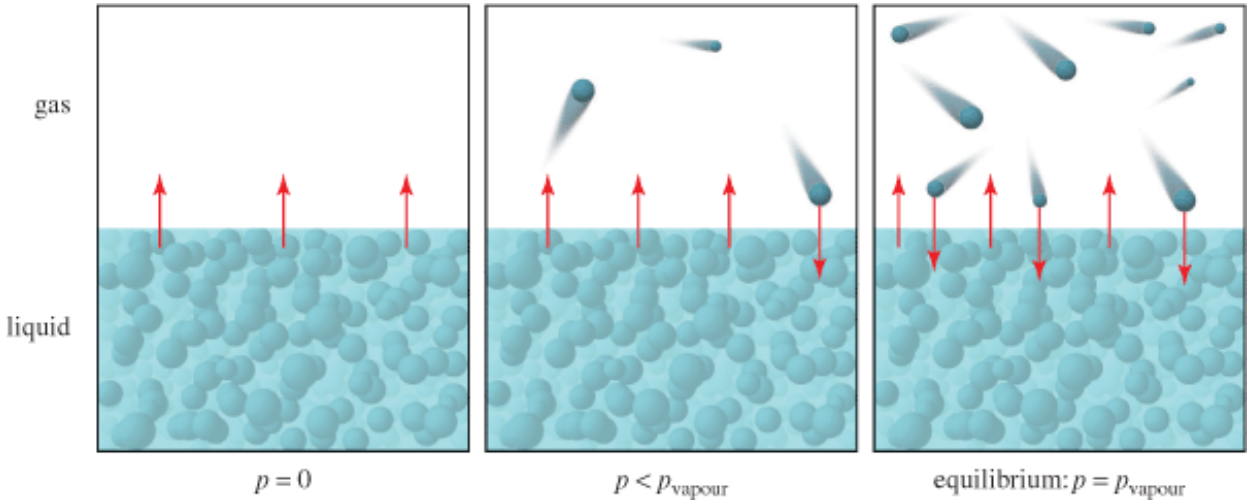


FIGURE 7.4 As the partial pressure of a substance in the gas phase above a liquid in a closed container increases (as indicated by the number of red arrows), the difference between the number of molecules escaping into the gas phase and the number re-entering the liquid phase decreases until, at the vapour pressure of the substance, equilibrium is established.

Once the vapour pressure of the liquid in an open container reaches the external pressure, the liquid starts to boil. Water, for instance, boils at 100 °C at average atmospheric pressure at sea level (1.013×10^5 Pa). As we learned in chapter 6, the temperature at which a liquid boils at this pressure is known as the normal boiling point. At lower pressure, such as we would find on top of a high mountain, the boiling point is lower because the required vapour pressure is reached at a lower temperature. For example, on top of New Zealand's Aoraki/Mount Cook, which is 3754 m high, average atmospheric pressure is 0.637×10^5 Pa and water boils at about 85 °C. Conversely, a pressure cooker works on the principle that if you increase the external pressure the boiling point increases. For instance, at normal atmospheric pressure, you cannot heat liquid water to above 100 °C, whereas in a household pressure cooker temperatures of up to 120 °C can be reached. Figure 7.5 shows the dependence of vapour pressure on temperature for a range of liquids. The variation between vapour pressures of different substances is due to the different strengths of intermolecular forces.

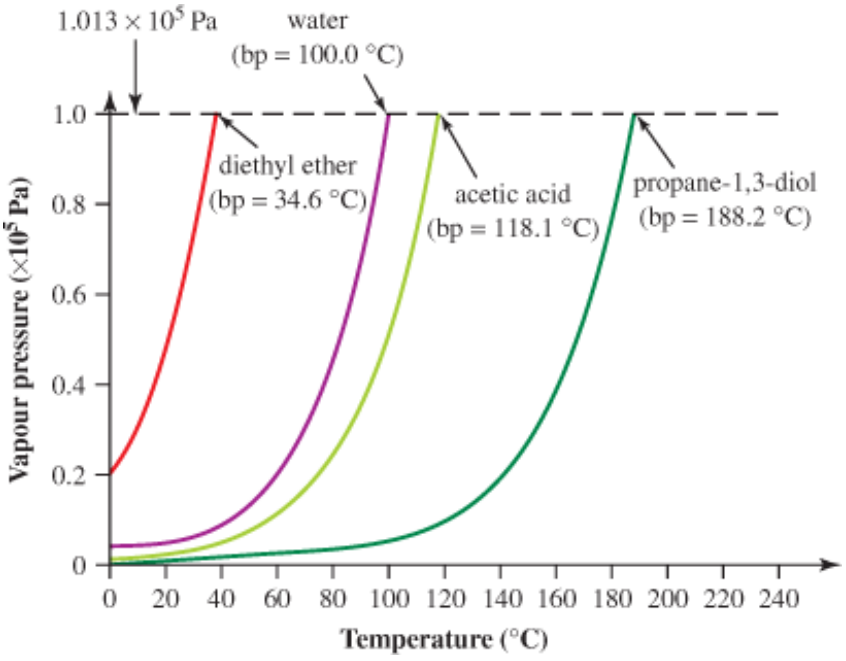


FIGURE 7.5 Vapour pressure as a function of temperature for diethyl ether, water, acetic acid and propane-1,3-diol.

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7.2 Solids

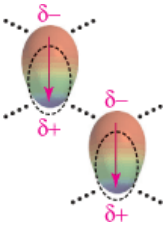
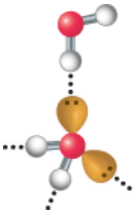
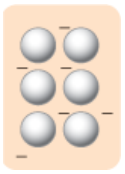
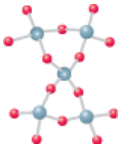
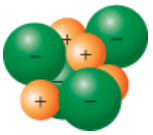
The vast majority of compounds are solids under ambient conditions. A substance is a solid when its ions, atoms or molecules are held together so strongly that they cannot easily move past each other. Unlike gases and liquids, solids are characterised by rigidity, which gives them the stable shapes that we see in structures ranging from bones to aeroplane wings. One of the most active areas of research in chemistry, physics and engineering is the development of new or improved solid materials. Solids continue to play a large role in society, from capacitors and solid-state battery components in mobile phones and laptops to new tissue-compatible solids for surgical implants. In this section, we describe the various types of solids.

Magnitudes of Forces

In chapter 6, we saw that the melting points of solids span an immense range, e.g. from 0.95 K (He) to 1808 K (Fe) for those presented in table 6.4 (p. 240). These values indicate that the forces in solids range from very small to extremely large. This is because the ions, atoms or molecules in solids can be bound together by various attractive forces: intermolecular forces, metallic bonding, covalent bonds and ionic interactions.

The molecules of a **molecular solid** are held in place by intermolecular forces: dispersion forces and dipolar interactions, including hydrogen bonds. The atoms of a **metallic solid** are held in place by delocalised bonding involving mobile electrons (p. 259). A **network solid** contains an array of covalent bonds linking every atom to its neighbours. An **ionic solid** contains cations and anions, attracted to one another by electrostatic forces as described in section 5.2. Table 7.1 contrasts the forces and energies associated with these four types of solids.

TABLE 7.1 Characteristics of different types of solids

Solid type	atomic/molecular	molecular	molecular	metallic	network	ionic
Attractive forces	dispersion	dispersion + dipolar	dispersion + dipolar + hydrogen bonding	delocalised bonding	covalent	electrostatic
Energy (kJ mol^{-1})	0.05–40	5–25	5–50	75–1000	150–500	400–4000
Example	Ar	HCl	H_2O	Cu	SiO_2	NaCl
Melting point (°C)	–189	–114	0	1088	1713	801
Schematic diagram						

Molecular Solids

Molecular solids are aggregates of molecules bound together by intermolecular forces. The forces can be dispersion forces, dipolar forces, hydrogen bonding or a combination of these.

Many larger molecules have sufficient dispersion forces to exist as solids at room temperature. One example is naphthalene, $C_{10}H_8$, the active substance in mothballs. Naphthalene is a white solid that melts at 80 °C. Naphthalene has a planar structure with a cloud of 10 π electrons delocalised above and below the molecular plane (figure 7.6). Naphthalene molecules are held in the solid state by strong dispersion forces involving these highly polarisable π electrons. The molecules in crystalline naphthalene are arranged to maximise these dispersion forces, thus leading to the formation of plate-like macroscopic crystals.

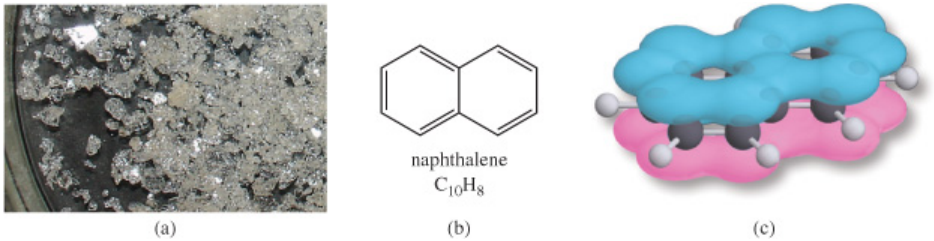


FIGURE 7.6 (a) Naphthalene, (b) the line structure of naphthalene and (c) a ball-and-stick model, overlaid with the lowest energy π bonding molecular orbital.

Dimethyl oxalate, $CH_3OC(O)C(O)OCH_3$ (figure 7.7) is an example of a molecular solid (mp = 52 °C) in which neighbouring molecules are held together predominantly by dipolar interactions. The two carbonyl C atoms have significant δ+ character, due to the fact that each is bonded to two electronegative O atoms. The δ+ C atoms are involved in attractive dipolar interactions with the δ- O atoms of neighbouring molecules.

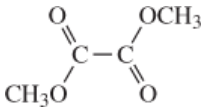


FIGURE 7.7 Structural formula of dimethyl oxalate.

In addition to dispersion and dipolar forces, molecular solids often involve hydrogen bonding. Benzoic acid, C_6H_5COOH, whose sodium salt is a common food preservative, provides a good example, as illustrated in figure 7.8. Molecules of benzoic acid are held in place by a combination of dispersion forces between the π electrons and hydrogen bonding between the —COOH groups. With fewer π electrons, benzoic acid has weaker dispersion forces than naphthalene, but its hydrogen bonding gives benzoic acid a higher melting point of 122 °C.

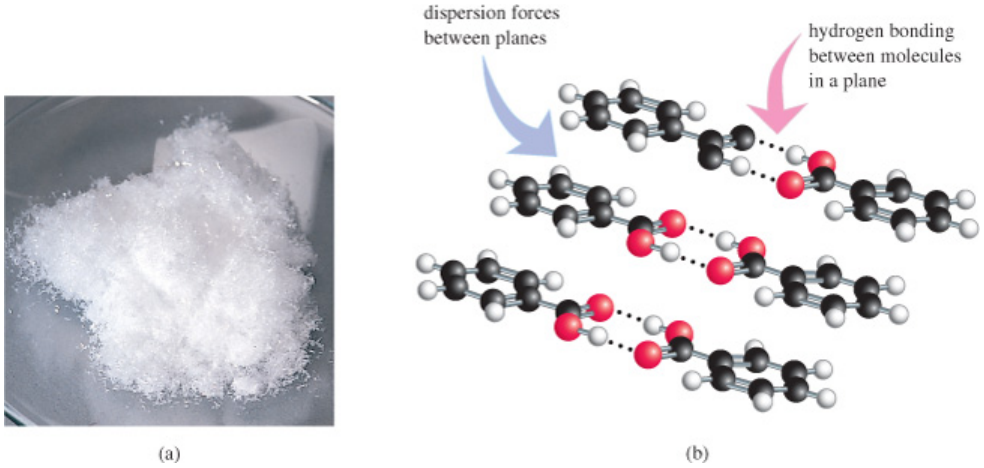


FIGURE 7.8 (a) Crystals of benzoic acid contain
(b) pairs of molecules held together head-to-head by hydrogen bonds. These pairs then stack in planes that are held together by dispersion forces.

The effect of extensive hydrogen bonding is revealed by the relatively high melting point of glucose, $C_6H_{12}O_6$, the sugar found in blood and human tissue. Glucose melts at 155 °C because each of its molecules has five —OH groups that form hydrogen bonds to neighbouring molecules (figure 7.9). Although glucose lacks the highly polarisable π electrons found in naphthalene and benzoic acid, its extensive hydrogen bonding gives this sugar the highest melting point of these three compounds.

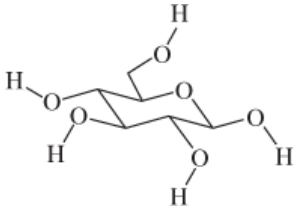


FIGURE 7.9 The structural formula of glucose, $C_6H_{12}O_6$.

Network Solids

In sharp contrast to molecular solids, network solids have very high melting points. Compare the behaviour of phosphorus and silicon, third-row neighbours in the periodic table. White phosphorus melts at 44 °C, but silicon melts at 1410 °C. White phosphorus is a molecular solid that contains individual P_4 molecules (see figure 7.10), but silicon is a network solid in which covalent bonds connect every Si atom to each of its four neighbours (see figure 7.11).

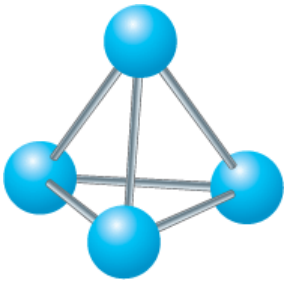


FIGURE 7.10 Representation of a P_4 molecule in white phosphorus.

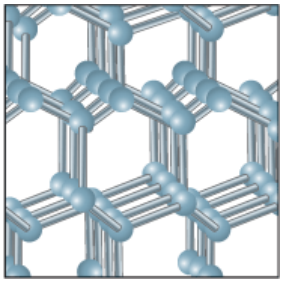


FIGURE 7.11 Part of the structural model of silicon, showing silicon atoms connected to each other to form a three-dimensional network.

The cause of the great difference in the melting points of these two elements is evident from table 7.1. Covalent bonds are much stronger than intermolecular forces. For solid silicon to melt, a significant fraction of its Si—Si covalent bonds must break. The average Si—Si bond energy is 225 kJ mol^{-1}, whereas attractive energies due to intermolecular forces in P_4 are much lower (as shown in table 7.1, intermolecular forces are generally less than 50 kJ mol^{-1}) so it takes a much higher temperature to melt silicon than white phosphorus.

Bonding patterns determine the properties of network solids. Diamond and graphite, the two forms of elemental carbon that occur naturally on Earth, have very different physical and chemical properties. Diamond contains a three-dimensional array of σ bonds, with each sp^3-hybridised carbon atom linked to each of its four neighbouring carbon atoms through covalent bonds resulting in a tetrahedral geometry around each carbon atom (identical to the Si structure mentioned above, see figure 7.12a). It is thus a network solid. Its three-dimensional network of strong covalent bonds makes diamond extremely strong and abrasive. Covalent bonds connecting atoms in three dimensions make network solids extremely durable. The sp^2 hybridised carbon atoms in graphite, in contrast, are connected to only three neighbouring carbon atoms via covalent bonds in a planar arrangement. The bonding is supplemented by delocalised π bonding above and below the plane of the σ bonds (see figure 7.12b). Each two-dimensional layer is attracted to its neighbouring layers only by dispersion forces between the π electrons. As a result, planes of carbon atoms easily slide past one another, making graphite a brittle lubricant.

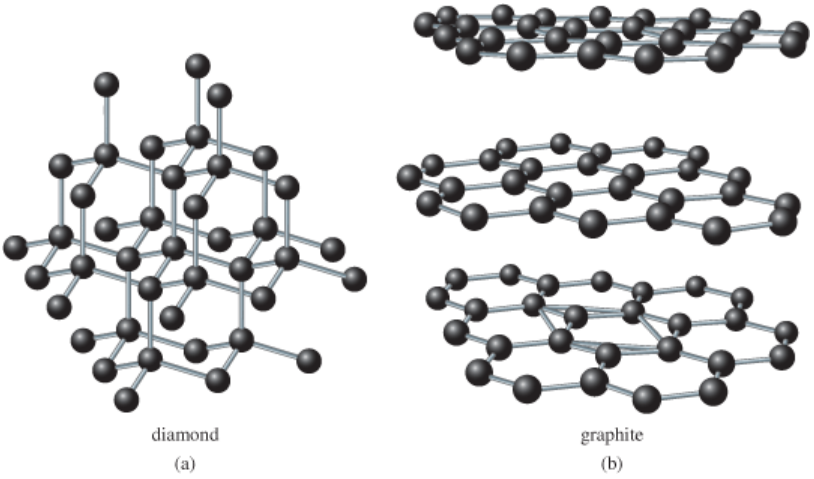


FIGURE 7.12 Part of the structural models of
(a) diamond showing carbon atoms connected to each other to form a three-dimensional network, and
(b) graphite, showing the two-dimensional layers.

Compounds such as silica (silicon dioxide, SiO_2) may also exist as network solids. Opals are composed of nanosized silica spheroids. Their prized colour is due to the way they diffract light, rather than the impurities that give most other gemstones their colour. Another example is silicon carbide, SiC, which has a similar structure to diamond and is used as an abrasive in sandpaper and as an edge on cutting tools as it is less expensive to produce. These substances have very high melting points because their atoms are held together by networks of strong σ covalent bonds.

Metallic Solids

The bonding in solid metals differs from that in other types of solids because it derives primarily from electrons in highly delocalised valence orbitals. Recall from the molecular orbital theory discussed in chapter 5 that overlap of *n* valence atomic orbitals gives rise to *n* molecular orbitals. When *n* is very large, as is the case in 1 mole of a solid metal, then a large number of molecular orbitals are formed. The energies of these molecular orbitals are

so close together that they essentially form a continuum of energies, called a band, which extends over all of the atoms in the metal. Therefore, an electron in a partially filled orbital is delocalised over all the atoms, and is consequently able to move throughout the entire metal. Hence, we can view a metal as consisting of a regular array of metal atom cores embedded in a 'sea' of mobile valence electrons (see figure 7.13). The properties of metals, such as electrical and thermal conductivity, can be explained on the basis of this model.

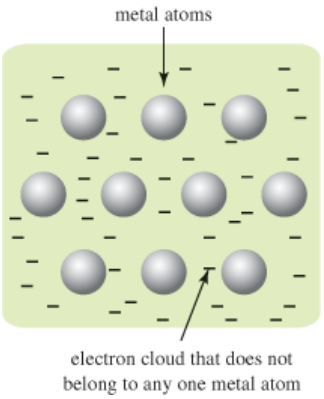
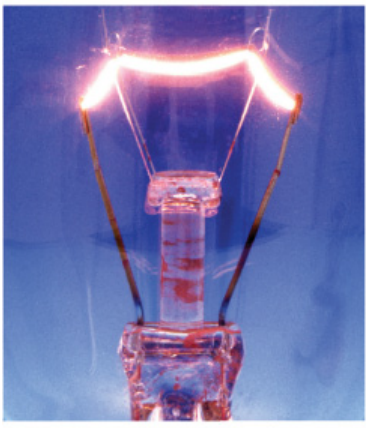


FIGURE 7.13 A diagrammatic representation of metallic bonding. The metal atoms are embedded in a 'sea' of mobile valence electrons.

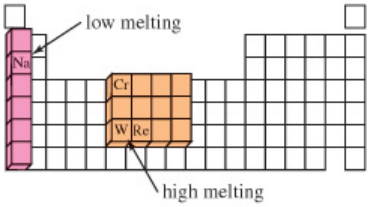
Metals display a wide range of melting points, indicating that the strength of metallic bonding is variable. The group 1 metals are quite soft and melt at relatively low temperatures (see figures 7.14a,c). Sodium, for example, melts at 98 °C and caesium melts at 28.5 °C. Bonding is weak in these metals because each atom of a group 1 metal contributes only one valence electron to the bond-forming energy band. Metals near the middle of the *d* block, on the other hand, are very hard and have some of the highest known melting points: tungsten melts at 3407 °C (figure 7.14b), rhenium at 3180 °C and chromium at 1857 °C. Atoms of these metals contribute several *d* electrons to bond formation, leading to extremely strong metallic bonding.



(a)



(b)



(c)

FIGURE 7.14

(a) Sodium, Na, can be cut with a knife.

(b) Tungsten, W, can be heated to incandescence without melting, which is why it is used as the filament in light bulbs.

(c) Group 1 metals melt at relatively low temperatures whereas metals near the middle of the *d* block have some of the highest known melting points.

Metals are ductile, meaning they can be drawn into wires, and malleable, meaning they can be hammered into thin sheets. When a piece of metal forms a new shape, its atoms change position. However, because the bonding electrons are fully delocalised, changing the positions of the atoms does not cause corresponding changes in the energy levels of the electrons. The 'sea' of electrons is largely unaffected by the pattern of metal atoms, as figure 7.15 illustrates. Thus, metals can be forced into many shapes, including sheets and wires, without destroying their bonding nature.

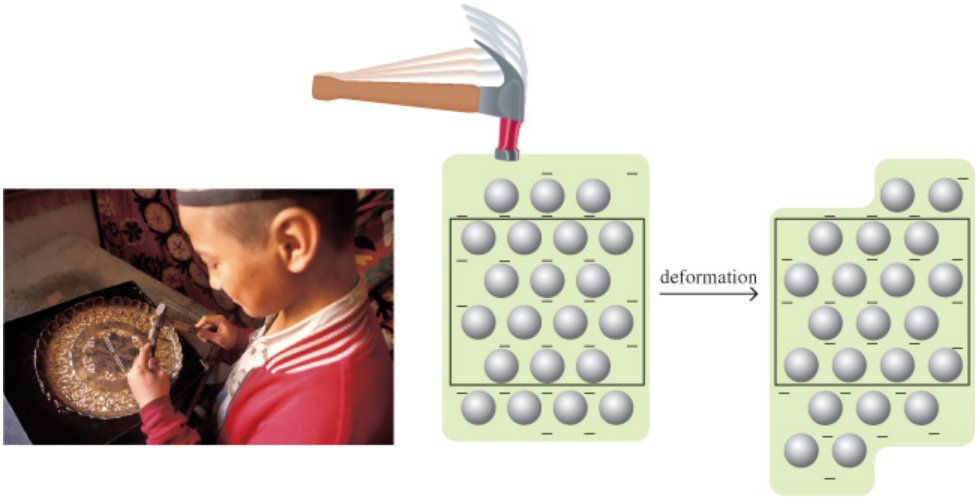


FIGURE 7.15 When a metal changes shape, its atoms shift position. However, because the valence electrons are fully delocalised, the energy of these electrons is unaffected.

The *d*-block metals display a range of properties. Copper and silver are much better electrical conductors than chromium. Tungsten has very low ductility. Mercury is a liquid at room temperature. These differences arise in part because of variations in the number of valence electrons. The *d*-block metals vanadium and chromium have five or six valence electrons per atom respectively, all of which occupy bonding orbitals in the metal atoms. As a result, there are strong attractive forces between the metal atoms, and vanadium and chromium are strong and hard. Beyond the middle of the *d*-block series, the additional valence electrons occupy antibonding orbitals, which reduces the net bonding. This effect is most pronounced at the end of the *d* block, where the number of antibonding electrons nearly matches the number of bonding electrons. Zinc, cadmium and mercury, with s^2 and d^{10} configurations, have melting temperatures that are more than 600 °C lower than those of their immediate neighbours.

Ionic Solids

As described in chapter 5, ionic solids contain cations and anions strongly attracted to each other by electrostatic forces. Ionic solids must be electrically neutral, so their stoichiometries are determined by the charges carried by the positive and negative ions.

Many ionic solids contain metal cations and polyatomic anions. Here again, the stoichiometry of the solid is dictated by the charges on the ions and

the need for the solid to maintain electrical neutrality. Some examples of 1 : 1 ionic solids containing polyatomic anions are NaOH, KNO_3, $CuSO_4$, $BaCO_3$ and $NaClO_3$. Some metallic ores have 1 : 1 stoichiometry, such as scheelite, $CaWO_4$ (contains WO_4^{2-}), zircon, $ZrSiO_4$ (contains SiO_4^{4-}) and ilmenite, $FeTiO_3$ (contains TiO_3^{2-}). Ilmenite is the source of TiO_2, which is used as a white pigment in paper and paints.

Minerals often contain more than one cation or anion. For example, apatite, $Ca_5(PO_4)_3OH$, the main substance in tooth enamel, contains both phosphate and hydroxide anions. Beryl, $Be_3Al_2Si_6O_{18}$, contains beryllium and aluminium cations as well as the $Si_6O_{18}^{12-}$ polyatomic anion. Beryl is the substance that makes up emeralds. An even more complicated mineral is garnierite, $(Ni, Mg)_6Si_4O_{10}(OH)_2$, which has a variable composition of Ni^{2+} and Mg^{2+} cations. Although the relative proportions of Mg^{2+} and Ni^{2+} vary, garnierite always has six cations and two anions of OH^- for every anion of $Si_4O_{10}^{10-}$.

Some mixed oxides that contain rare earth metals are *superconductors*. Below a certain temperature, a superconductor can carry an immense electrical current without incurring losses from resistance. Optimal superconducting behaviour often requires a slight deviation from stoichio-metric composition, which we will learn more about in section 7.8.

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7.3 Phase Changes

In chapter 6 and the first two sections of this chapter, we have examined the three most common phases of matter (gas, liquid and solid) in isolation. We will now investigate what governs a **phase change** — the transition of a substance from one phase to another. Substances can undergo phase changes given the appropriate conditions. Phase changes depend on temperature, pressure, and the magnitudes of bonding and intermolecular forces.

We are all familiar with the phase changes of water at ambient pressure, which are illustrated in figure 7.16. Consider taking ice cubes from the freezer at -18 °C and placing them in a container at room temperature. At first the water is in the solid phase (stage 1). Outside the freezer, the temperature of the ice cubes begins to increase. When the temperature of the ice cubes reaches 0 °C, they begin to melt and we get a mixture of solid and liquid water (stage 2). The temperature of this mixture does not increase until all the ice has melted. Once the ice has completely melted, the temperature of the liquid will start increasing (stage 3). If we apply heat to the container the liquid will increase in temperature (stage 3) until it reaches 100 °C. The water then starts to boil (stage 4) and we get water vapour. The system remains at 100 °C until all of the water has evaporated. Continued heating of the water vapour once all of the water has evaporated will result in its temperature increasing above 100 °C (stage 5). The temperature of the container will also increase once all the water has evaporated, which is why it is not a good idea to allow a saucepan to boil dry on a hotplate.

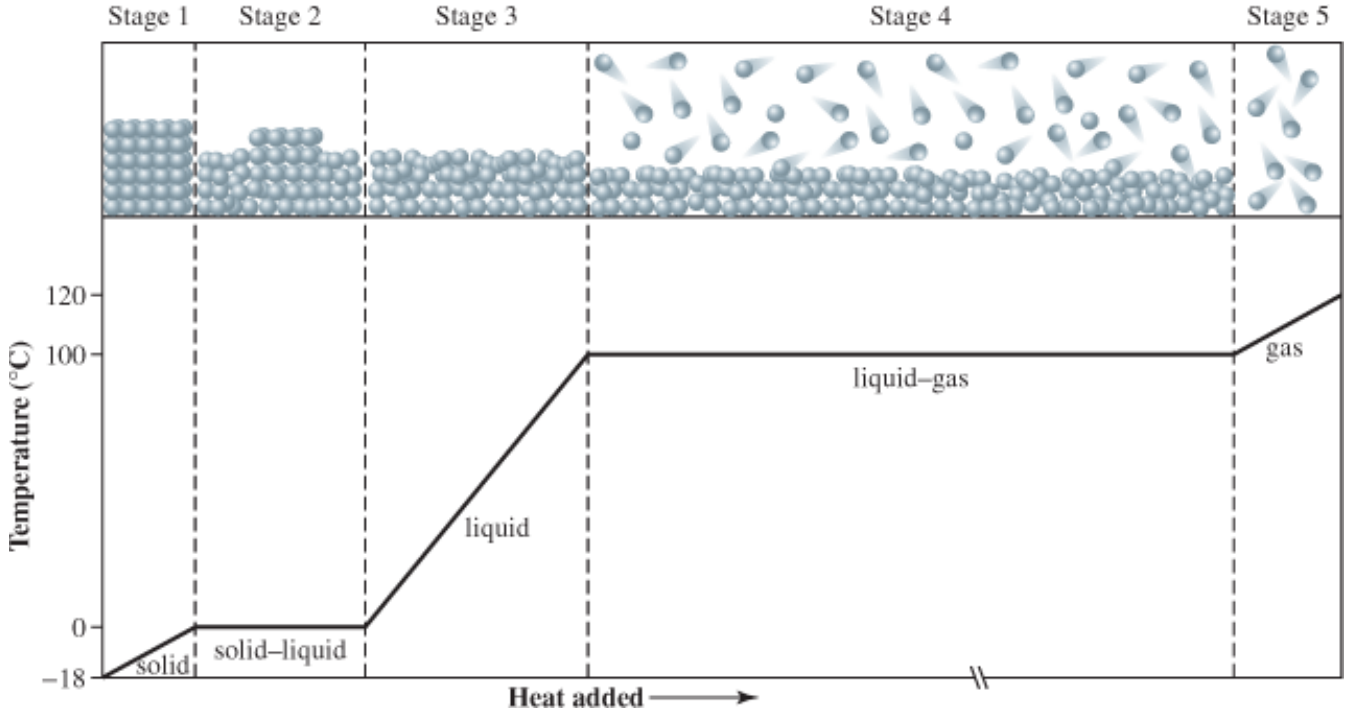


FIGURE 7.16 When heat is supplied to a sample of H_2O at a constant pressure of 1.013×10^5 Pa, phase changes occur at 0 °C and 100 °C. The *x*-axis represents the heat required for each individual process. It should be noted that there are molecules in the vapour phase above both solid and liquid water, but these have been omitted in stages 1, 2 and 3 for clarity.
Adapted from: *Chemistry: The molecular nature of matter and change*, 3rd edition, Martin S Silberberg, p. 424, © 2003 The McGraw-Hill Companies, Inc.

Phase changes require that energy (usually in the form of heat) be either supplied to or removed from the substance undergoing the phase change. Restricting ourselves to molecular substances, but recognising that similar arguments hold for atomic and ionic substances, a molecular perspective reveals why this is so. Any phase change that results in increased molecular mobility requires that intermolecular forces be overcome. For example, hydrogen bonds in ice must be broken to change the ice to liquid water, and hydrogen bonds in liquid water must be broken to convert it to water vapour. About 41 kJ of heat must be supplied to transfer 1 mole of water molecules from the liquid phase into the vapour phase. Similarly, 41

kJ of heat must be removed to liquefy 1 mole of water vapour. As figure 7.16 indicates, the heat required to change between the liquid and solid phases is considerably less.

As you will see in more detail in chapter 8, the amount of heat transferred at constant pressure is equal to a quantity called the enthalpy change (ΔH). The magnitude of the change depends on the strength of intermolecular forces in the substance undergoing the phase change.

The amount of heat required to vaporise a substance also depends on the amount in the sample. The energy required to vaporise 2 moles of water is twice that needed for 1 mole. The heat needed to vaporise 1 mole of a substance at its normal boiling point is called the **molar enthalpy of vaporisation ($\Delta_{vap}H$)**. For example, $\Delta_{vap}H$ of water is about 41 kJ mol^{-1}.

Energy must also be provided to melt a solid substance. This energy is used to overcome the intermolecular forces that hold molecules in fixed positions in the solid phase. The heat needed to melt 1 mole of a substance at its normal melting point is called the **molar enthalpy of fusion ($\Delta_{fus}H$)**. For example, $\Delta_{fus}H$ of water is about 6 kJ mol^{-1}.

Phase changes between solid and liquid, and between liquid and gas, are the most common, but a phase change in which a solid converts directly to a gas without passing through the liquid phase is also possible. This transition is known as **sublimation** (**deposition** is the opposite transition). Dry ice (solid CO_2) sublimes at 195 K with the **molar enthalpy of sublimation ($\Delta_{sub}H$)** = 25.2 kJ mol^{-1}. Mothballs contain naphthalene, $C_{10}H_8$ (Δ_{sub} = 73 kJ mol^{-1}), a crystalline white solid that sublimes to produce a vapour that repels moths. The purple colour of the gas above iodine crystals in a closed container (figure 7.17) provides visible evidence that this solid also sublimes at room temperature ($\Delta_{sub}H$ = 62.4 kJ mol^{-1}). Both naphthalene and iodine melt at ambient pressure (at 80 °C and 114 °C, respectively), indicating that, while a small amount can sublime at ambient pressure, it is not a thermodynamic equilibrium.



FIGURE 7.17 The purple colour of the vapour above solid iodine is due to I_2 molecules in the gas phase.

Phase changes can go in either direction; ice melts upon adding heat, and liquid water freezes on removing heat from the system. Heat is absorbed as a solid melts to a liquid and is released as a liquid freezes to a solid. To make ice cubes, for instance, water is placed in a freezer that absorbs the heat released during the formation of ice. The heat released when liquid water changes to ice is equal in magnitude to the heat required to change ice to liquid water.

By convention, tabulated values of enthalpies of phase changes are always specified in terms of the phase change that requires the addition of heat. The reverse processes have the same magnitude but the opposite

sign.

$$\begin{array}{lcll} \text{solid} \rightarrow \text{liquid} & \Delta_{\text{fus}}H & \text{liquid} \rightarrow \text{solid} & \Delta H_{\text{solidification}} = -\Delta_{\text{fus}}H \\ \text{liquid} \rightarrow \text{gas} & \Delta_{\text{vap}}H & \text{gas} \rightarrow \text{liquid} & \Delta H_{\text{condensation}} = -\Delta_{\text{vap}}H \\ \text{solid} \rightarrow \text{gas} & \Delta_{\text{sub}}H & \text{gas} \rightarrow \text{solid} & \Delta H_{\text{deposition}} = -\Delta_{\text{sub}}H \end{array}$$

Table 7.2 lists values of $\Delta_{\text{fus}}H$, $\Delta_{\text{vap}}H$, melting points and boiling points for selected chemical substances.

TABLE 7.2 Phase change data for selected chemical substances

Substance	Formula	mp (K)	$\Delta_{\text{fus}}H$ (kJ mol^{-1})	bp (K)	$\Delta_{\text{vap}}H$ (kJ mol^{-1})
argon	Ar	83	1.3	87	6.3
oxygen	O_2	54	0.45	90	9.8
methane	CH_4	90	0.84	112	9.2
ethane	C_2H_6	90	2.85	184	15.5
diethyl ether	$(C_2H_5)_2O$	157	6.90	308	26.0
bromine	Br_2	266	10.8	332	30.5
ethanol	C_2H_5OH	156	7.61	351	39.3
benzene	C_6H_6	278	10.9	353	31.0
water	H_2O	273	6.01	373	40.79
mercury	Hg	234	23.4	630	59.0

WORKED EXAMPLE 7.1

Enthalpy of Phase Change

A swimmer emerging from a pool is covered with a film containing about 75 g of water. How much heat must be supplied to evaporate this water?

Analysis

Energy in the form of heat is required to evaporate the water from the swimmer's skin. The energy needed to vaporise the water can be found using the molar enthalpy of vaporisation and the amount of water.

Solution

$\Delta_{\text{vap}}H$ of water is 40.79 kJ mol^{-1} (see table 7.2). The molar mass of water is 18.02 g mol^{-1}, so 75 g of water is 4.16 mol. Therefore, the heat that must be supplied is:

$$n\Delta_{\text{vap}}H = (4.16\,\text{mol})(40.79\text{KJ mol}^{-1}) = 1.7 \times 10^2\,\text{kJ}$$

Is our answer reasonable?

If the swimmer's body must supply all this heat, a substantial chilling effect occurs. Thus, swimmers usually towel off (to reduce the amount of water that must be evaporated) or lie in the sun (to let the sun provide most of the heat required).

PRACTICE EXERCISE 7.1

Determine how much heat is involved in freezing 125 g of water in an ice-cube tray. What is the direction of heat flow in this process?

Recall from our discussion of figure 7.16 that adding heat to boiling water does not cause the temperature of the water to increase. Instead, the added energy is used to overcome inter-molecular attractions as more molecules leave the liquid phase and enter the gas phase. Other two-phase systems show similar behaviour. This can be used to hold a chemical system at a fixed temperature. A temperature of 100 °C can be maintained by a boiling water bath, and an ice bath holds a system at 0 °C. Lower temperatures can be achieved with other substances. Dry ice (solid CO_2) suspended in liquid acetone maintains a temperature of -78 °C (195 K); a bath of liquid nitrogen has a constant temperature of -196 °C (77 K); and liquid helium, which boils at 4.2 K, is used for research requiring ultracold temperatures.

At the start of this section we mentioned that pressure is also involved in phase changes. The effect of pressure is mainly seen for phase transitions involving gases. Recall from chapter 6 that gas density increases with pressure. A gas at constant temperature can be liquefied by increasing the pressure. This is important in the storage of liquefied petroleum gas (LPG), a mixture of propane and butane that is used as a fuel for cars, barbecues and heaters. Propane and butane are gases at room temperature and normal atmospheric pressure. To make the storage and transport of the fuel practicable, it is liquefied by placing it under pressure. The pressure at which a gas liquefies at a specific temperature is known as the condensation point.

Supercritical Fluids

We have learned about the three phases we are familiar with from everyday life: solids, liquids and gases. We have seen that we can liquefy gases by cooling or increasing the pressure. As the pressure on a gas increases, the gas is compressed into an ever-smaller volume. If the temperature is low enough, this compression eventually results in liquefaction. At high enough temperature, however, no amount of compression can cause liquefaction; that is, the liquid–gas transition is no longer possible. Instead, the substance becomes a **supercritical fluid**. A supercritical fluid is a fluid that has certain characteristics of both liquids and gases but is neither.

Imagine that you have a liquid in a sealed container. On heating, the vapour pressure increases as more molecules from the liquid escape into the gas phase, thus increasing the density in the gas phase while also decreasing the density in the liquid phase. As we continue heating the container, the densities in the gas phase and the liquid phase approach the same value. At the point where they become equal we can no longer distinguish between the liquid and gas phases, i.e. we cannot observe a phase boundary. The temperature at which this occurs is called the **critical temperature (T_c)**; the associated pressure is called the **critical pressure**. The combination of the critical temperature and the critical pressure is called the

critical point. The substance is now in its supercritical state (figure 7.18). It has the viscosity typical of a liquid, but it is able to expand or contract like a gas.

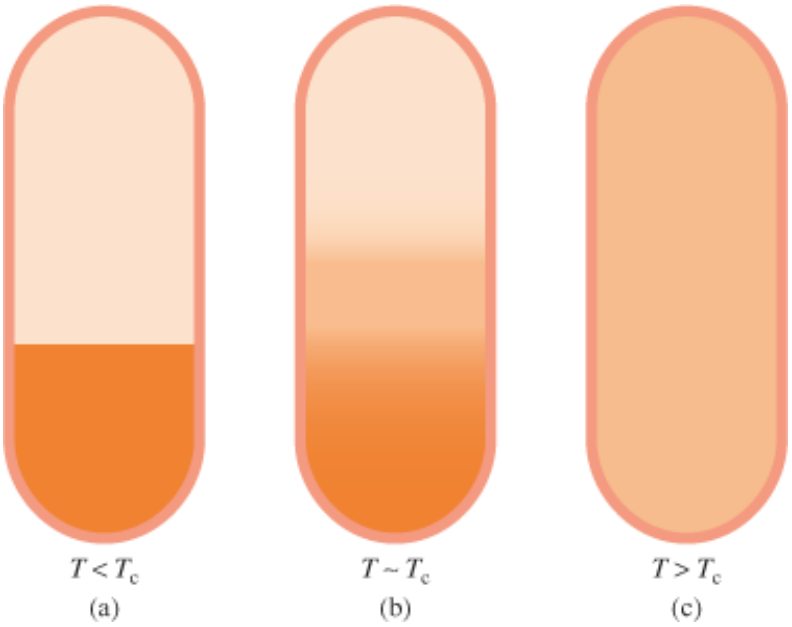


FIGURE 7.18

(a) Below the critical temperature for CO_2 you can clearly see the phase boundary between the liquid and the gas phase.

(b) As the temperature rises the liquid becomes less dense, the vapour phase becomes more dense, and the phase boundary blurs.

(c) Above the critical temperature the phase boundary has disappeared and only a supercritical fluid exists.

The critical point of water is $T = 647$ K, $p = 221 \times 10^5$ Pa, that of CO_2 is $T = 304$ K, $p = 73.9 \times 10^5$ Pa, and that of N_2 is $T = 126$ K, $p = 33.9 \times 10^5$ Pa. Although critical pressures are many times greater than atmospheric pressure, supercritical fluids have important commercial applications. The most important of these is the use of supercritical carbon dioxide as a solvent. Supercritical CO_2 diffuses through a solid matrix rapidly, and it transports materials well because it has a lower viscosity than liquids. Supercritical CO_2 is currently used as a solvent for dry cleaning, for petroleum extraction, for decaffeination and for polymer synthesis. Compared with solvents used previously for some of these processes, such as dichloromethane, CH_2Cl_2, and tetrachloromethane, CCl_4, supercritical CO_2 is a much better choice.

Phase Diagrams

The phase behaviour of a substance can be conveniently summarised in a **phase diagram** as a function of temperature and pressure. An example is provided in figure 7.19. Pressure is plotted along the *y*-axis, and temperature is plotted along the *x*-axis. In the region of low *T* and high *p*, the substance exists as a solid. In the region of high *T* and low *p*, the substance exists as a gas. In some intermediate range of *T* and *p*, the substance exists as a liquid.

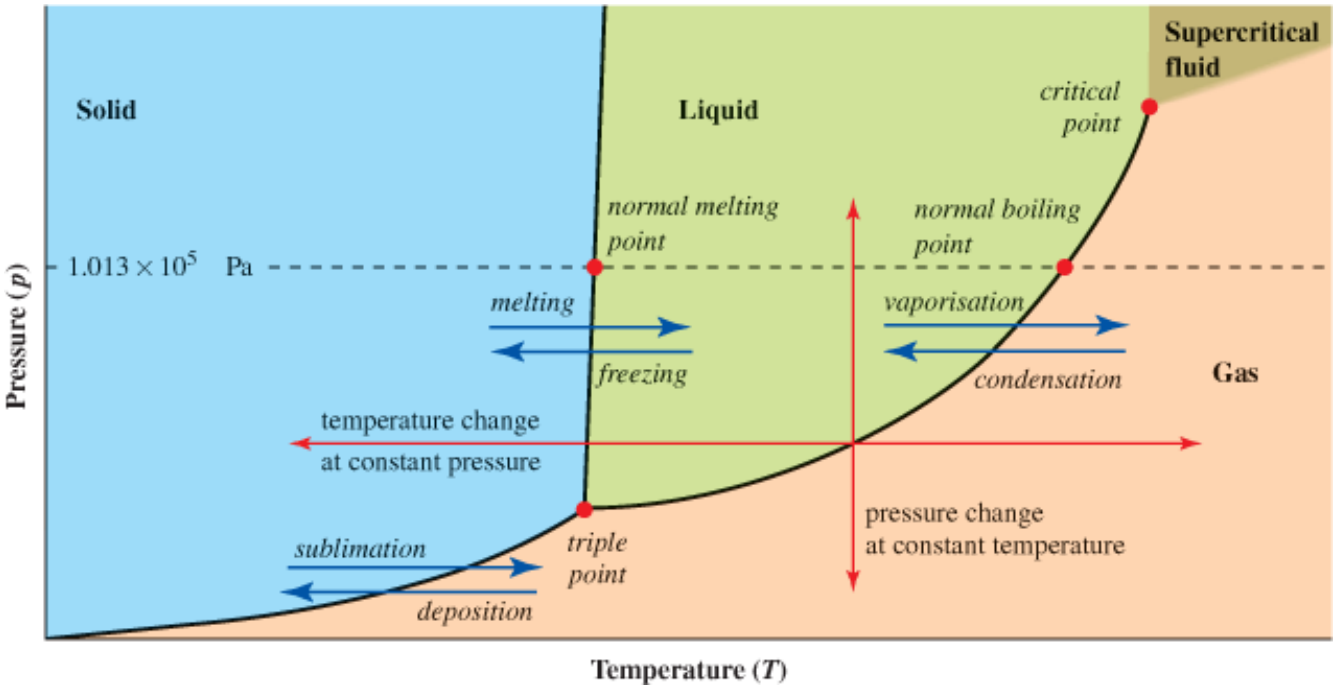


FIGURE 7.19 The general form of a phase diagram. Any point on the diagram corresponds to a specific temperature and pressure. Boundary lines trace conditions where neighbouring phases exist in equilibrium, and the blue arrows show six types of phase transitions. The red arrows highlight a sequence of phase changes on changing temperature at constant pressure, or on changing pressure at constant temperature.

Figure 7.19 illustrates many of the characteristic features of phase diagrams:

1. Boundary lines between phases separate the regions where each phase is thermodynamically stable. (Substances can exist as a metastable phase outside their thermodynamically determined boundaries, e.g. carbon can exist as diamond, rather than graphite, under ambient conditions.
2. Movement across a boundary line corresponds to a phase change. The blue arrows on the figure show six different phase changes: sublimation and its reverse, deposition; melting and its reverse, freezing; and vaporisation and its reverse, condensation.
3. On a boundary line, the two neighbouring phases coexist in a dynamic equilibrium. In addition, at a given pressure, for example, when heat is added or removed, the temperature of this two-phase system does not change until all of one phase has converted to the other. The normal melting point and normal boiling point of a substance (shown by red dots) are the points where the phase boundary lines intersect the horizontal line that represents $p = 1.013 \times 10^5$ Pa.
4. Three boundary lines meet at a single point (shown by another red dot), called a **triple point**. All three phases are present simultaneously at this unique combination of temperature and pressure. Notice that, although two phases are stable under any of the conditions specified by the boundary lines, three phases can be simultaneously stable only at a triple point.
5. Above the temperature specified by the critical point (again shown by a red dot), the gas cannot be liquefied under any pressure. Instead if the pressure is high enough a supercritical fluid forms. It has the viscosity typical of a liquid, but it is able to expand or contract like a gas.
6. What happens to a substance as temperature changes at constant pressure can be determined by drawing a horizontal line at the appropriate pressure on the phase diagram (shown as a horizontal red line).
7. What happens to a substance as pressure changes at constant temperature can be determined by drawing a vertical line at the appropriate temperature on the phase diagram (shown as a vertical red line).
8. The temperature for conversion between the gas phase and a condensed phase depends strongly on pressure. Qualitatively, this is because compressing a gas increases the collision rate and makes condensation more favourable.

9. The melting temperature is almost independent of pressure, making the boundary line between solid and liquid nearly vertical. Qualitatively, this is because moderate pressure has hardly any effect on the condensed liquid and solid phases.
10. The solid–gas boundary line extrapolates to $p = 0$ Pa and $T = 0$ K. This is a consequence of the direct link between temperature and energy. At 0 K, atoms, ions and molecules have minimum energy, so they cannot escape from the solid lattice. At 0 K, the vapour pressure of every solid substance would be 0 Pa.

The phase diagram for water, shown in figure 7.20, illustrates these features for a familiar substance. The figure shows that liquid water and solid ice coexist at the normal melting point (mp), $T = 273.15$ K and $p = 1.013 \times 10^5$ Pa. Liquid water and water vapour coexist at the normal boiling point (bp), $T = 373.15$ K and $p = 1.013 \times 10^5$ Pa. The triple point (tp) of water occurs at $T = 273.16$ K and $p = 0.0061 \times 10^5$ Pa. The figure shows that when p is lower than 0.0061×10^5 Pa, there is no temperature at which water is stable as a liquid. At those low pressures, ice sublimes but does not melt.

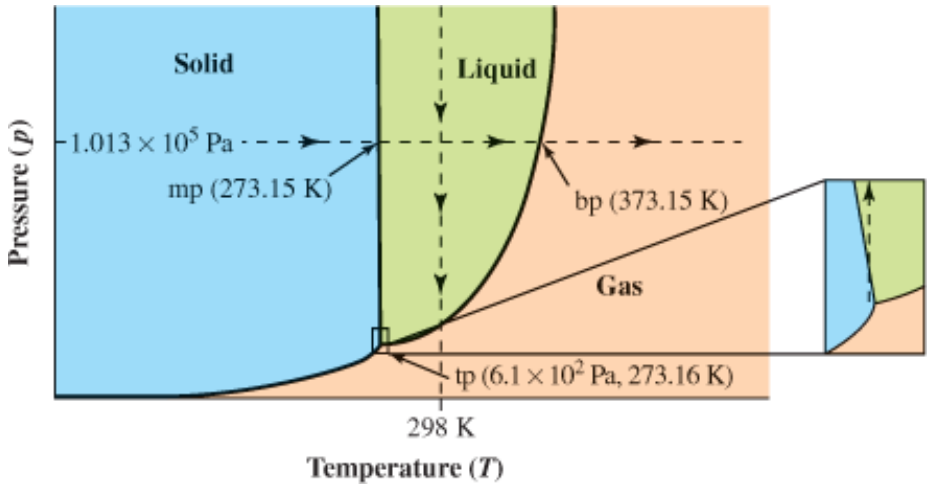


FIGURE 7.20 The phase diagram for water. The critical point is at $T = 647$ K, $p = 221 \times 10^5$ Pa, well outside this diagram.

The dashed lines on figure 7.20 show two paths that involve phase changes for water. The horizontal dashed line shows what happens as the temperature increases at a constant pressure of 1.013×10^5 Pa. As ice warms from a low temperature, it remains in the solid phase until the tempera ture reaches 273.15 K. At that temperature, solid ice melts to liquid water, and water remains liquid as the temperature increases, until it reaches 373.15 K. At 373.15 K, liquid water changes to water vapour. When the pressure is 1.013×10^5 Pa, water exists in the gas phase at all higher temperatures. The vertical dashed line shows what happens as the pressure on water is reduced at a constant temperature of 298 K (approximately room temperature). Water remains in the liquid phase until the pressure drops to 3.04×10^3 Pa. At 298 K, water exists in the gas phase at any pressure lower than this. Notice that at 298 K there is no pressure at which water exists in the solid state.

Given that the temperature of the triple point is slightly higher than the temperature of the normal melting point, we can conclude that the slope of the boundary line between the solid and liquid phases has to be negative. As shown in the magnified section of figure 7.20, if you start with solid H_2O at a temperature just below the triple point and increase the pressure at constant temperature you will effect a phase change from solid to liquid (dashed line). This shows, as we discussed in the opening paragraph of this chapter, that the density of the liquid is higher than the density of the solid, which is why ice floats on water. Ice-skaters make use of this pressure-induced phase transition. The thin blades of their ice skates put pressure on the ice, changing it to liquid water which refreezes once the pressure is removed. This property of water is relatively uncommon among substances. Most solids have higher density than their corresponding liquids. For water, the lower density is caused by the larger number of hydrogen bonds per water molecule in ice compared with liquid water.

All phase diagrams of pure substances share the 10 common features listed previously. However, the detailed appearance of a phase diagram is different for each substance, as determined by the strength of the interactions between its constituents. Figure 7.21 shows two examples, the phase diagrams for nitrogen and carbon dioxide. Both of these substances are gases under normal conditions. In contrast to H_2O, which has a triple point close to 298 K, N_2 and CO_2 have triple points that are well below room temperature. Although both are gases at ambient temperature and pressure, they behave differently when cooled at atmospheric pressure. Molecular nitrogen liquefies at 77.4 K and then solidifies at 63.29 K, whereas carbon dioxide condenses directly to the solid phase at 195 K. This difference in behaviour arises because the triple point of CO_2, in contrast to the triple points of H_2O and N_2, occurs at a pressure greater than 1.013×10^5 Pa. The phase diagram of CO_2 shows that at a pressure of 1.013×10^5 Pa, there is no temperature at which CO_2 exists in the liquid phase.

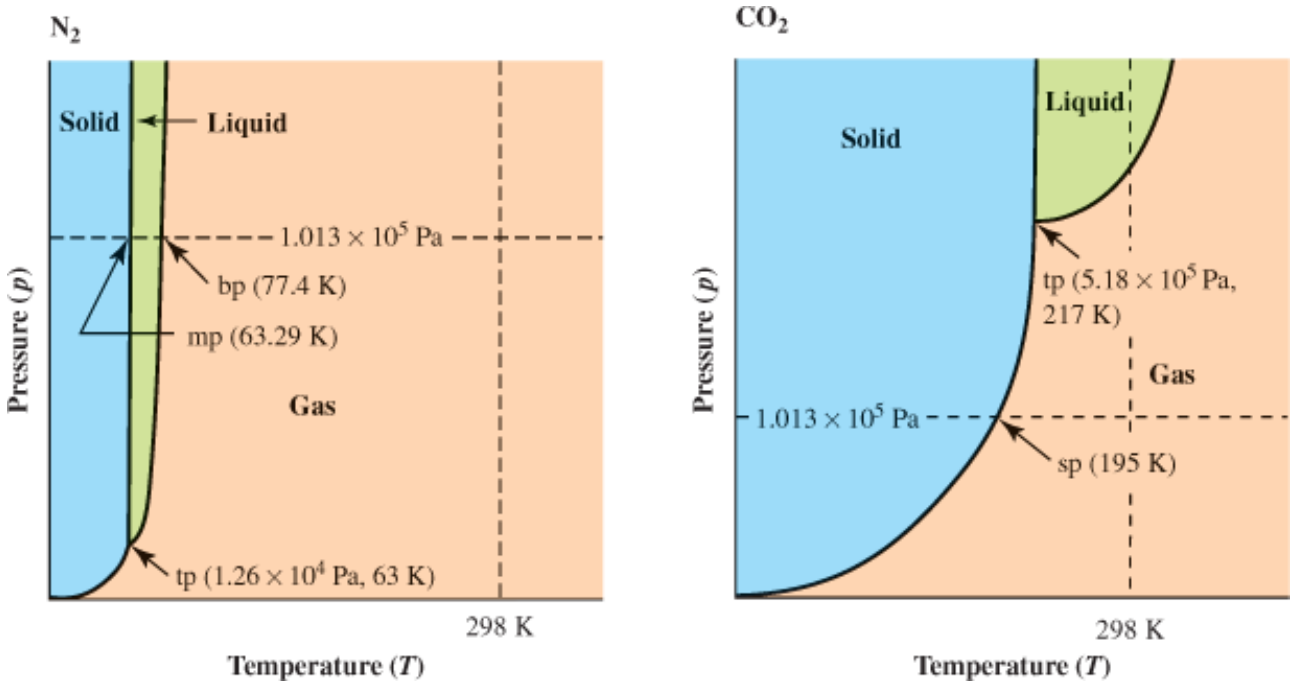


FIGURE 7.21 Phase diagrams for nitrogen and carbon dioxide, two substances that are gases at room temperature and pressure (sp = normal sublimation point).

Phase diagrams are constructed by measuring the temperatures and pressures at which phase changes occur. Approximate phase diagrams such as those shown in figures 7.20 and 7.21 can be constructed from the triple point, normal melting point and normal boiling point of a substance.

WORKED EXAMPLE 7.2

Constructing a Phase Diagram

Ammonia is a gas under ambient conditions. Its normal boiling point is 239.8 K, and its normal melting point is 195.5 K. The triple point for NH_3 is $p = 0.0612 \times 10^5$ Pa and $T = 195.4$ K. Use this information to construct an approximate phase diagram for NH_3.

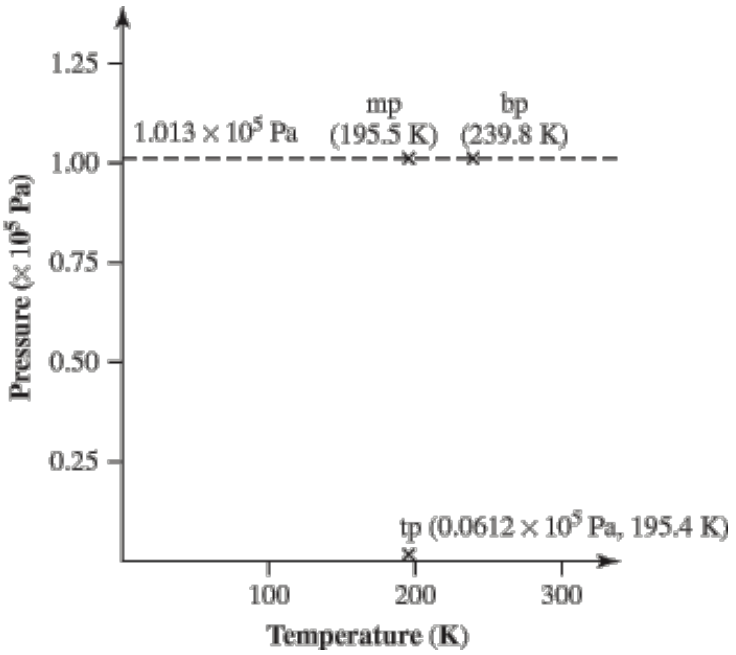
Analysis

The normal melting and boiling points and the triple point give three points on the phase

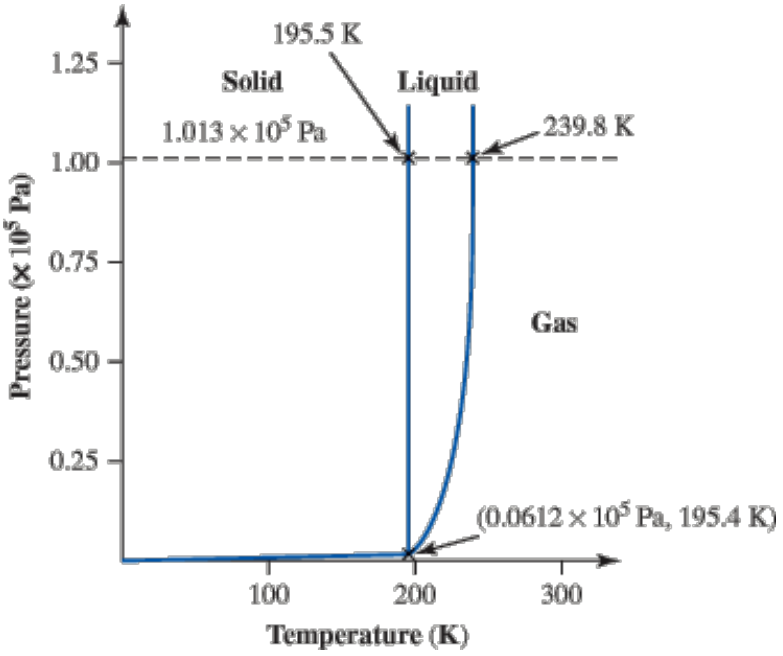
boundary curves. To construct the curves from knowledge of these three points, use the common features of phase diagrams: the gas–liquid and gas–solid boundaries of phase diagrams slope upwards, the liquid–solid line is nearly vertical, and the gas–solid line begins at $T = 0$ K and $p = 0$ Pa.

Solution

Begin by choosing appropriate scales, drawing the $p = 1.013 \times 10^5$ Pa line and locating the given data points. An upper temperature limit of 300 K encompasses all the data.



Next, connect the points and label the domains.



Is our answer reasonable?

Check that pressure is on the y-axis and temperature is on the x-axis and that you have not accidentally interchanged the solid, liquid and gas phases. Also check that the slope of the solid–gas phase boundary is less steep than that of the liquid–gas phase boundary near the triple point and that the solid–liquid phase boundary is nearly vertical.

PRACTICE EXERCISE 7.2

Molecular chlorine melts at 172 K, boils at 239 K and has its triple point at 0.014×10^5 Pa and 172 K. Sketch the phase diagram for this compound.

Phase diagrams can be used to determine which phase of a substance is stable at any particular pressure and temperature. They also summarise how phase changes occur as either condition is varied.

WORKED EXAMPLE 7.3

Interpreting a Phase Diagram

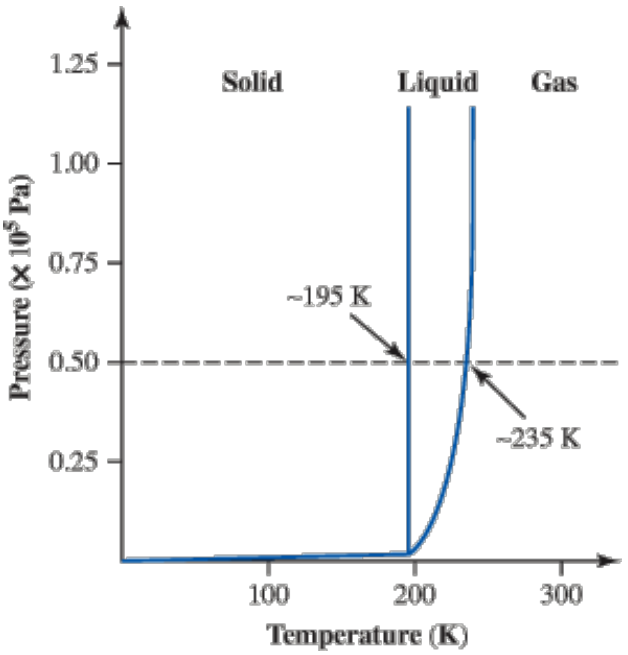
A chemist wants to perform a synthesis in a vessel at $p = 0.50 \times 10^5$ Pa using liquid NH_3 as the solvent. What temperature range would be suitable? When the synthesis is complete, the chemist wants to boil off the solvent without raising T above 220 K. Is this possible?

Analysis

The phase diagram for NH_3 (refer to worked example 7.2) shows the boundary lines for the liquid domain. These boundary lines can be used to determine the conditions under which phase changes occur.

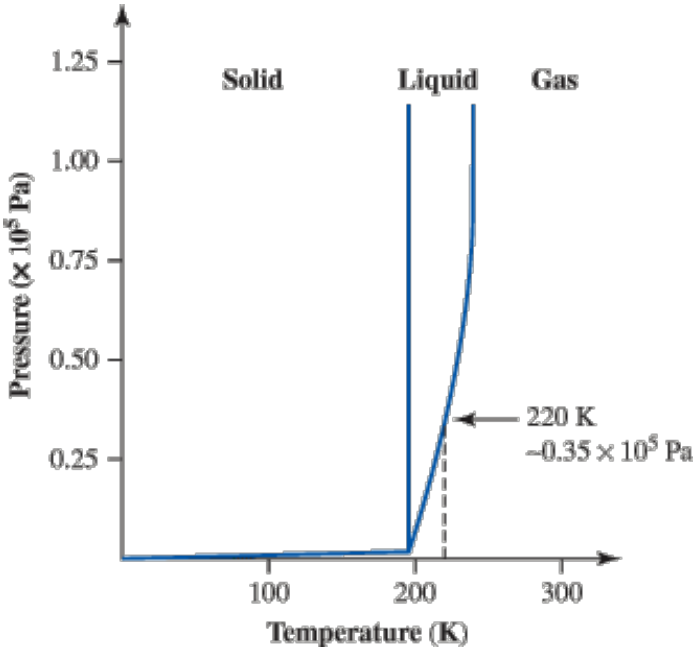
Solution

Because the chemist wants to work at $p = 0.50 \times 10^5$ Pa, draw a horizontal line across the phase diagram at $p = 0.50 \times 10^5$ Pa. Here is an expanded view of the phase diagram between 150 and 300 K.



The horizontal line intersects the boundary lines at about 235 K and 195 K. Liquid NH_3 is stable between these temperatures at this pressure.

At the completion of the synthesis, the chemist wants to remove the solvent without raising *T* above 220 K. A vertical line at 220 K on the phase diagram represents this condition.



The line intersects the liquid–gas boundary at about 0.35×10^5 Pa. A vacuum pump capable of reducing *p* below 0.35×10^5 Pa can be used to vaporise and remove the NH_3 while keeping the temperature below 220 K.

Is our answer reasonable?

Check that the lines for pressure and temperature are entered correctly. Since $NH_3(l)$ boils at 235 K and 0.5×10^5 Pa, for $NH_3(l)$ to boil at the lower temperature of 220 K we need a reduced pressure, as we have determined.

PRACTICE EXERCISE 7.3

A sample of N_2 gas is at $p = 0.1 \times 10^5$ Pa and $T = 63.1$ K. Use figure 7.21 to determine what will happen to this sample if the temperature remains fixed while the pressure slowly increases to 1×10^5 Pa.

The phase diagrams we have studied are the simplest ones that occur for pure substances. However, many substances have more than one solid phase (there are 14 different known forms of ice!). Phase diagrams of solids are particularly useful in geology, because many minerals undergo solid–solid phase transitions at the high temperatures and pressures found deep in the Earth's crust. Figure 7.22 is the phase diagram for silica (silicon dioxide, SiO_2), an important geological substance. Notice that the scale reflects geological pressures and temperatures. Notice also that there are six different forms of crystalline silica, each stable in a different temperature–pressure region. A geologist who encounters a sample of stishovite can be confident that it solidified under extremely high pressure conditions.

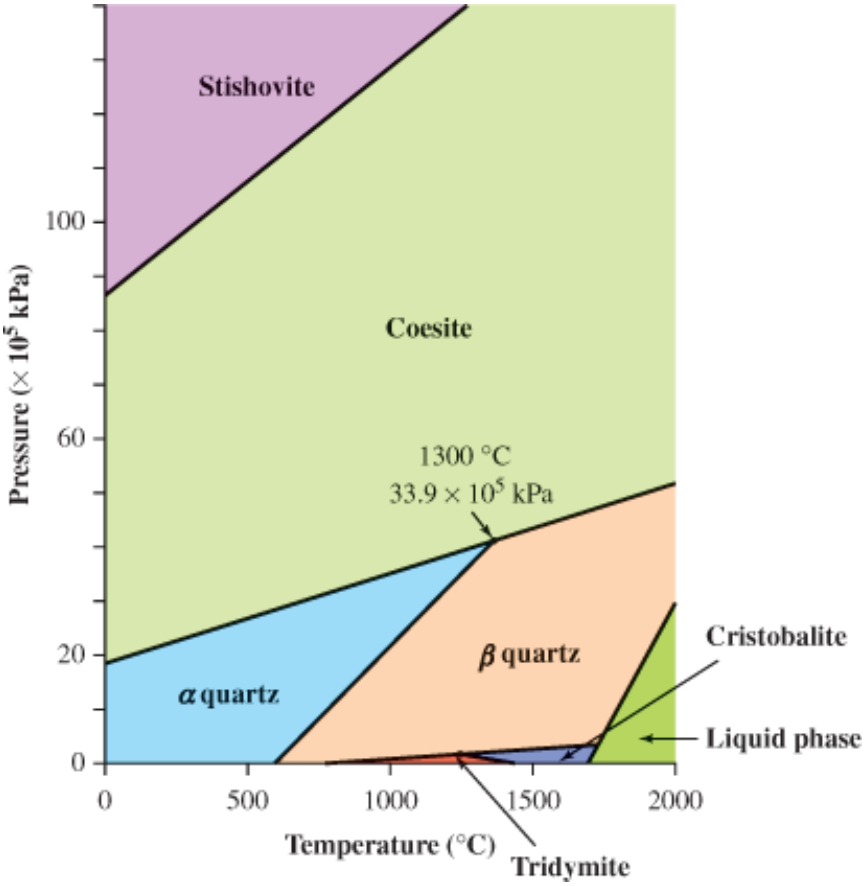


FIGURE 7.22 The phase diagram for silica shows six different forms of the solid, each stable under different temperature and pressure conditions.

If we have more than one component in a mixture, phase diagrams become even more complicated, and treatment of these is beyond the scope of this book.

Chemical Connections

Chemistry and Cool Jackets

Researchers at RMIT University have developed an advanced cooling jacket to help athletes reduce their body temperatures before major events. Cooling the body prior to an event enhances the athlete's performance and delays the onset of exhaustion by minimising the stress and strain on the body, which reduces the reliance on the body's store of sugar. Athletes have long used ‘ice jackets’ to reduce their body temperature before big races to take advantage of these benefits, but they have often suffered undesirable side effects such as shivering, ‘ice burn’ and headaches. The RMIT team, led by Professor David Mainwaring, and including Professor Robert Shanks, developed a jacket that is filled with solid phase change material (PCM, figure 7.23). In order to effect cooling, a PCM must undergo an endothermic phase change (one that requires heat from the surroundings to occur). Many compounds do of course do this, most notably water (the ‘ice jackets’ mentioned above operate on this principle) but in order for the wearer to be comfortable, the phase change needs to occur at around room temperature. The PCM developed by RMIT consists of a mixture of two or more straight-chain alkanes. While low-molar-mass alkanes are either gases or liquids, those with more than about 12 carbon atoms have melting points above 0 °C. The actual alkanes used are chosen so as to give the most desirable thermal properties, and, in this case, at least 90% of the alkanes have between 14 and 18 carbon atoms. At temperatures below about 18 °C, the PCM exists as a waxy semi-solid in which the chains of the alkane molecules are aligned. When the jacket is worn, the body heat of the wearer causes a phase change to occur in the PCM from a semi-solid to a liquid at about 20 °C. This is an endothermic process that removes heat from the surroundings, thereby leading to a cooling effect for the wearer. The jacket can be regenerated for use simply by cooling it to a temperature below about 18 °C in, for example, an airconditioned room. This causes an exothermic phase change (one that gives out heat to the surroundings) of the PCM back to a semi-solid and the jacket is again ready for use.



FIGURE 7.23 An 'ice jacket' that uses solid phase change material (PCM) which changes from a semi-solid to a fluid at about 20 °C.
© 2005 RMIT University, Educational Technology Advancement Group. Photographer Margund Sallowsky.

Because heat is withdrawn from the body at close to normal skin temperature, and not at ice temperature, the cooling processes are more comfortable, efficient and effective.

The jackets were developed in conjunction with the Australian Institute of Sport and are used by many of Australia's elite athletes in preparation for major sporting events such as the Olympic Games.

The vests also have potential in the treatment of medical conditions. Applications might include control of heat-induced hand tremors and dizziness in people with multiple sclerosis, as well as the effective and safe cooling of people who have suffered brain injuries or cardiac trauma.

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7.4 Order in Solids

In contrast to molecules in gases and liquids, which can move relatively freely, the atoms, molecules or ions in a solid are in fixed positions. Generally, their motions are restricted to vibrations about these fixed positions. In this section, we examine the principles that govern the relative arrangements of atoms, molecules and ions in solids. To start our exploration of order in solids we will look at some simple cases.

Close-packed Structures

Most elements in the periodic table are metals and, apart from mercury, all metals are solids at standard conditions. In order to develop a picture of metal structures, we will assume that we can approximate a metal atom with a sphere. Figure 7.24 shows both square and hexagonal arrangements of identical spheres. We can see that the hexagonal arrangement is able to fit more spheres into the same area; every sphere in the hexagonal arrangement has six direct neighbours, but only four in the square arrangement. This hexagonal arrangement of identical spheres is the most dense packing that you can achieve in one layer of spheres. You can see this when you place pool balls in the triangle at the start of the game (figure 7.25). Only if you arrange them this way can all of the balls fit into the triangle.

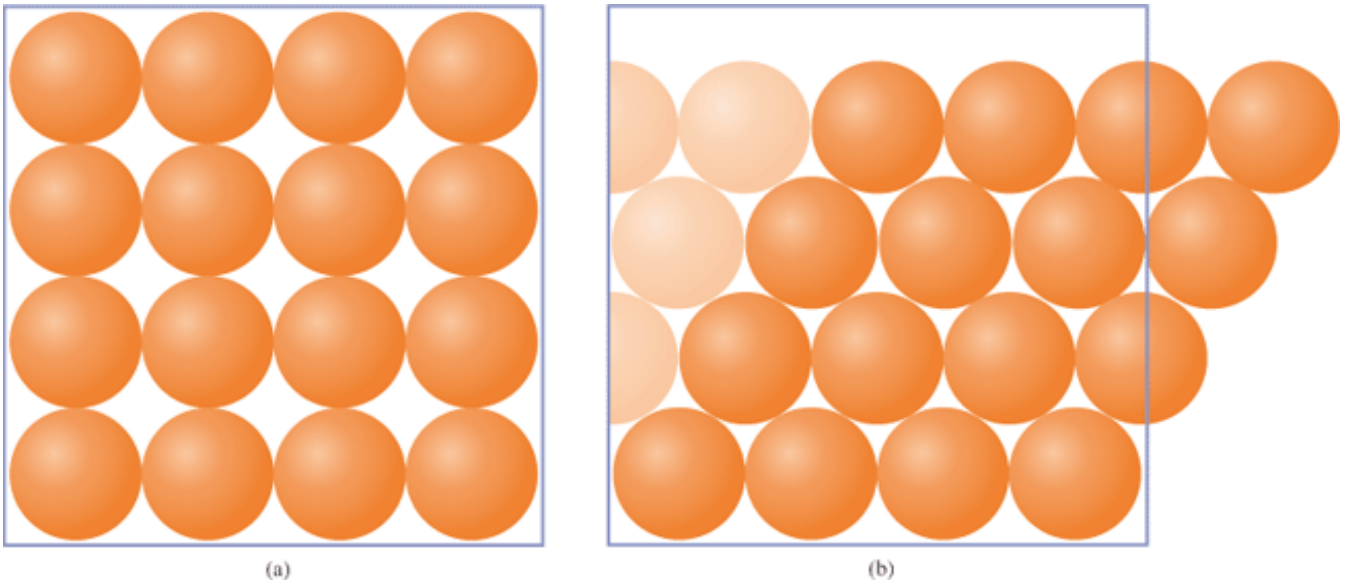


FIGURE 7.24 Comparison of **(a)** square and **(b)** hexagonal arrangement of identical spheres. You can see that both squares fit 16 spheres (moving the spheres outside the square in (b) into the empty space at the other side of the square (lighter shaded spheres). In (b), there is space left over at the top of the square, while in (a) there is no space left over, indicating that the spheres in the hexagonal arrangement are closer together.



FIGURE 7.25 Pool balls fit into the triangle in a hexagonal arrangement.

Now add a second layer of spheres to the hexagonal arrangement. Let's call the first layer ‘layer A’ and the second layer ‘layer B’. To achieve the most compact arrangement, each sphere in layer B sits in one of the ‘dimples’ between a trio of spheres in layer A. There are six dimples around any sphere in layer A. You can see that the centres of two neighbouring dimples are closer together than the diameter of the spheres. Hence, it is impossible to place a sphere over every dimple. For example, if we place spheres as indicated by the red rings in figure 7.26, we can see that it is impos sible to place spheres in the positions indicated by the blue rings at the same time.

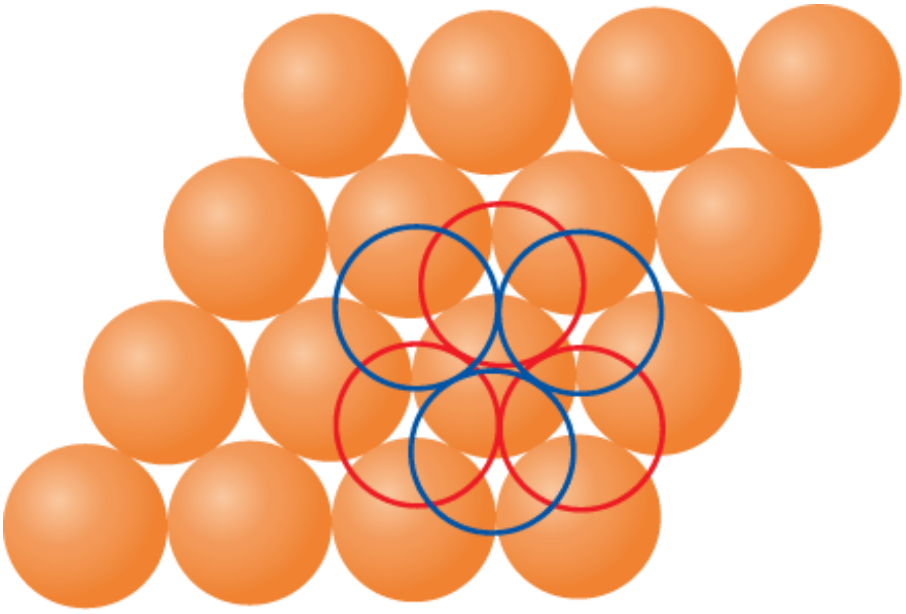


FIGURE 7.26 It is impossible to place a sphere over every dimple. We can place spheres only in the red positions or blue positions, not both at the same time.

If we fill all the dimples corresponding to the red rings in figure 7.26a, we create a second layer as shown in figure 7.27b. This adds three more adjoining spheres for each sphere in layer A, one in each set of three neighbouring dimples. As additional spheres are added, layer B eventually looks identical to layer A, except that it is offset slightly to allow the spheres to nestle in the dimples formed by the layer below. There is no difference between filling all dimples corresponding to the red rings or the blue rings; the resulting arrangements of spheres are indistinguishable.

Now consider adding a third layer of spheres. This new layer can be placed in two different ways because there are two sets of dimples in layer B. Figure 7.28 shows a close-up of figure 7.27b. Notice in figure 7.28 that the view through one set of dimples (highlighted in orange) reveals the orange spheres of layer A. The view through the other set of dimples (high-lighted in blue) reveals the unfilled dimples of layer A.

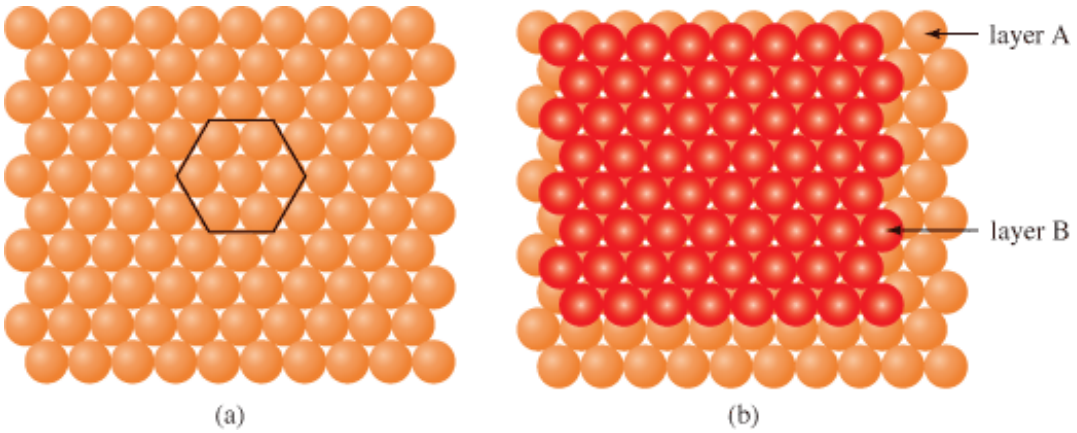


FIGURE 7.27 (a) Spheres close-packed in a layer generate a hexagonal pattern.
(b) When a second layer is packed on top of the first, each sphere in the second layer nestles in the dimple formed between three adjacent spheres in the lower layer.

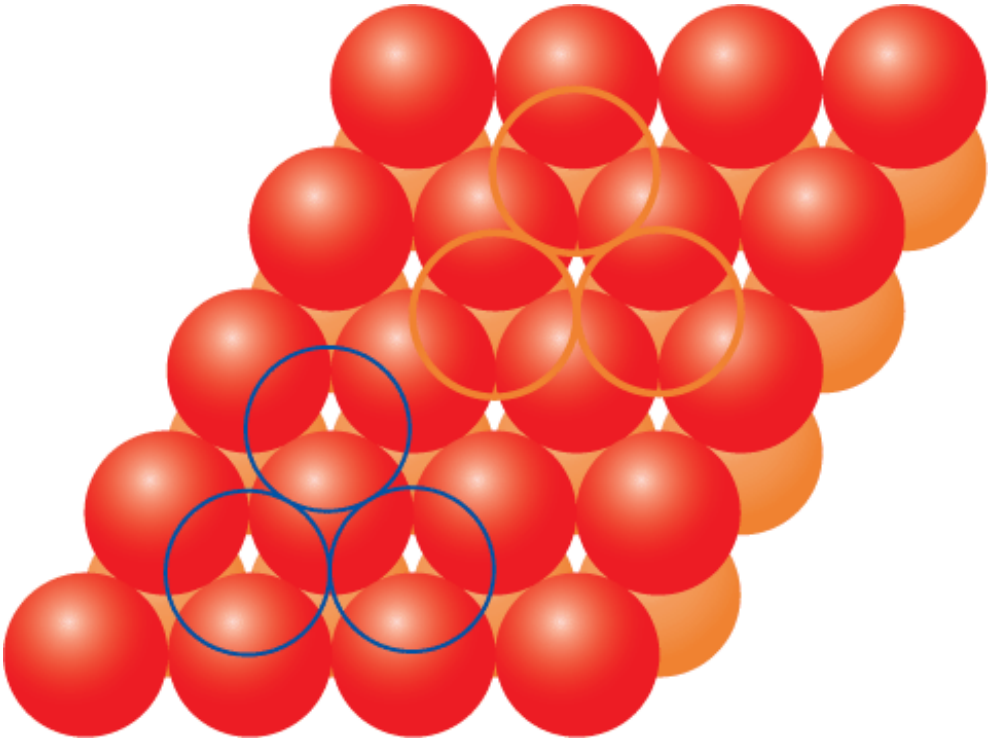


FIGURE 7.28 A third layer of spheres can be placed in two different ways.

If spheres in the third layer lie in the dimples highlighted in orange, the third layer is directly above the first, and the structure is called **hexagonal close-packed (hcp)**. If the spheres of the third layer lie in the dimples highlighted in blue, the third layer is offset from both of the lower layers. This arrangement is called **cubic close-packed (ccp)**. Figure 7.29 shows that in the hexagonal close-packed structure the positioning of the third layer corresponds to that of layer A and therefore we also label it A. In the cubic close-packed structure, the positioning is different and so we label the third layer 'layer C'. Comparing the two diagrams, we can see that in the hexagonal close-packed structure one set of dimples is never covered, while in the cubic close-packed structure, they are. If we continue this layering pattern, we find that a hexagonal close-packed structure has the pattern ABAB etc., while a cubic close-packed structure has the pattern ABCABC etc.

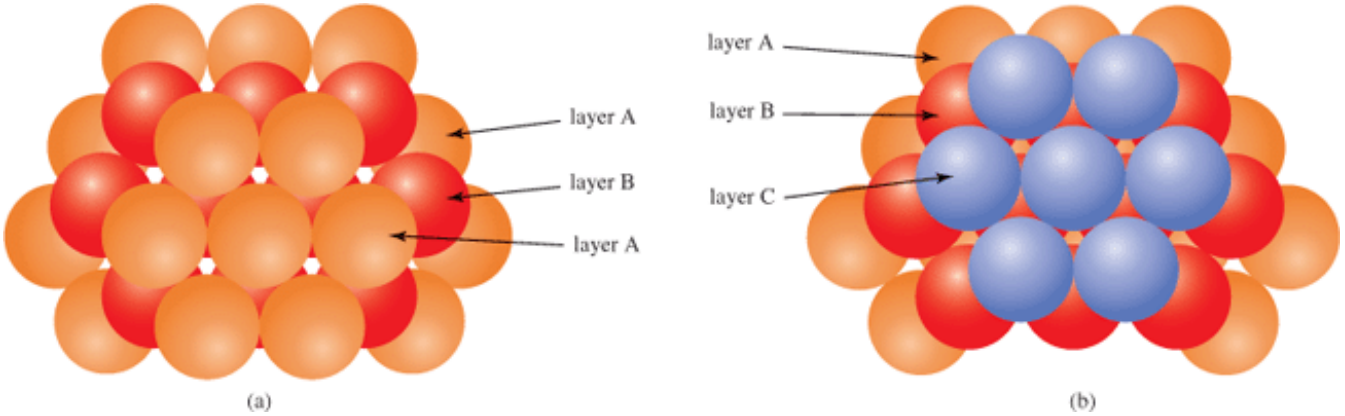


FIGURE 7.29 Top-down views of hexagonal and cubic close-packed arrangements:
(a) The hexagonal close-packed structure has a layer repeating pattern ABAB etc.
(b) The cubic close-packed structure has a layer repeating pattern ABCABC etc.

The two structure types described are called **close-packed structures** because they achieve maximum space filling for identical spheres. In either of these arrangements, 74% of the total space is filled, and each sphere has 12 nearest neigh bours (i.e. neigh bours with the same shortest distance to that sphere): six in the same plane, three in the dimples above and three in the dimples below. This is shown for the hexagonal and cubic close-packed structures in figure 7.30. The number of nearest neighbours is also called the coordination number, and therefore spheres in close-packed structures have a coordi nation number of 12.

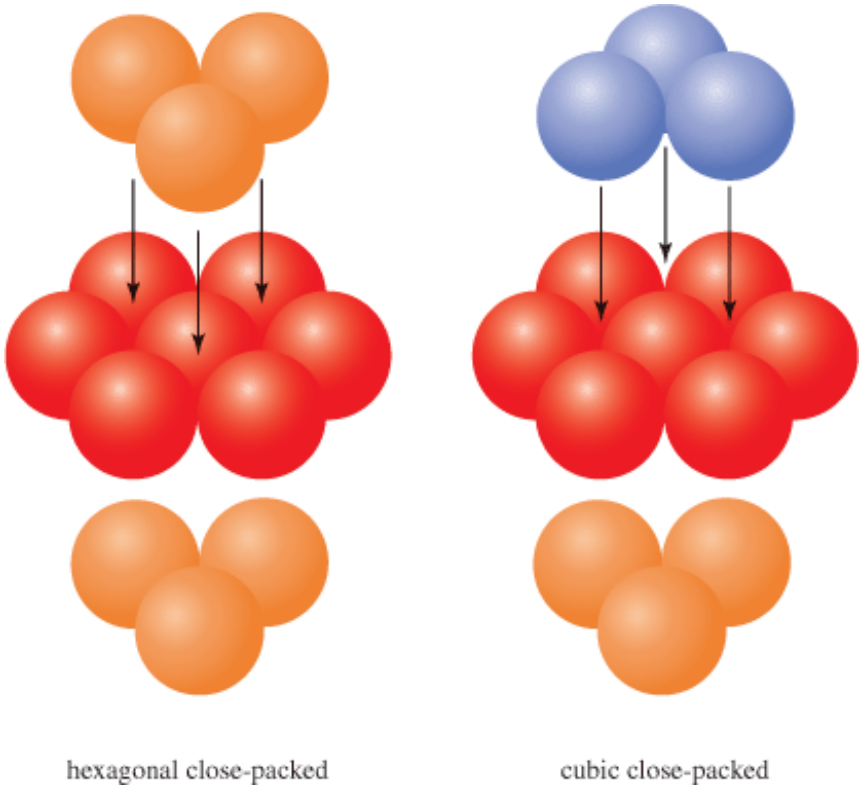


FIGURE 7.30 In close-packed structures, each sphere has 12 nearest neighbours: six in the same plane, three in the dimples above and three in the dimples below.

Many metals form crystals with hexagonal or cubic close-packed geometries, since metal bonding that involves sharing valence electrons benefits from close contact between participating metal atoms. For instance, magnesium and zinc crystallise with their atoms in a hexagonal close-packed array, while silver, aluminium and gold crystallise in the cubic close-packed arrangement. Other spherical entities, such as argon atoms, and methane and C_{60} molecules, also form close-packed arrangements. Argon solidifies at low temperature as a cubic close-packed crystal, and neon can solidify in either the hcp or ccp form.

The Crystal Lattice and the Unit Cell

In a solid, the number of atoms, ions or molecules is enormous. If you could imagine being at the centre of even a small sample of a solid, you would find that the atoms, ions or molecules go on as far as you can see in every direction. Describing all the individual positions is impossible and, fortunately, unnecessary if we are able to identify a repeating pattern within the solid.

There are a number of rules to consider when defining such a repeating pattern, and to start off we will look at examples in two dimensions. We can recognise a repeating motif in the wallpaper design of figure 7.31a. How can we describe this pattern? In order to concentrate on the repeating features of the pattern, we start by randomly selecting a point and then mark every other point on the wallpaper that has an identical environment (to make that easier to see we choose the eye of the rearmost of the three fish) as shown in figure 7.31b.

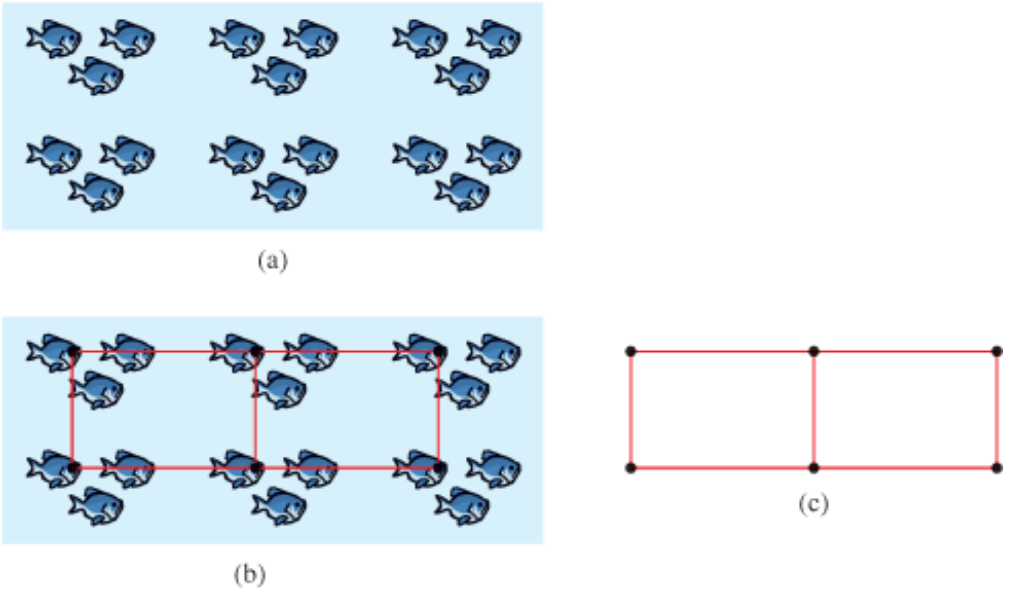


FIGURE 7.31 Defining a repeating pattern:
(a) There is a repeating pattern in the wallpaper design.
(b) The pattern can be described by a set of points with identical environments.
(c) The resulting pattern is a lattice and each black dot is a lattice point.

Figure 7.31b shows this set of points, which have been connected by lines. In figure 7.31c we take away the wallpaper, leaving just the connected points. We call this pattern of points a **lattice**, and every individual point is a **lattice point**. Since we selected a set of points by requiring each one to have an identical environment, this set of points represents the repeating feature of our wallpaper design, and every lattice point represents one repeating motif.

In the next step, we must find the smallest repeating unit within our lattice, which in this case is one of the rectangles in figure 7.31c. We call the smallest unique repeating unit of a lattice the **unit cell** (there are a number of rules for the correct choice of unit cell, but they are beyond the scope of this book). Repeating the unit cell in two dimensions will create the lattice. Therefore, all we need to describe any pattern is the lattice and the content of the unit cell.

An important fact about lattices is that the same lattice can be used to describe many different designs or structures. For example, take the square lattice and unit cell in figure 7.32a. In figure 7.32b, we see a design formed by associating a blue heart with each lattice point. Using a square lattice, we could form any number of designs just by using different design elements (for example, a rose or a diamond), or by changing the lengths of the edges of the unit cell. The only requirement is that the same design element must be associated with each lattice point; that is, each lattice point must have an identical environment. There is no requirement, however, that the lattice point is centred on the object, as illustrated in figure 7.32c,d. You are

allowed to shift the entire lattice as long as you still end up with all lattice points having identical environments.

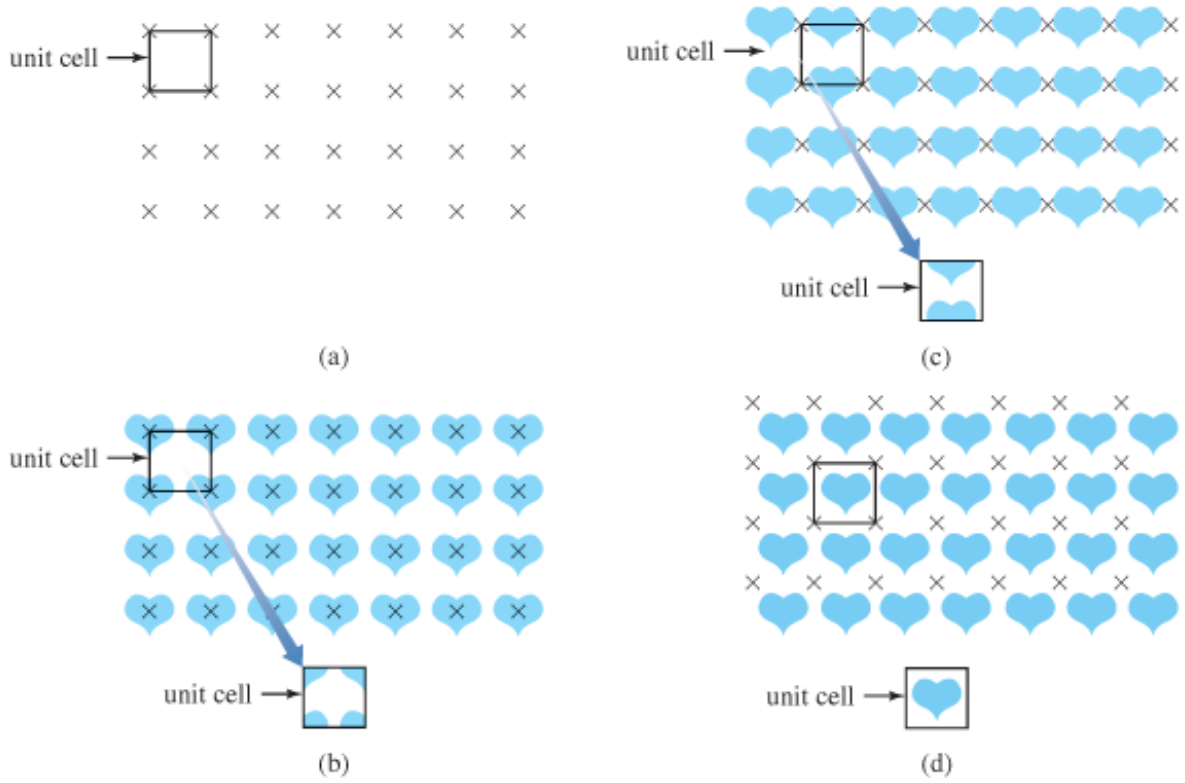


FIGURE 7.32 A two-dimensional lattice:

(a) a simple square lattice, for which the unit cell is a square with lattice points at the corners,

(b) a wallpaper pattern formed by associating a design element (blue heart) with each lattice point. The x centred on each heart corresponds to a lattice point. Notice that the unit cell contains portions of a heart at each corner. (The rest of each heart lies in adjacent unit cells.)

(c) and

(d) There is no requirement that the lattice point is centred on any object. In (a), (b), (c) and (d), all the information needed to generate the entire array is present in the unit cell, which is repeated over and over.

Another example is shown in the picture by the Dutch artist MC Escher (1898–1972) reproduced in figure 7.33. Escher often used symmetrical patterns aligned together to create an overall design. The repeating units can be visualised as tiles placed edge to edge. The faces of unit cells can be squares, rectangles or parallelograms. In figure 7.33a each tile is a parallelogram. Once you have chosen the size and shape of the unit cell, you can move its origin and still create the same overall pattern (figure 7.33b).

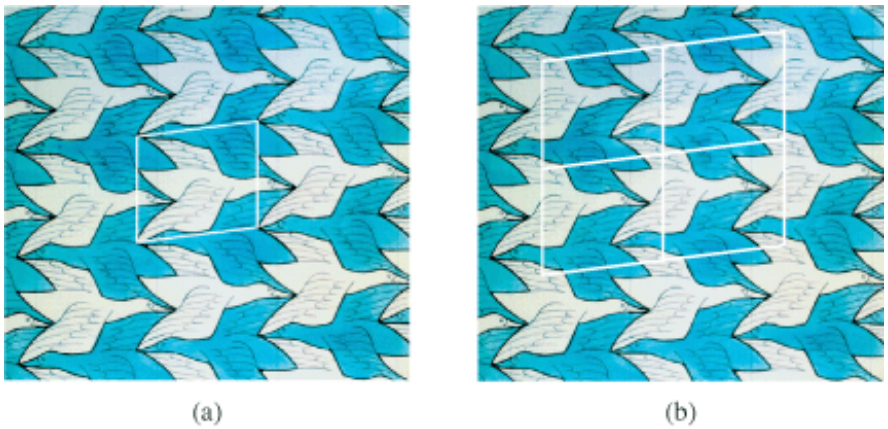


FIGURE 7.33 A drawing by MC Escher that contains a repeating pattern. A two-dimensional unit cell is highlighted in **(a)**. In **(b)**, the unit cell has been shifted and it is shown how repeating it in two dimensions will produce the entire pattern. (*Source:* M.C. Escher's 'Symmetry Drawing E18', © 2007 The M.C. Escher Company–Holland. All rights reserved. www.mcescher.com)

For the sake of simplicity we have looked at lattices and unit cells in two dimensions. We can also apply these concepts to three-dimensional patterns. The ions, atoms or molecules in many solids are arranged in regular three-dimensional patterns. Such solids are classified as **crystalline solids**. Diamonds are an example. We can describe crystalline solids using the concepts of a **crystal lattice**, that is, the lattice of a crystalline solid and a unit cell. It is possible to describe limitless numbers of different compounds with just a limited set of three-dimensional lattices. In fact, it has been shown mathematically that there are only 14 different types of three-dimensional lattices possible, which means that essentially all crystalline chemical substances must form crystals with one of these 14 lattice types, albeit with different unit cell dimensions. On the following pages, we describe some metal structures with cubic unit cells. These crystal structures can be described such that all the atoms in a unit cell are associated with the lattice points, i.e. the number of atoms in the unit cell and the number of lattice points will be identical. This is because all metal atoms in each of these very simple structures have identical surroundings and therefore all can be associated with lattice points. This is not so for most other crystalline solid structures.

Cubic Structures

The easiest three-dimensional structure to visualise has a simple cube as the unit cell. In a simple cubic crystal, layers of atoms stack one directly above another, so that all atoms lie along straight lines at right angles, as figure 7.34 shows. Each atom in this structure has a coordination number of 6; there are four nearest neighbours within the same plane, one above the plane and one below the plane. Within one layer of the crystal, any set of four atoms forms a square. Adding four atoms directly above or below the first four forms a cube. This structure is called the **primitive cubic structure**, because it has a primitive cubic lattice. (In this context, primitive means that there is only one lattice point per unit cell. A method for determining the number of lattice points is described below.) The unit cell of the primitive cubic structure is shown in the cutaway portion of figure 7.34. To calculate how many atoms are in the unit cell, we count only that proportion of the atom that is within the unit cell boundaries. An atom that is located on the corner of a cube is shared by eight cubes in total. Therefore, only $\frac{1}{8}$ of that atom counts for any one of those cubes. The unit cell contains $\frac{1}{8}$ of an atom at each of the eight corners of a cube. The total number of atoms in the unit cell is thus $8\left(\frac{1}{8}\right) = 1$. The same applies to counting lattice points; a unit cell with lattice points only on the corners ends up with one lattice point, i.e. a primitive lattice. The fraction of space that is filled by the atoms in this primitive cubic unit cell is only 52%. This is much less than the most efficient packing, which achieves 74% space filling (see p. 270). Consequently, this structure is adopted by only one metal: polonium.

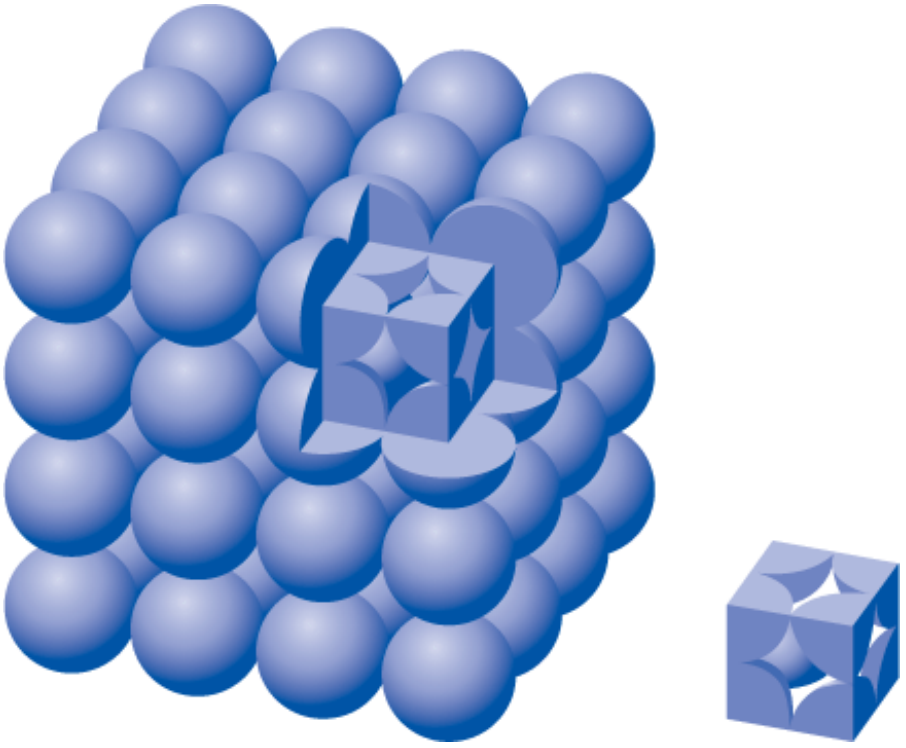
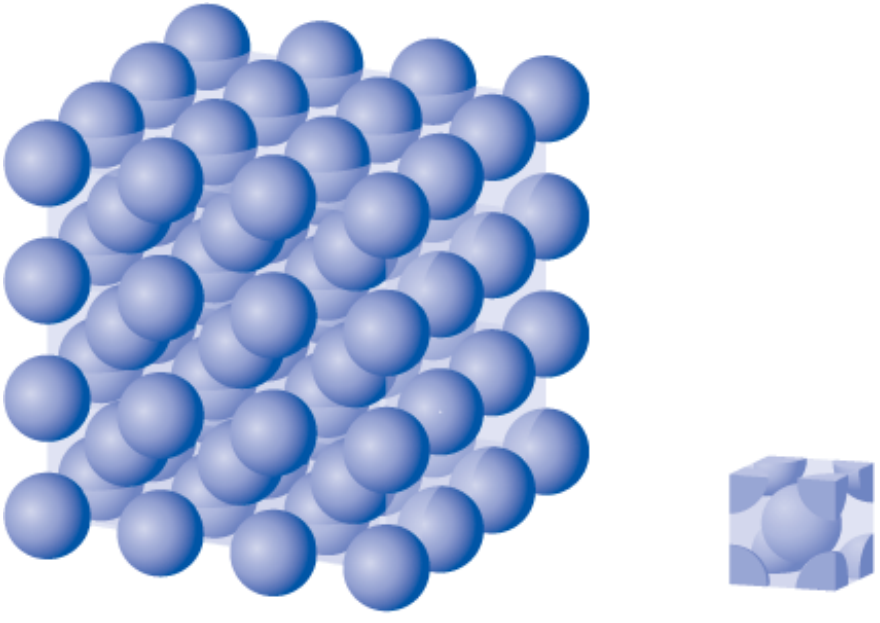


FIGURE 7.34 The simple cubic structure is built from square layers of spheres stacked one directly above another. The cutaway view shows one unit cell.

When eight atoms form a cube, there is a cavity at the centre of the cube. The cavity is not large enough to hold an additional atom, but moving the eight corner atoms slightly away from each other does allow the structure to accommodate another atom of the same type in the centre. The result is the body-centred cubic structure, described by a **body-centred cubic lattice (bcc)**, which now has two lattice points: one on a corner and one in the centre of the cube. Each atom in a body-centred cubic lattice is at the centre of a cube and contacts eight neighbouring corner atoms (see figure 7.35). In other words, every atom in the structure can be viewed as the centre atom of one body-centred cube or as a corner atom in another cube. The unit cell of a body-centred cube contains a total of $\left[1+8(\frac{1}{8})\right]=2$ atoms. The views of the iron crystal structure in figure 7.35 on the next page illustrate this arrangement.



(a) (b)

FIGURE 7.35 Views of the arrangement of atoms in iron:
(a) a view of the body-centred crystal lattice and
(b) the unit cell.

Although the corner atoms are further apart in a body-centred cube than in a primitive cube, the extra atom in the centre of the structure makes the body-centred cubic structure more compact than the primitive cubic structure. It fills 68% of the total space, which is close to the maximum possible. All of the group 1 metals, as well as iron and the transition metals from groups 5 and 6, form crystals with body-centred cubic structures.

Another common cubic crystal structure is the **face-centred cubic structure (fcc)**, which is the same as the cubic close-packed structure that we encountered on p. 270. When four atoms form a square, there is open space at the centre of the square. A fifth atom can fit into this space by moving the other four atoms away from one another. Additional atoms can be placed in the centres of all six faces of the simple cube, as figure 7.36 shows.

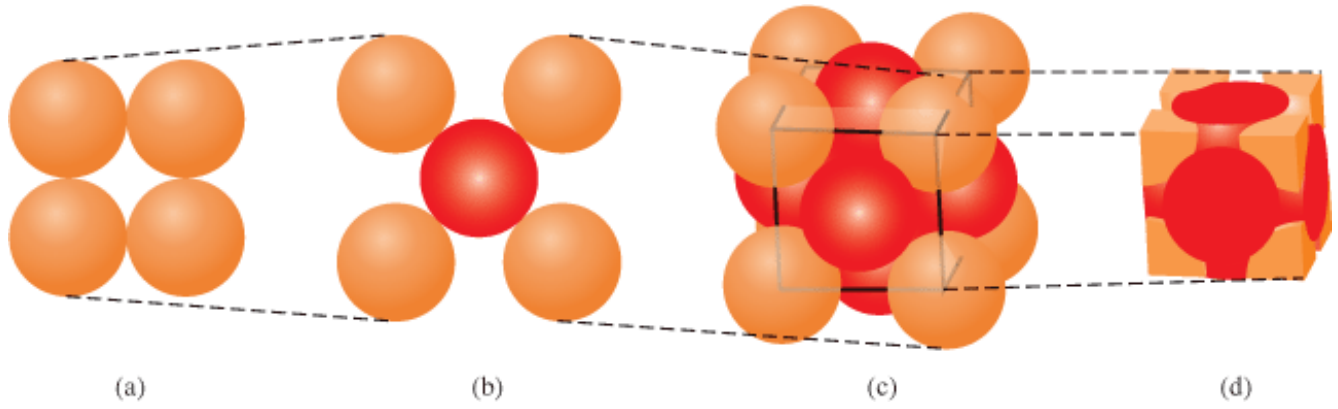


FIGURE 7.36 The face-centred cubic lattice can be viewed as:
(a) a simple cube,
(b) with each face expanded just enough to fit an additional atom in the centre,
(c) giving eight atoms at the corners and six atoms embedded in the faces.
(d) The unit cell has $\frac{1}{2}$ of an atom at the centre of each face and $\frac{1}{8}$ of an atom at each corner.
(All atoms in this arrangement are the same. Different colours are used only for clarity.)

The unit cell of the face-centred cube consists of six $\frac{1}{2}$-atoms embedded in the faces of the cube and eight $\frac{1}{8}$-atoms at the corners of the cube. This unit cell contains $\left[6(\frac{1}{2}) + 8(\frac{1}{8})\right] = 4$ atoms. Each atom in a face-centred cube contacts 12 neighbouring atoms. Consequently, the face-centred cube is more compact than either of the other cubic structures and fills 74% of the total space. The cubic close-packed structure that we

encountered at the beginning of section 7.4 can be described by this face-centred cubic unit cell.

Figure 7.37 shows the relationship between a set of hexagonal layers and a face-centred cubic unit cell. Figure 7.37a shows a top-down view of the hexagonal layers. In figure 7.37b we have removed all but one of the atoms from the top and bottom layers, and have removed all but six atoms in each of the two middle layers. We can see from figure 7.37c that a line drawn between the orange atoms (from the top and bottom layers) represents the body diagonal of a cube. Each face of the cube has an atom at each corner and one atom in the centre, as shown by figure 7.37c. Since all the atoms are identical, this is a face-centred cubic arrangement as revealed in the perspectives of figures 7.37c and 7.37d.

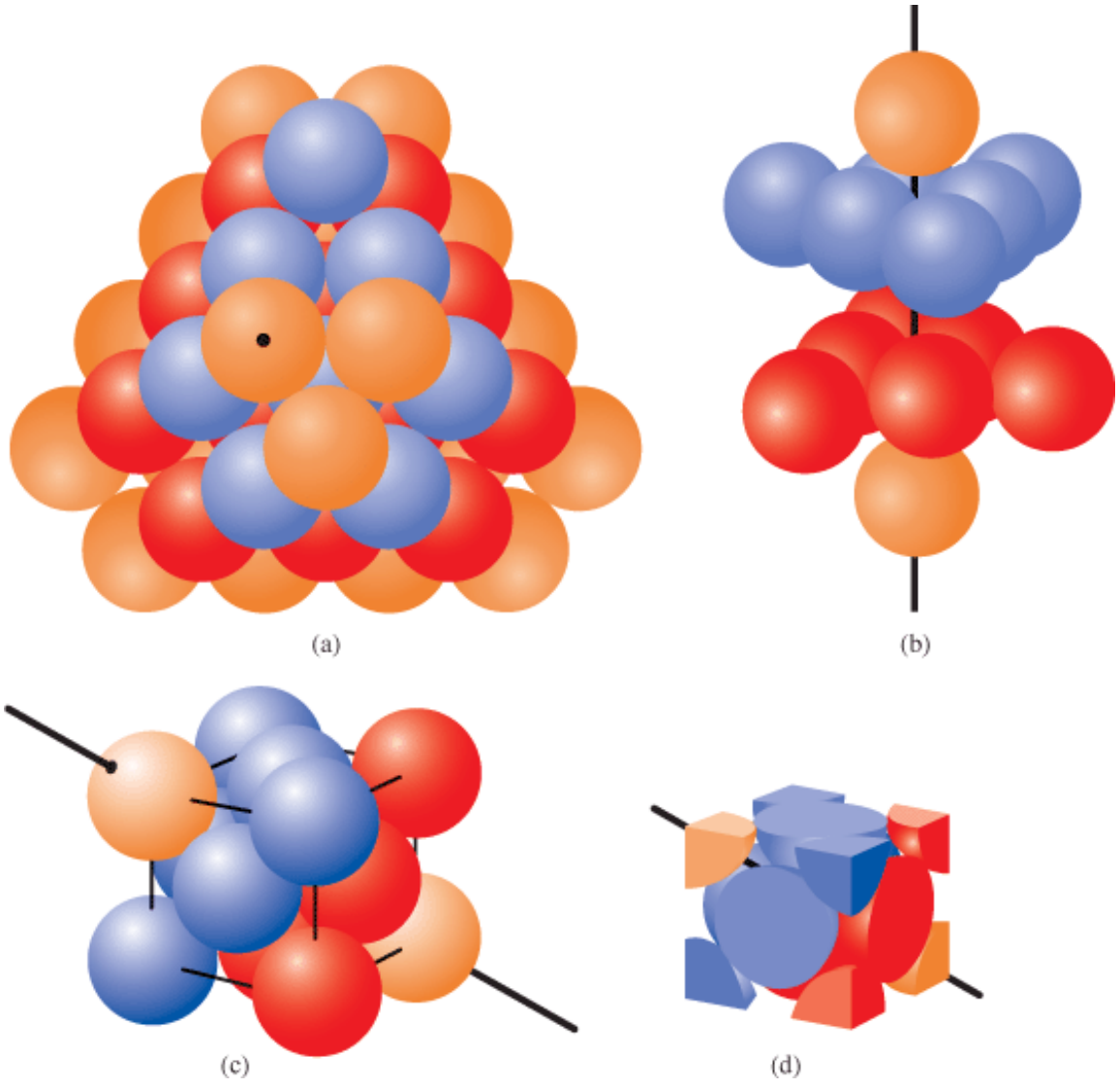


FIGURE 7.37 Four views of the hexagonal layers contained within a face-centred cubic arrangement:
(a) a top-down view of the hexagonal layers, with an axis shown as a black dot,
(b) a side view showing four layers along the axis,
(c) tilting (b) leads to the arrangement shown here, with the vertical black line in (b) now the body diagonal of this cube, and
(d) the unit cell. (All atoms in this arrangement are the same. Different colours are used for clarity only.)

We can now see that the arrangement of hexagonal layers in an ABCABC fashion is called a cubic close-packed structure, because the structure can be described by a face-centred cubic unit cell (the terms ‘cubic close-packed structure’ and ‘face-centred cubic structure’ are often used synonmously). Equally, the hexagonal close-packed structure gets its name because it can be described by a hexagonal unit cell as shown in figure 7.38.

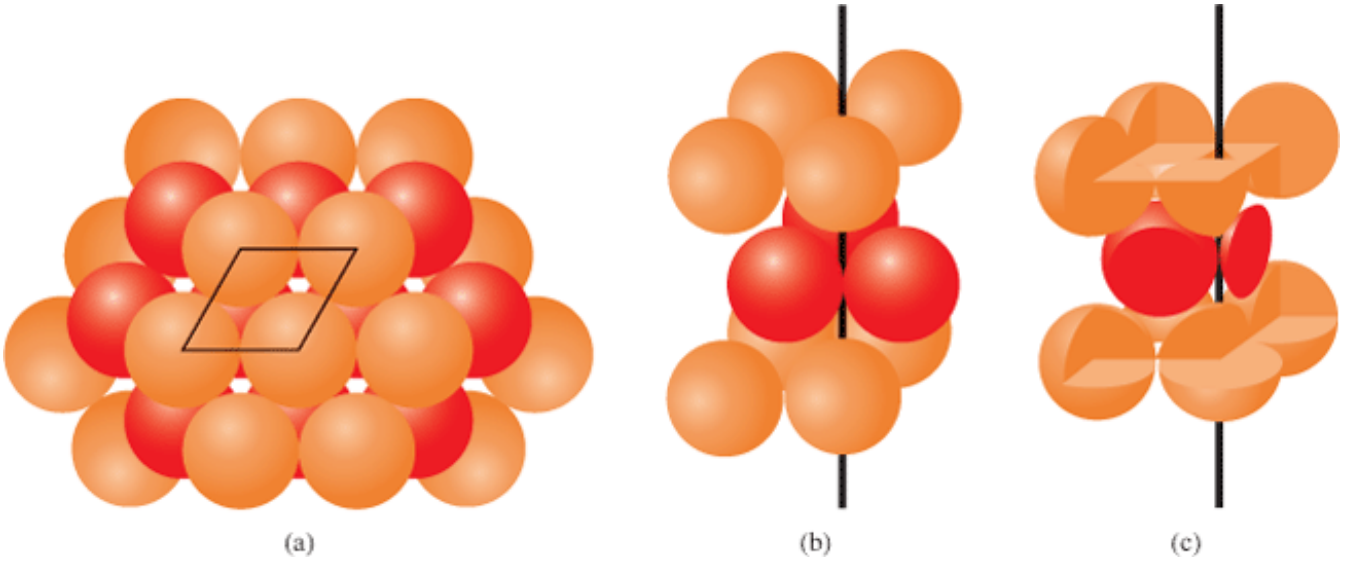


FIGURE 7.38 Three views of the hexagonal layers contained within a hexagonal close-packed structure:
(a) a top-down view of the hexagonal layers with the unit cell shown,
(b) a side view showing three layers and
(c) the unit cell. This unit cell contains two atoms and fills 74% of the space. (All atoms in this arrangement are of the same type. Different colours are used for clarity only.)

Up to now, we have described the crystalline arrangements favoured by spherical objects such as atoms, but most molecules are far from spherical. Nonspherical objects require different arrays to achieve maximal stability. To illustrate, compare a stack of bananas with a stack of oranges (figure 7.39). Just as the stacking pattern for bananas is less symmetrical than that for oranges, the structural patterns for most molecular crystals are less symmetrical than those for crystals of spherical atoms, reflecting the lower symmetry of the molecules.

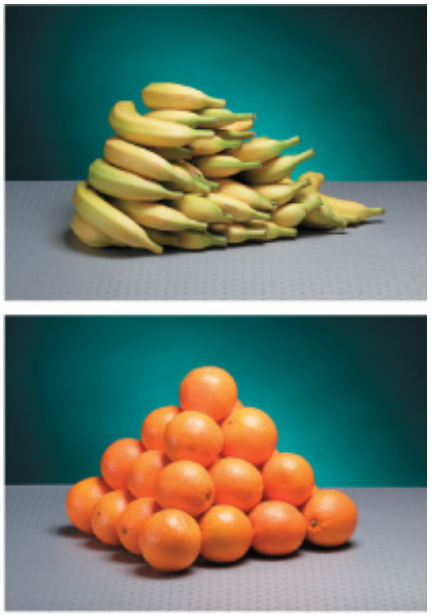


FIGURE 7.39 Nonspherical bananas require different packing schemes from spherical oranges.

Ionic Solids

We will now show how the principles discussed previously relate to the actual structures of ionic solids. Recall from figure 7.28 that two sets of dimples are created when we add two hexagonal layers of spheres. This is shown again in figure 7.40a. One set of dimples has an atom directly below (shown in orange), while the other set does not (shown in blue). The open space between the two layers of spheres directly below the first set of dimples is surrounded by four spheres (one below and three above), while the open space between the two layers of spheres directly below the second set of dimples is surrounded by six spheres (three below and three above). Figure 7.40b shows that the four spheres associated with the first set of dimples form a tetrahedron, while figure 7.40c shows that the six spheres associated with the second set form an octahedron. The space between the spheres is called an **interstitial hole**. The interstitial holes take up much less space than the spheres that surround them. In general, the more spheres that surround an interstitial hole, the larger the hole is, that is, an octahedral hole is larger than a tetrahedral hole. The number of octahedral holes equals the number of spheres that form the structure, while the number of tetrahedral holes is twice the number of spheres that form the structure.

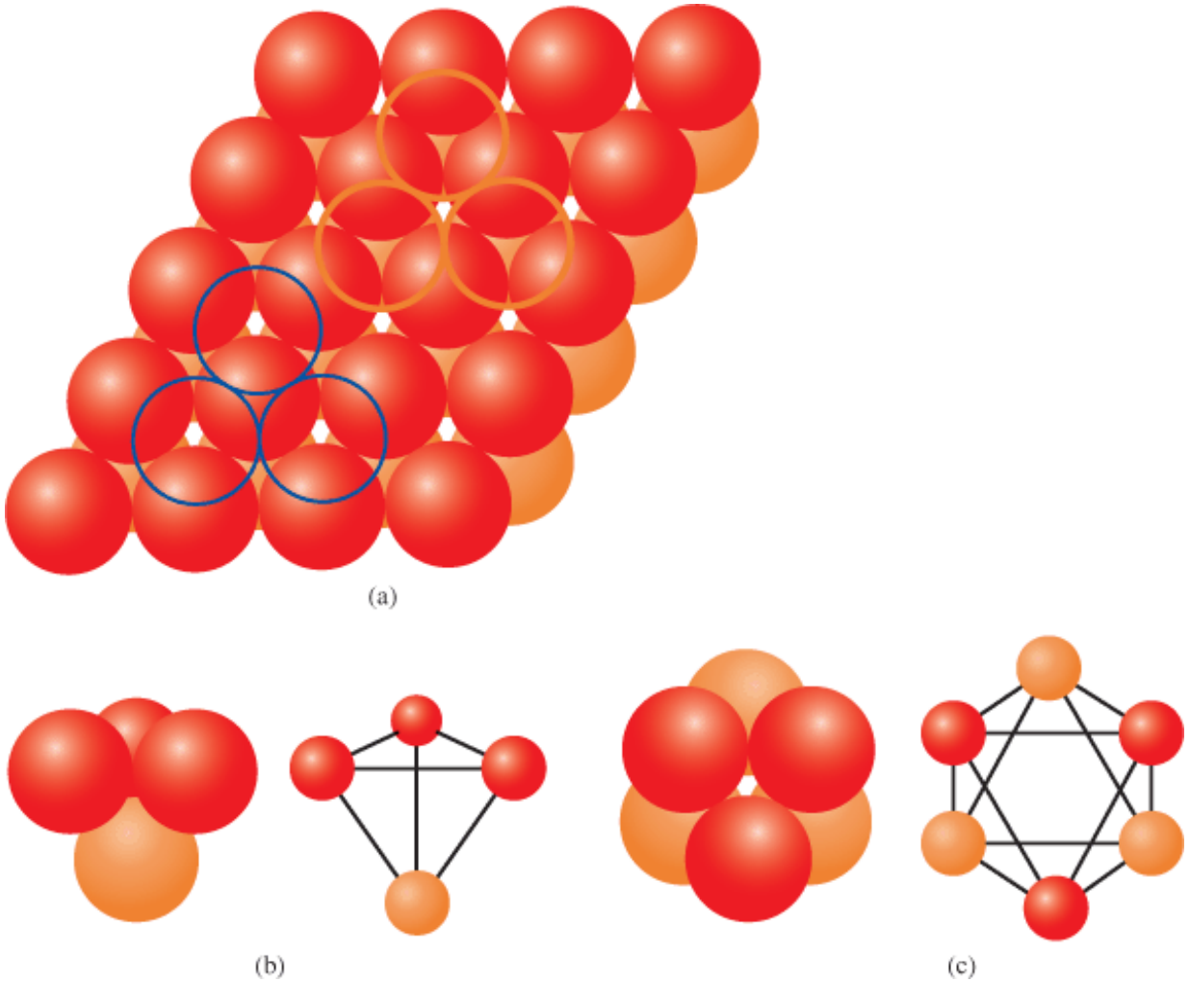


FIGURE 7.40

(a) Two sets of dimples are created when two hexagonal layers of spheres are combined.
(b) The four spheres associated with each dimple shown in orange surround a tetrahedral hole.
(c) The six spheres associated with each dimple shown in red surround an octahedral hole.

The packing in ionic crystals requires that ions of opposite charge alternate with one another to maximise attractions and minimise repulsions. The cations and anions are usually different sizes (often the cations are smaller). We can understand ionic structures by assuming that the close-packed structure is formed by the larger ions, while the smaller ions fill the interstitial sites. We can identify a crystal lattice for the larger ions, and then describe how the smaller ions pack within that lattice. Because the crystal is made up of a huge number of identical unit cells, the stoichiometry within the unit cell must match the overall stoichiometry of the compound.

Ionic compounds adopt a variety of structures that depend on the stoichiometry and relative sizes of the ions. For many 1 : 1 ionic crystals such as NaCl, the most stable arrangement is a face-centred cubic array of anions (Cl^-) with the cations (Na^+) packed into the octahedral holes between the anions. This structure appears in figure 7.41a. Notice that every cation is surrounded by six anions and every anion is surrounded by six cations. The unit cell based on close packing of Cl^- is shown. In addition to the face-centred cubic arrangement of chloride ions, the unit cell in figure 7.41b shows $\frac{1}{4}$ of a sodium cation along each edge of the cell, and there is an additional sodium cation in the centre of the unit cell. Summing the components reveals that each unit cell contains four complete NaCl units, thus giving the correct 1 : 1 stoichiometry.

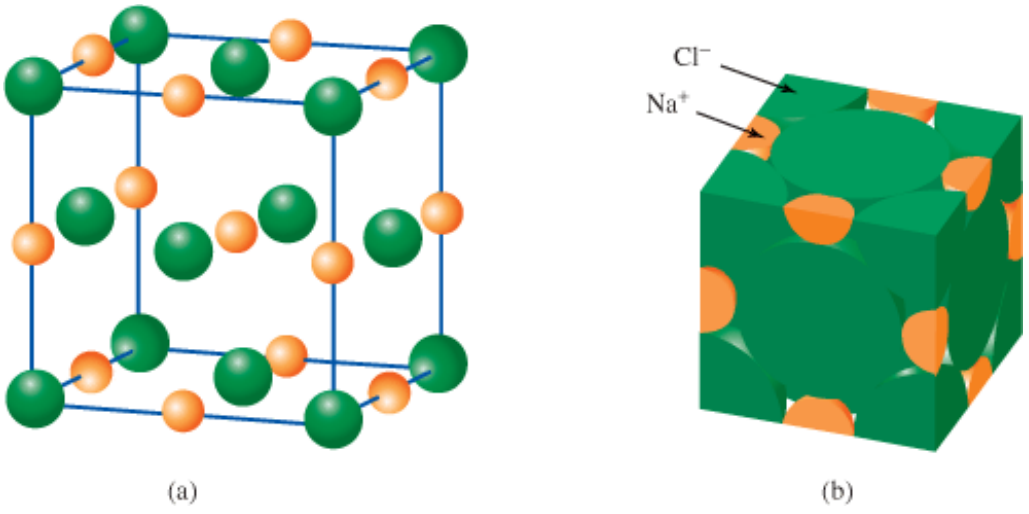


FIGURE 7.41

(a) The structure of sodium chloride can be described as a face-centred cubic arrangement of Cl^- anions (green), with the Na^+ cations (orange) occupying the interstitial octahedral sites.
(b) Because Cl^- anions are considerably larger than Na^+ cations, the commonly used unit cell

places anions at the corners. There is a cation at the centre of this unit cell.

$$\text{chloride anions: 6face } (\tfrac{1}{2}\text{anion/faces}) + 8 \text{ corners } (\tfrac{1}{8}\text{anion/corner}) = 4\ Cl^- \text{ anions}$$

$$\text{sodium cations: 12 edges } (\tfrac{1}{4}\text{ cation/edge}) + 1 \text{ in center} = 4\ Na^+ \text{ cations}$$

Many ionic solids have the same structure type as sodium chloride. Examples are all the halides of Li^+, Na^+, K^+ and Rb^+, as well as the oxides of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}.

Caesium chloride, in which the relative size of the cation is much larger than in sodium chloride, forms a different type of structure. Because its cation and anion are close to the same size, caesium chloride is most stable in a primitive cubic lattice. There are Cl^- anions at the corners of the cube, with a Cs^+ in the centre, as figure 7.42 shows. The unit cell contains $8(\frac{1}{8}) = 1$ chloride ion and 1 caesium ion. The caesium chloride structure type is also found for CsBr, CsI and several other 1 : 1 ionic crystals in which the cations and anions have similar sizes.

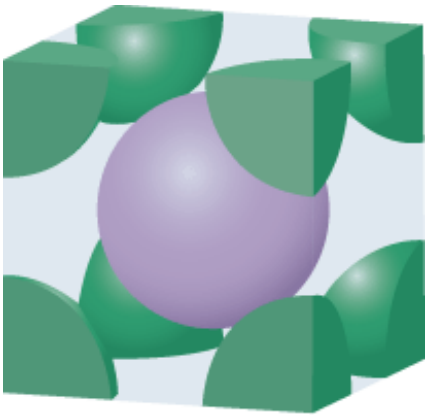


FIGURE 7.42 The caesium chloride structure consists of a primitive cubic array of chloride anions with a caesium cation at the centre of each unit cell.

In zinc sulfide, ZnS, the relative size ratios are such that the zinc cation is too small for octahedral sites and instead occupies tetrahedral holes in the structure. Since there are twice as many tetrahedral sites as spheres that form the structure, only half will be occupied by Zn^{2+} cations in a regular fashion. We have seen previously that a face-centred arrangement of anions leads to four anions in the unit cell. We can see in figure 7.43 that there are also four cations within the unit cell, resulting in the correct 1 : 1 stoichiometry. In this structure, as seen in figure 7.43b, every cation is surrounded by four anions, and every anion is surrounded by four cations in a tetrahedral arrangement.

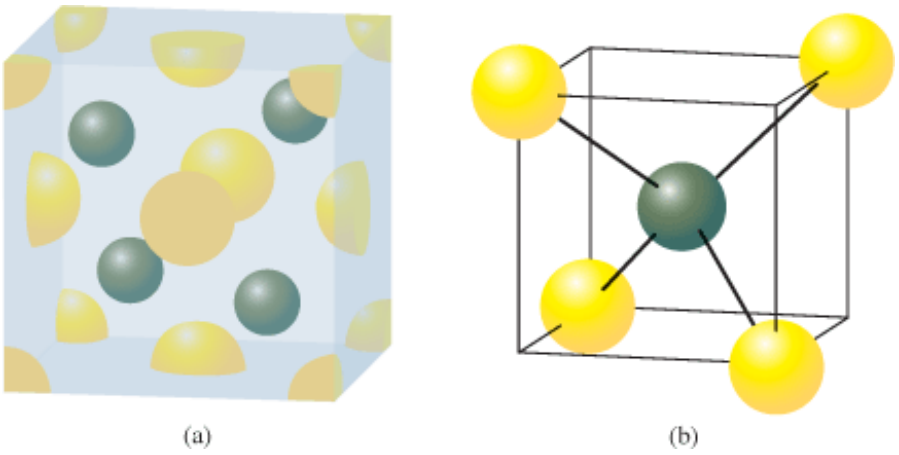
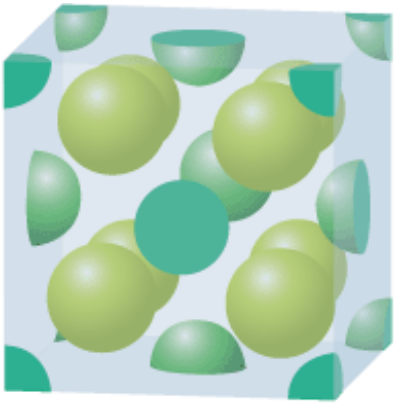


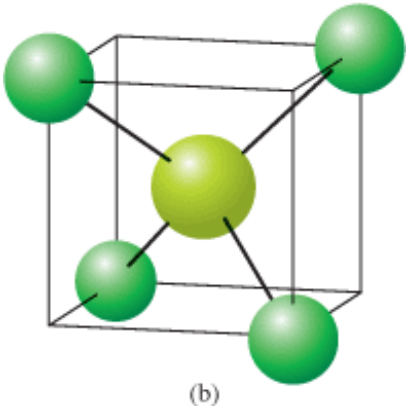
FIGURE 7.43 Zinc sulfide.
(a) The unit cell of cubic zinc sulfide has anions in a face-centred cubic arrangement.

(b) Each cation is surrounded by four anions in the form of a tetrahedron.

Many ionic compounds have stoichiometries that differ from 1 : 1. To give an example, the fluorite structure is named for the naturally occurring form of CaF_2 and is common for salts of the general formula MX_2X. It is easiest to describe this structure by thinking of the Ca^{2+} cations arranged in a face-centred cubic structure. In this arrangement, the F^- anions fill all the tetrahedral holes in the lattice, forming a simple cube of eight anions in the interior of the face-centred cube. This is in contrast to zinc sulfide, where only half of the tetrahedral holes were filled. Figure 7.44a shows the unit cell of the fluorite structure, which contains a total of four Ca^{2+} cations and eight F^- anions (consistent with the number of tetrahedral holes being twice the number of spheres that form the structure).



(a)



(b)

FIGURE 7.44

(a) The unit cell of the fluorite structure has cations in a face-centred cubic arrangement, with a simple cube of anions within the unit cell.

(b) All fluoride ions are surrounded by four calcium ions in a tetrahedral arrangement.

$$\text{calcium anions: } 6\,\text{face}\left(\frac{1}{2}\,\text{cation/face}\right) + 8\,\text{corners}\left(\frac{1}{8}\,\text{cation/corner}\right) = 4\,Ca^{2+}\,\text{cations}$$

$$\text{fluoride anions: } 8\,\text{complete anions within the face-centred cube} = 8\,F^{-}\,\text{anions}$$

This gives the correct 1 : 2 stoichiometry, resulting in electrical neutrality.

The calcium ions are arranged in a tetrahedron about the fluoride ions as shown in figure 7.44b. We have briefly mentioned four simple ionic lattices, but there are many others. Moreover, the structures of many crystalline network solids can also be described by the methods we have introduced here for NaCl, CsCl, ZnS and CaF_2.

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7.5 X-ray Diffraction

X-ray diffraction can be used to determine the arrangement of atoms, molecules or ions in a crystalline structure. When atoms are exposed to X-rays, they act like tiny X-ray sources. If we look at radiation from two such atoms (see figure 7.45), we find that the X-rays are in phase in some directions but out of phase in others. In chapter 4 you learned about constructive (in-phase) and destructive (out-of-phase) interferences of waves, and these create a phenomenon called *diffraction*. X-ray diffraction by crystals has enabled scientists to determine the structures of extremely complex compounds in a particularly elegant way.

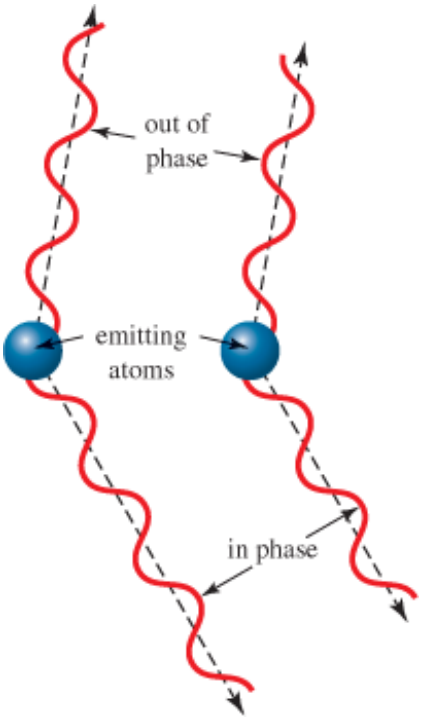


FIGURE 7.45 Diffraction of X-rays from atoms in a crystal. X-rays emitted from atoms are in phase in some directions and out of phase in other directions.

In a crystal, there are enormous numbers of atoms, and these can be described by a lattice and a unit cell. When the crystal is exposed to X-rays, diffracted beams due to constructive interference appear only in specific directions. In other directions, no X-rays appear because of destructive interference. The X-rays coming from the crystal are recorded and form a **diffraction pattern** (see figure 7.46).

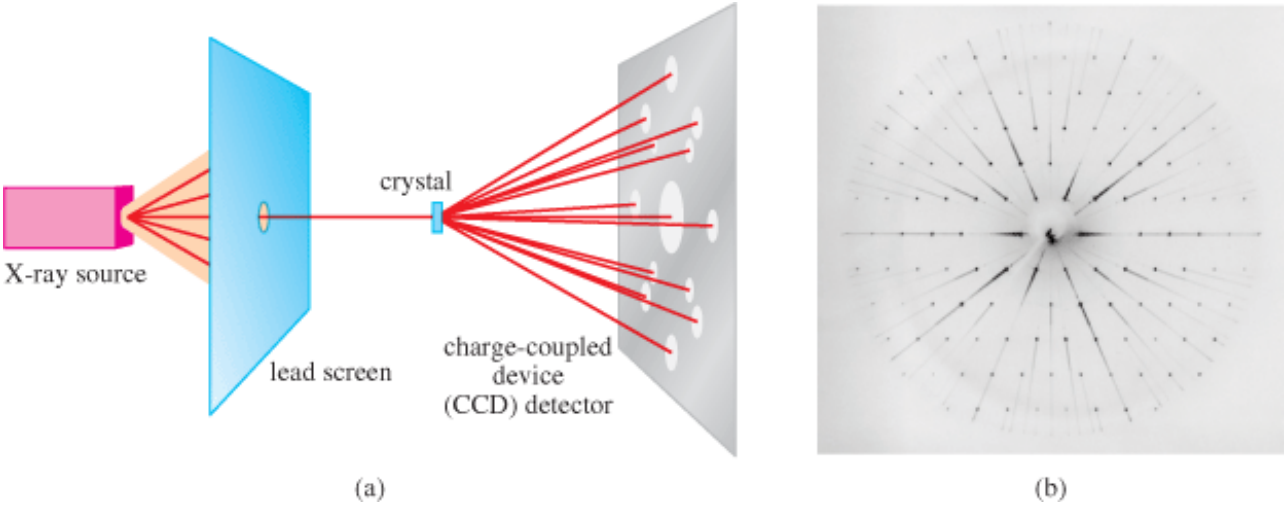


FIGURE 7.46 X-ray diffraction:
(a) schematic set-up for recording an X-ray diffraction pattern and
(b) an X-ray diffraction pattern.

In 1913, William Henry Bragg and his Australian-born son William Lawrence Bragg discovered that just a few variables control the appearance of an X-ray diffraction pattern. Figure 7.47 illustrates the conditions necessary to obtain constructive interference of the X-rays from successive layers (planes) of atoms in a crystal. A beam of X-rays with a wavelength λ strikes the layers at an angle θ. For certain distances, *d*, between the layers, constructive interference causes an intense diffracted beam to emerge at the same angle, θ.

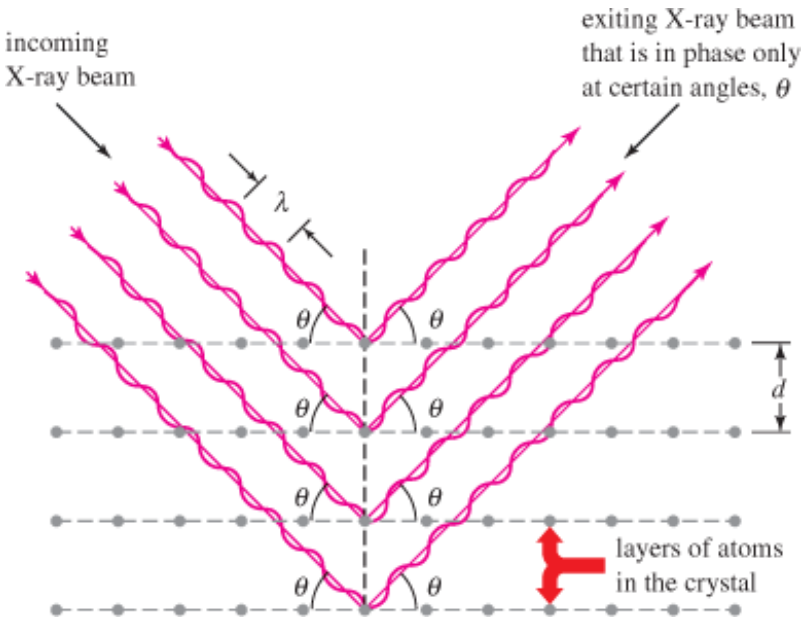


FIGURE 7.47 Diffraction of X-rays from successive layers of atoms i n a crystal. The layers of atoms are separated by a distance *d*. The X-rays of wavelength λ enter and emerge at an angle θ relative to the layers of the atoms. For the emerging beam of X-rays to have any intensity, the condition $n\lambda = 2d \sin\theta$ must be fulfilled, where *n* is an integer.

The **Bragg equation** relates λ, θ and the distance between the planes of atoms, *d*:

$$n\lambda = 2d \sin\theta$$

where *n* is any integer. The Bragg equation is the basic tool used by scientists in the study of solid structures. Let us briefly see how it is used.

In any crystal, many different sets of imaginary planes can be passed through the structure. Figure 7.48 illustrates this idea in two dimensions for a simple pattern of points. When a crystal is exposed to X-rays, many diffracted beams are produced because of the diffraction from the many sets of planes. An apparatus called a diffractometer (figure 7.49) is used to record the diffraction pattern and allows the determination of the angles at which the diffracted beams emerge from each distinct set of planes. Using the Bragg equation, we can calculate the distances between planes of atoms from the measured angles of diffraction, the wavelength of the X-rays (source dependent) and the value of *n* (usually 1). The next step is to use the calculated interplanar distances to deduce the unit cell of the lattice. The locations of the atoms within the unit cell are then determined from the relative intensities of the diffracted beams. If this sounds like a difficult task, it is! For all but the simplest crystalline structures, sophisticated mathematics and computers are needed to accomplish it. The efforts, however, are well rewarded because the calculations give very accurate locations for the atoms within the unit cell. This enables us to understand the bonding, intermolecular interactions and properties of crystalline materials.

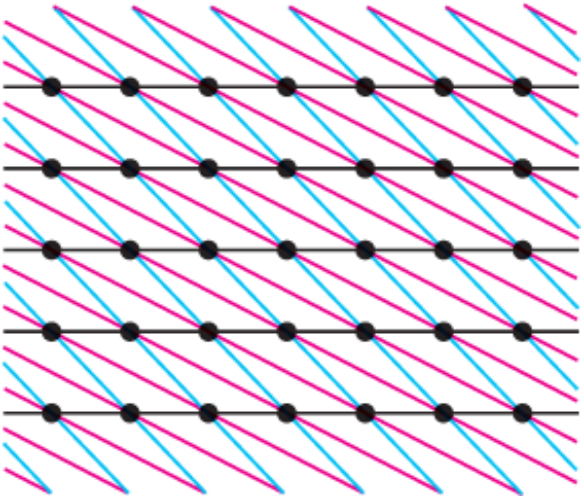


FIGURE 7.48 A two-dimensional pattern of points with many possible sets of parallel lines. In a three-dimensional crystal lattice there are many sets of parallel planes.

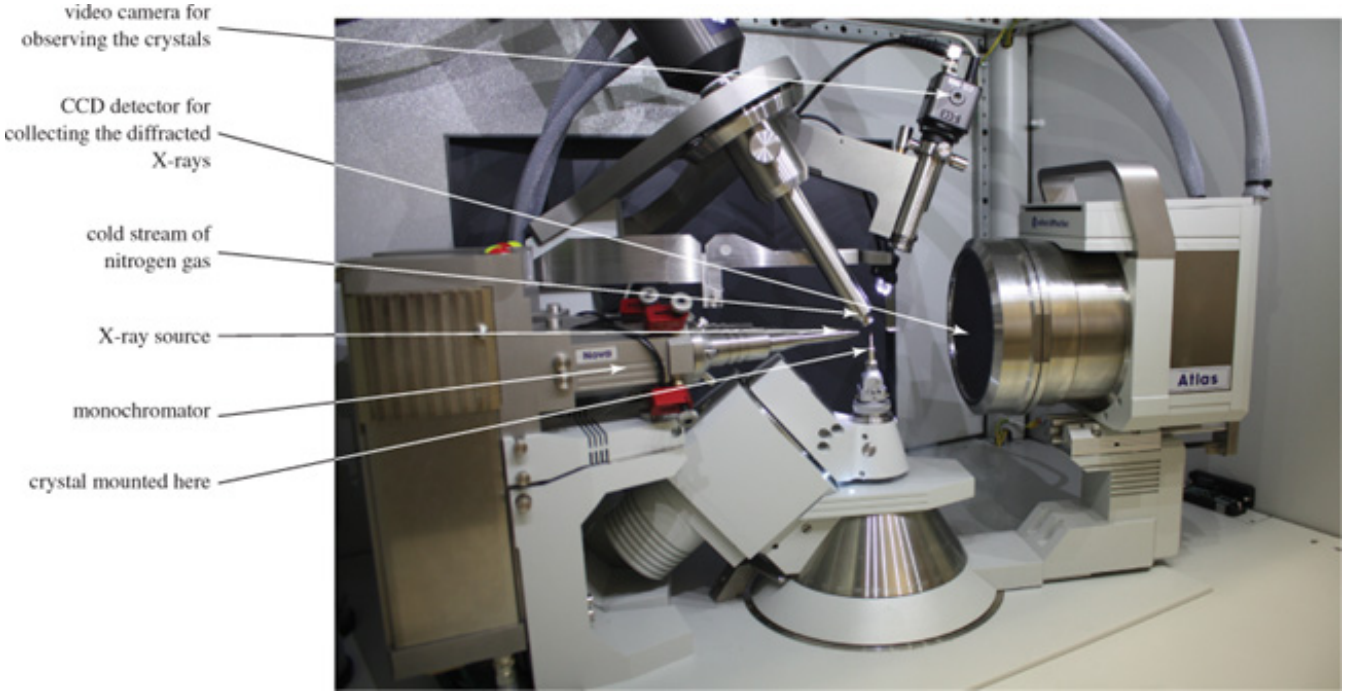


FIGURE 7.49 A modern X-ray diffractometer.

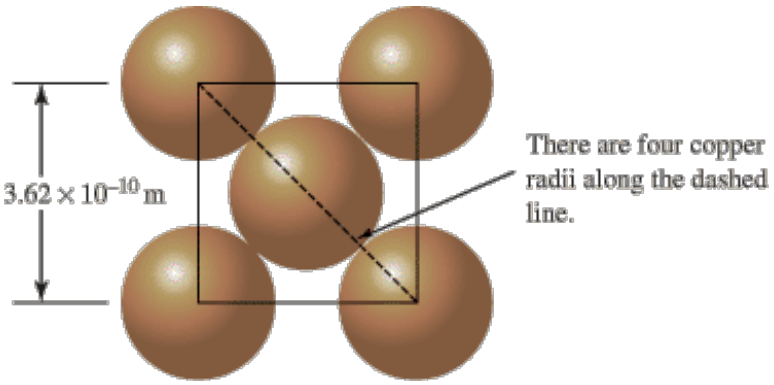
WORKED EXAMPLE 7.4

Using Crystal Structure Data to Calculate Atomic Sizes

X-ray diffraction measurements reveal that copper crystallises with a face-centred cubic lattice in which the unit cell length is 3.62×10^{-10} m. What is the radius of a copper atom? What is the copper–copper bond length?

Analysis

Copper atoms are in contact along a face diagonal (the dashed line at right) that runs from one corner of a face to another corner.



Using geometry, we can calculate the length of this diagonal, which equals four times the radius of a copper atom.

Solution

From geometry, the length of the diagonal is $\sqrt{2}$ times the length of the edge of the unit cell.

$$\text{diagonal} = \sqrt{2} \times (3.36 \times 10^{-10}) = 5.12 \times 10^{-10}\text{m}$$

If we call the radius of the copper atom r_{Cu}, then the diagonal equals $4 \times r_{Cu}$. Therefore:

$$\begin{aligned} 4 \times r_{Cu} &= 5.12 \times 10^{-10}\ \text{m} \\ r_{Cu} &= 1.28 \times 10^{-10}\ \text{m} \end{aligned}$$

The calculated radius of the copper atom is 1.28×10^{-10} m.

The copper–copper bond length is twice this number: i.e. 2.56×10^{-10} m.

Is our answer reasonable?

Depending on the size of the atom, you should know from chapter 5 that bond distances between atoms are about $1–3 \times 10^{-10}$ m and atomic radii are about half of this. The calculated Cu radius and Cu—Cu bond length fall within this range, so our answer is reasonable.

X-ray diffraction has had a profound impact on the study of biochemistry. Biochemists often use X-ray diffraction to determine the structures of enzymes and other large molecules produced by living systems. The most famous example is the experimental determination of the molecular structure of DNA. DNA (see chapter 25) is found in the nuclei of cells, and serves to carry an organism's genetic information. In 1953, using X-ray diffraction photographs of DNA fibres (figure 7.50) obtained by Rosalind Franklin and New Zealand-born Maurice Wilkins, James Watson and Francis Crick came to the conclusion that the DNA structure consists of the now-famous double helix (see figure 7.51). Watson, Crick and Wilkins shared the 1962 Nobel Prize in physiology or medicine for their discovery (Franklin had died of cancer in 1958, and it was not possible to nominate her for the Nobel Prize posthumously).

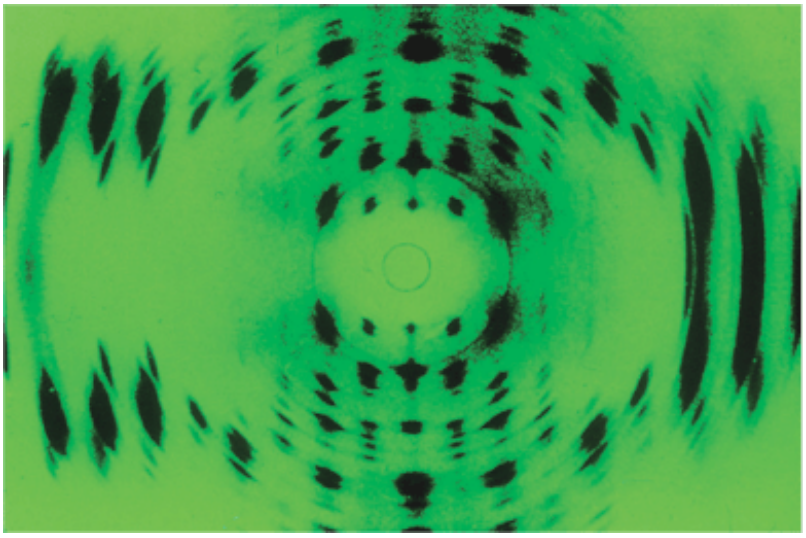


FIGURE 7.50 X-ray diffraction photograph of DNA.

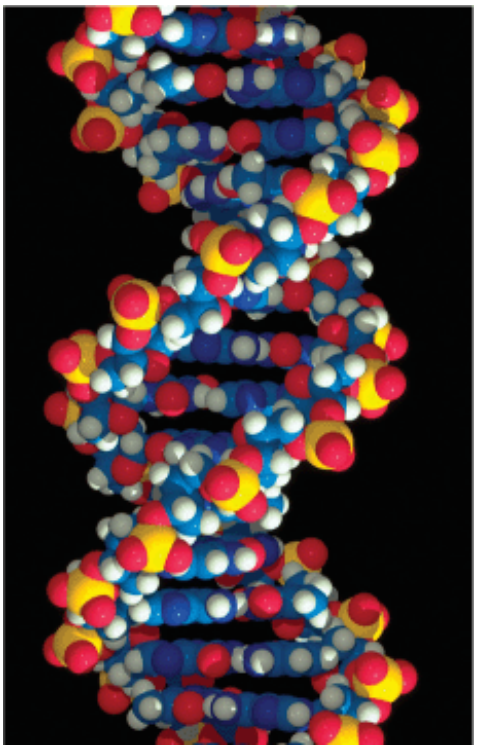


FIGURE 7.51 A computer-generated model of the DNA double helix.

X-ray diffraction continues to be one of the main tools used to determine the structures of complex proteins and enzymes.

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7.6 Amorphous Solids

When a pure liquid or a melt is cooled slowly, it often solidifies as a well-ordered crystalline solid. When solids form rapidly, on the other hand, their atoms, molecules or ions may become locked into positions other than those of a regular crystal, giving materials that are **amorphous**, meaning 'without form'. For example, ordinary cane sugar is crystalline, but rapidly cooling melted sugar gives fairy (or candy) floss, which contains long threads of amorphous sugar (figure 7.52). While amorphous solids can be formed in a variety of ways and by different mechanisms, one feature that clearly distinguishes them from crystalline solids is the fact that they do not diffract X-rays (see section 7.5).



(a)



(b)

FIGURE 7.52 (a) Fairy floss is amorphous, while (b) ordinary cane sugar is crystalline.

What we call **glass** is an entire family of amorphous solids based on silica, SiO_2. Pure SiO_2 is usually found as a crystalline solid containing a regular array of Si and O atoms. This is known as quartz. When quartz is melted and then quickly cooled, it forms fused silica, an amorphous solid glass. Silica glass has many desirable properties. It resists corrosion, transmits light well and withstands wide variations in temperature. Unfortunately, pure silica is very difficult to work with because of its high melting point (1983 K). Consequently, silica glass is used only for special applications.

Mixing sodium oxide, Na_2O, with silica results in a glass that can be shaped at a lower temperature. Sodium—oxygen bonds are ionic, and incorporating sodium ions into the mixture breaks the Si—O—Si chain of covalent bonds. This weakens the lattice strength of the glass, lowers its melting point and reduces the viscosity of the resulting liquid. However, the weakened lattice also means that glass made from mixed sodium and silicon oxides is vulnerable to chemical attack.

A desirable glass melts at a reasonable temperature, is easy to work with and yet is chemically inert. Such a glass can be prepared by adding a third component that has bonding characteristics between those of purely ionic sodium oxide and purely covalent silicon dioxide. Several different components are used, depending on the properties required for the glass.

The glass used for windowpanes and bottles is soda–lime–silica glass, a mixture of sodium oxide, calcium oxide and silicon dioxide. The addition of CaO strengthens the lattice enough to make the glass chemically inert to most common substances (strong bases and HF, however, attack this glass). Pyrex®, the glass used in coffeepots and laboratory glassware, is a mixture of B_2O_3, CaO and SiO_2. This glass can withstand rapid temperature changes that would crack soda–lime– silica glass. Lenses and other optical components are made from glass that contains PbO. Light rays are strongly bent as they pass through lenses made of this glass. Coloured glasses contain small amounts of coloured metal oxides such as Cr_2O_3 (amber), NiO (green) or CoO (brown).

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7.7 Crystal Imperfections

The two extremes of ordering in solids are perfect crystals with complete regularity and amorphous solids that have little order. Many solid materials are crystalline but contain defects. **Crystalline defects** can profoundly alter the properties of a solid material, often in ways that have useful applications. Doped semiconductors are solids into which impurity 'defects' are introduced deliberately in order to modify electrical conductivity. Some gemstones are crystals containing impurities that give them their colour. Sapphires and rubies are imperfect crystals of colourless Al_2O_3; Ti^{3+} or Fe^{3+} makes sapphires blue, and Cr^{3+} makes rubies red (figure 7.53).

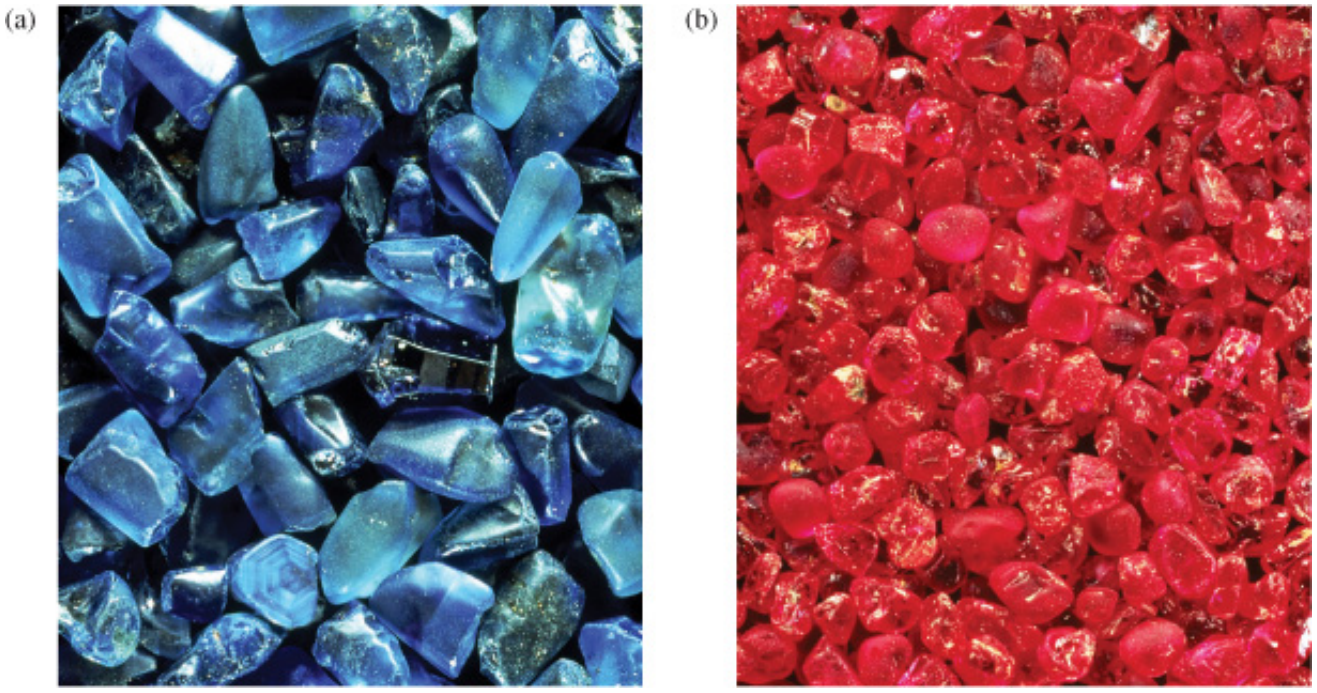


FIGURE 7.53 (a) Sapphires are blue; (b) rubies are red.

Yttrium barium copper oxide superconductors have optimal properties when they have a slight deficiency of oxygen, as indicated by the δ sign in the formula $YBa_2Cu_3O_{7-\delta}$. This departure from stoichiometric composition is accommodated by defects in the crystal structure. The superconductor crystal has oxygen anions missing from some positions in the crystal lattice, and the number of missing anions can vary sufficiently to give the material a variable composition. The solid remains electrically neutral when its anion content is varied because some of the cations take on different charges. The copper cations in the superconductor can have a +2 or +3 charge. The relative number of Cu^{3+} ions decreases as oxygen anions are removed from the structure.

Substitutional impurities replace one atom with another, while interstitial impurities occupy the spaces between regular atoms. Interstitial impurities create imperfections that play important roles in the properties of metals. For example, small amounts of impurities are deliberately added to iron to improve its mechanical properties. Pure iron is relatively soft, easily deformed and corrodes readily, but the addition of a small amount of carbon creates steel, a much harder material. Carbon atoms fill some of the open spaces between iron atoms in the crystalline structure of steel. Although carbon atoms fit easily into these spaces, their presence reduces the ability of adjacent layers of iron atoms to slide past each other, as figure 7.54 illustrates.

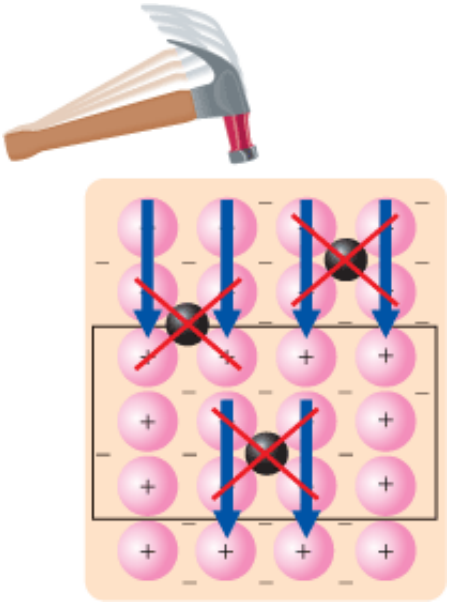


FIGURE 7.54 The presence of even a few carbon atoms (black spheres) in the interstitial holes in an iron lattice prevents adjacent layers of iron atoms from sliding past one another and hardens the iron into steel.

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7.8 Modern Ceramics

Ceramics are materials composed of inorganic components that have been heat treated. They have a long history, dating to prehistoric times. Examples of pottery about 13 000 years old have been found in several parts of the world. Today, ceramics include common inorganic building materials such as brick, cement and glass. We find ceramics around the home as porcelain dinner-ware, tiles, sinks, toilets, and artistic pottery and figurines. We also find ceramics in places we might not expect, such as mobile phones, diesel engines and bullet-proof vests.

Many manufactured ceramics are made from inorganic minerals such as clay, silica (sand) and other silicates (compounds containing anions composed of silicon and oxygen), which are taken from the Earth's crust. In recent times, an entirely new set of materials with high-tech applications, generally referred to as advanced ceramics, has been prepared by chemists. We will focus our discussions mainly on these.

Properties of Ceramics

There are some properties that ceramics have in common, and there are others that can be tailored by controlling the ceramic's composition and method of preparation. For example, many ceramic materials are very hard and have very high melting points. Table 7.3 contains a list of some advanced ceramic materials and their properties, along with the properties of some metals in common use. The hardest substance known is diamond, and some ceramics have hardnesses that approach diamond. Silicon carbide, which is relatively inexpensive to make in bulk, has long been used as an abrasive in sandpaper and grinding wheels.

TABLE 7.3 Some properties of ceramic materials, diamond, steel and aluminium

Ceramic material	Hardness ([a]) (GPa)	Melting point (°C)	Elastic modulus ([b]) (GPa)	Density (g mL^{-1})
diamond, C	80	3800	910	3.52
boron nitride, BN	50	2730	660	3.48
titanium carbide, TiC	28	3067	470	4.93
silicon carbide, SiC	26	2760	480	3.22
zirconium carbide, ZrC	25	3445	400	6.63
tungsten carbide, WC	23	2776	720	15.72
titanium nitride, TiN	21	2950	590	5.40
aluminium oxide, Al_2O_3 (alumina)	21	2047	400	3.98
beryllium oxide, BeO (beryllia)	15	2550	390	3.03
zirconium oxide, ZrO_2 (zirconia)	12	2677	190	5.76
aluminium nitride, AlN	12	2250	350	3.36
titanium dioxide, TiO_2 (titania)	11	1867	205	4.25

stainless steel	2.35	1420	200	7.89
aluminium	1.51	658	69	2.70

(a) Pressure required to dent the material: the larger the value, the harder the material.
(b) Force per unit cross-sectional area required to elongate (stretch) the solid: the larger the value, the stronger the material and the more it resists stretching.

Notice that all of the listed ceramics are harder than steel and also have lower densities and very high melting points. Those with high strength and relatively low density are useful, for example, for applications in space.

Because of their high melting points, we often find ceramics used as **refractories** (heat-resistant materials) for lining furnaces and rocket engine exhausts. When given a glassy porcelain surface, ceramics are impervious to water, but under the right conditions they can be made porous and used as filters in applications where high temperatures would destroy other materials.

Most ceramics do not conduct electricity, so they are used as insulators for high-voltage power lines, car spark plugs and in TV sets. However, some ceramic materials become excellent conductors of electricity when cooled to very low temperatures. There is a whole class of these materials that are superconductors with many potential applications (see pp. 283–6).

Table 7.3 shows that ceramics generally contain metals in relatively high positive oxidation states, combined with small nonmetals (e.g. O, N and C) with high negative oxidation states. As we discussed earlier, the assignment of a formal oxidation state does not mean that the electrons have completely transferred from one bonding partner to another; i.e. it allows for all forms of chemical bonding.

Actually, the ceramic compounds listed in table 7.3 possess substantial covalent bonding between the atoms. Imagining that the compounds were purely ionic, small cations with high charges would be able to pull electron density from highly charged anions into the region between the ions, causing the bonds to become substantially covalent. Furthermore, elements such as oxygen, nitrogen and carbon are able to form covalent bonds between two or more atoms. Therefore, a mixture of ionic and covalent bonding between the atoms, i.e. very polar covalent bonds, causes both the strength and high melting points of ceramic materials.

Applications of Advanced Ceramics

The field of high-tech ceramics is very competitive new materials with new applications are continually being developed. Their uses are extremely varied and a few examples are given on the following pages.

Thin ceramic films are used as antireflective coatings on optical surfaces and as filters for lighting. Tools such as drill bits are given thin coatings of titanium nitride, TiN, to make them more wear resistant (figure 7.55).



FIGURE 7.55 A drill bit with a thin golden coating of titanium nitride, TiN, will retain its sharpness longer than steel drill bits.

Partially stabilised zirconia (ZrO_2 with small amounts of other metal oxides) is used to make portions of hip-joint replacements. This application is possible because of the toughness of the ceramic.

One form of boron nitride powder, BN, is composed of flat, platelike crystals that can easily slide over one another. It is used in cosmetics, where it gives a silky texture. Another boron-containing ceramic, boron carbide, is used along with Kevlar^{tm} polymer to make bullet-proof vests. When a bullet strikes the vest, it is either shattered by the ceramic, or it cracks the ceramic, which then absorbs most of the kinetic energy. Residual energy is absorbed by the Kevlar backing.

Silicon nitride, Si_3N_4, is used to make engine components for diesel engines because it is wear resistant and extremely hard. It has a high stiffness with low density, and can withstand extremely high temperatures and harsh chemical environments.

Piezoelectric ceramics produce an electric potential when their shape is deformed. They also deform when an electric potential is applied to them. A company makes ‘smart skis’ that incorporate piezoelectric devices that use both properties. Vibrations in the skis are detected by the potential developed when they deform. A potential is then applied to cancel the vibration. Smart materials possess both sensing and action capability. They adaptively respond to changing stimuli.

Chemistry Research

Molecular Materials

Professor Cameron Kepert, University of Sydney

Once regarded as little more than arrangements of discrete molecules, over the past decade molecular solids have been recognised as extended lattices that can have interesting and useful cooperative effects. The diversity of molecular solids allows a potentially limitless degree of complexity and, therefore, the ability to design materials to perform specific functions.

Research into molecular materials aims to improve our understanding of how chemical structure leads to a material's specific function. By exploiting this know ledge in the design of new systems with new properties, we are seeking the answers to questions such as:

- Can we create materials that change colour, shape, magnetism etc. in response to changes in their environment and, therefore, act as sensors or data storage media?
- Can we store hydrogen gas efficiently in nanoporous materials?

Nanoporous Molecular Frameworks

A principal focus of the Kepert research group at the University of Sydney is the synthesis of new materials that display nanoporosity, i.e. they retain their structure following the absorption and desorption of guest molecules from within pores in the host materials. Nanoporosity and the ability to customise the types of guests that can be placed in the pores of materials have exciting practical implications including use in chemical sensing, molecular separations, catalysis, hydrogen storage and controlled release.

Electronic Switching

The group has developed ‘smart’ nanoporous materials that can switch between different electronic states. This occurs in response both to the exchange of guest molecules, an effect that provides a new mechanism for chemical sensing, and to changes in temperature, pressure and irradiation. The coupling of these effects is expected to lead to highly unusual host–guest properties and to instances where guest-exchange processes can be stimulated externally, e.g. by shining a light on the material.

Magnetism

Materials displaying both nanoporosity and magnetic ordering — properties that are generally mutually exclusive — have long been sought for systematic investigations of molecular magnetism and magnetic host–guest interactions. The Kepert research group has recently created the first truly nanoporous magnets by bridging inorganic chains and layers through short molecular linkers. Of particular interest is a material that converts to a magnet when dehydrated, despite there being no associated change to the framework structure (see figure 7.56). Efforts are underway to determine the influence of other guests on the magnetic properties of such host lattices.

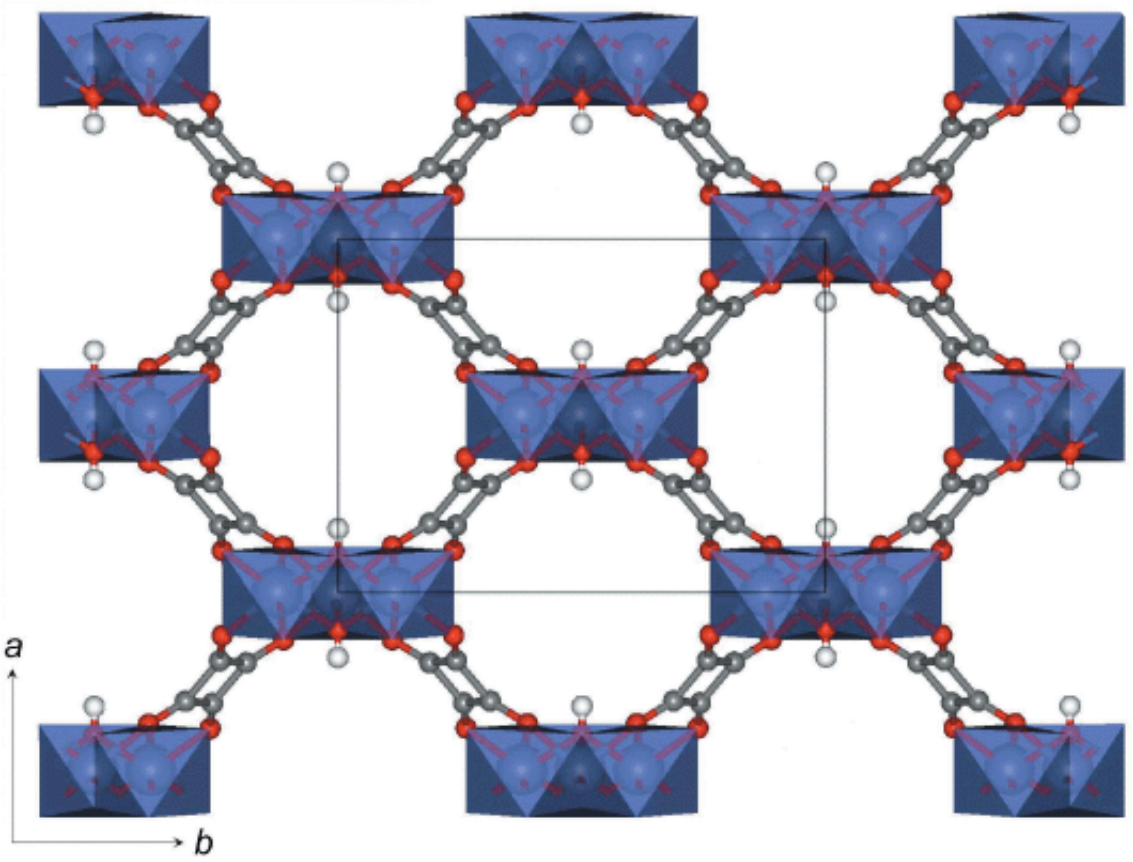


FIGURE 7.56 The nanoporous molecular framework material $[Co^{II}_3(OH)_2(C_4O_4)_2]$ consists of Co(II) ions (transparent blue octahedra connected edge-to-edge) linked by squarate ($C_4O_4^{2-}$) and hydroxide units. The material converts from a ferromagnet to an antiferromagnet (see chapter 13) upon inclusion of water molecules into the nanopores.

Hydrogen Storage

Recent results have shown that nanoporous molecular frameworks (see figure 7.57) are outstanding candidates for the efficient storage of hydrogen gas, an essential step if hydrogen is to be used to replace fossil fuels. Current methods for hydrogen transport and storage require very high pressures or very low temperatures. The Kepert research group has recently shown that materials can be designed in which hydrogen binds directly to bare metal sites on the interior pore surfaces. This advance points the way to possible future technologies in which hydrogen is stored and released under non-extreme temperatures and pressures.

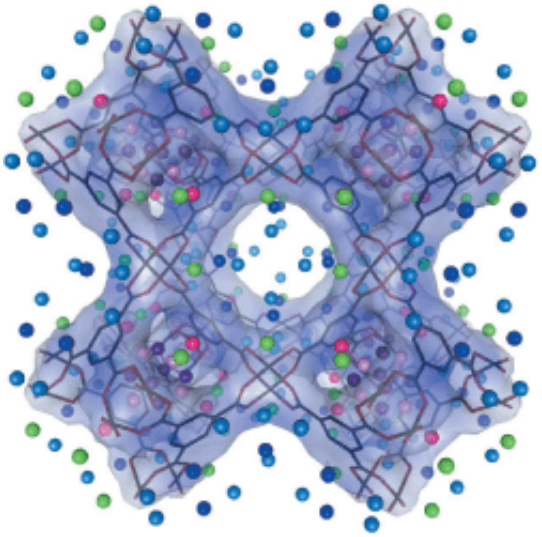


FIGURE 7.57 The nanoporous molecular framework material $[Cu^{II}_3(btc)_2]$ (btc = 1,3,5-benzenetricarboxylate) is able to store large quantities of hydrogen gas within its open pore structure. Framework atoms are shown as sticks and the locations of hydrogen molecules are shown as coloured spheres.

Chemistry Research

High-temperature Superconductors — an Ongoing Revolution

Jeff Tallon, MacDiarmid Institute and Industrial Research Ltd, New Zealand

Superconductivity represents the point where quantum mechanics meets the everyday world. It offers a technology that, throughout the twenty-first century, will have an impact on our world in countless practical ways.

Superconductors, first discovered in 1911 by the Nobel Prize-awarded Dutch physicist Heike Kamerlingh-Onnes, become perfect electrical conductors when cooled below a critical temperature, referred to as T_c; in other words, they show no resistance to the flow of electrical current below T_c and therefore superconducting wires can potentially be used to carry electricity with no loss. Superconductivity is a quantum mechanical effect that occurs when electrons of opposite momentum and opposite spin pair up to form a macroscopic wave function that extends across the entire superconductor, which could be a metre or even a kilometre in size.

Until 1986, all known superconductors had to be cooled using liquid helium. The record T_c at the time was 23 K. That year, Bednorz and Müller discovered the first of the so-called high-temperature superconductors (HTS) with $T_c \approx 30$ K. This was raised to 52 K under high pressure and set in motion an international race to discover HTS with still higher T_c values. Over the next few years, T_c increased an astounding seven fold.

Today there are more than 70 known HTS. They are based on the perovskite structure (see question 7.11, p. 288) and all have a layered structure with two-dimensional copper oxide sheets. However, only two of these HTS materials have proven amenable to manufacture into wires, as the majority of HTS are brittle ceramics. The most useful is $Bi_2Sr_2Ca_2Cu_3O_{10}$, often referred to as BSCCO (figure 7.58). Its T_c of 108 K means that it can be cooled using liquid nitrogen, which is much cheaper than liquid helium. It was first identified by a group working in New Zealand at Industrial Research Ltd, a government research institute. Their work was published in *Nature* in 1988 and they were eventually awarded US and European patents for this material after many years of patent battles among some of the world's largest corporations.

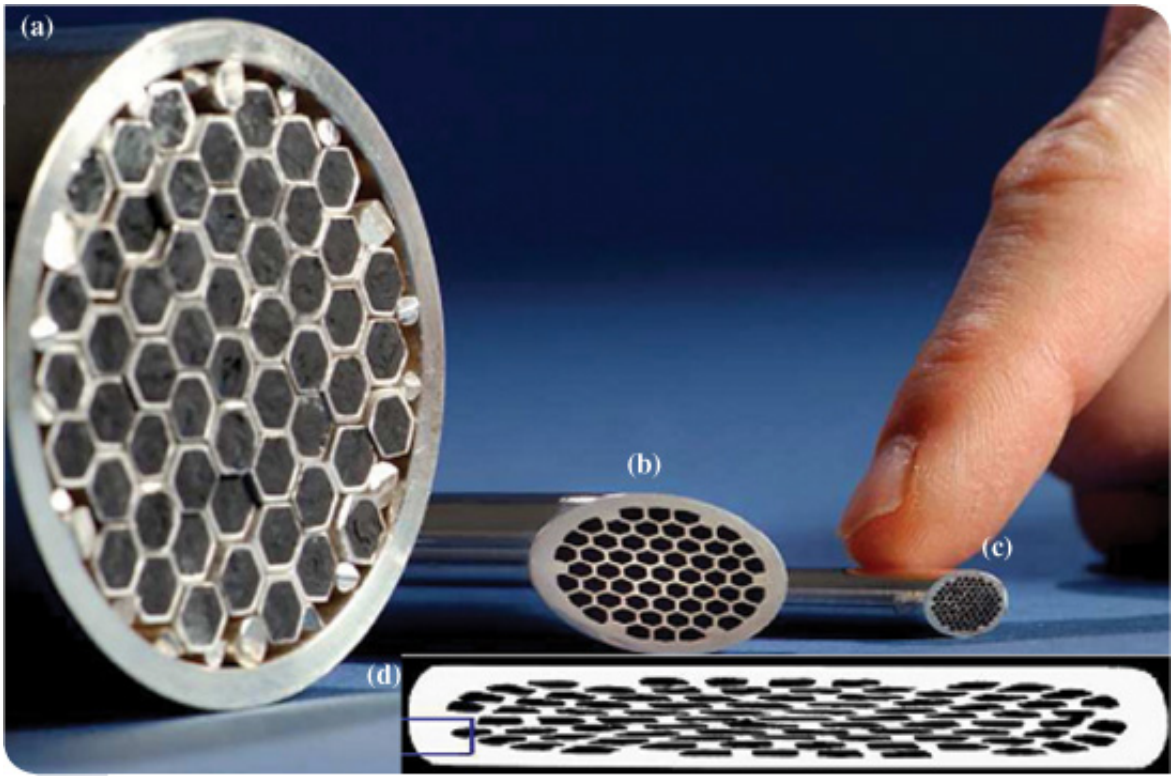


FIGURE 7.58 BSCCO wires:
(a) precursor materials are loaded into a silver billet, extruded,
(b) rebundled into 55 hexagonal tubes, re-extruded,
(c) drawn down to about 1 mm diameter, and then
(d) rolled flat to form a multifilamentary tape. This is then reacted at high temperature to complete the formation of the final BSCCO product.

This group spun out the business HTS-110 Ltd, which manufactures HTS-based products. These products include magnets for ion implantation, research, testing of computer hard drives, synchrotron dipole magnets, coils for motors and generators, and NMR instruments. Each of these devices has its own refrigerator and is made using BSCCO. A second New Zealand company, General Cable Superconductors, manufactures superconducting cable for AC and large current applications such as grid-scale generators and transformers.

There are many aspects of HTS science yet to be understood and this is an ongoing research focus for Dr Tallon's group. The ultimate goal is the production of room temperature superconductors, a discovery which would revolutionise the production and use of electricity on planet Earth. The HTS revolution is not finished yet!

High-temperature superconductors

A **superconductor** is a material which offers no resistance to the flow of electricity. Many compounds are superconductors at very low temperatures, which can be reached only by using liquid helium for cooling. Because liquid helium is very expensive, materials have been sought with critical temperatures, T_c (the temperature at which they become superconductors), above 77.4 K, the boiling point of liquid nitrogen. The refrigeration technology for producing and handling liquid nitrogen is well known and relatively simple, and liquid nitrogen costs about as much as milk or orange juice. In 1987, a ceramic mixed metal oxide, $YBa_2Cu_3O_7$, was discovered with a T_c of 93 K. Materials that have T_c values above

about 30 K are called *high-temperature super-conductors*. Materials with T_c values above 130 K (at atmospheric pressure) have been found.

The chief problem with ceramic superconductors is that they are brittle, but during the 1990s scientists and engineers successfully made wire-like superconducting materials that could be used to build electrical cables. The cables can carry up to three times more electricity than standard electrical cables. New-generation magnets made with high-temperature superconducting wires are now commercially available.

One of the most fascinating properties of superconducting materials is that they can be levitated by a magnetic field. Besides zero electrical resistance, a substance in its superconducting state permits no magnetic field within itself. A weak magnetic field is actually *repelled* by a superconductor (the Meisner effect), and this is what makes the levitation of superconductors possible (figure 7.59). Corporations in Germany and Japan have been investigating the use of this property to develop new train technology. They have successfully levitated entire trains and propelled them at high speed with no more frictional resistance than that offered to aeroplanes by the surrounding air. Prototypes of such ‘maglev’ trains are still being tested. The first commercial maglev train began operating in China in 2002, while a superconducting Japanese version set the world speed record for a train (581 km h^{-1}) in 2003.



FIGURE 7.59 (a) Levitation of a magnet above a superconductor. When a ceramic is cooled below T_c, it becomes superconducting and repels a magnetic field. That repulsion is sufficient to hold a magnet suspended above it.
(b) This principle is used by maglev trains.

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SUMMARY

Liquids

Liquids, like gases, are fluid, but cannot expand or contract much. Three properties of liquids, viscosity, surface tension and capillary action, depend mostly on the strengths of intermolecular attractions within the liquid. Cohesive forces occur between molecules in a liquid and are responsible for surface tension. Adhesive forces occur between the liquid molecules and the walls of the container and give rise to a curved meniscus at the surface of a liquid. Adhesive forces are also responsible for capillary action. Viscosity is related to both the shape of the molecules and the magnitude of the intermolecular forces in a liquid.

Liquids evaporate when their molecules have sufficient energy to overcome attractive intermolecular forces. The equilibrium vapour pressure of a liquid is the pressure at which the number of molecules escaping from the liquid exactly matches the number being captured by the liquid. Vapour pressure increases with increasing temperature until the normal boiling point, the point where the vapour pressure equals the external atmospheric pressure, is reached.

Solids

Solids are rigid, meaning that their constituent atoms, molecules or ions occupy well-defined positions relative to one another. Solids may be classified as molecular, metallic, network or ionic solids according to the nature of their constituents. Each category has characteristic interactions between its constituents. Molecular solids are held together by dispersion forces. In some solids and liquids, dipolar and hydrogen bonding forces may also occur depending on the nature of the individual molecules. In network solids, the constituents are covalently bonded together, while ionic solids are held together by electrostatic attractions between oppositely charged ions. The bonding in metallic solids is due to a delocalised ‘sea’ of electrons.

Phase Changes

A phase change occurs when a substance undergoes a transition from one phase to another. Energy must be either supplied to, or removed from, a substance undergoing a phase change. This can be quantified by considering the values of the molar enthalpy of vaporisation $\Delta_{vap}H$ or the molar enthalpy of fusion $\Delta_{fus}H$, which are the enthalpy changes that occur on vaporising or melting 1 mole of substance, respectively. In addition to these phase changes, sublimation, the direct conversion of a solid to a gas, can also occur, and it has an associated molar enthalpy of sublimation, $\Delta_{sub}H$. The reverse of this process is called deposition.

Heating a liquid in a closed container results in gradual evaporation and a corresponding increase in pressure. Eventually, a point may be reached at which the liquid and gas phases cannot be distinguished and the substance exists as a supercritical fluid. The temperature and pressure at which this occurs are called the critical temperature and critical pressure.

Temperatures and pressures at which equilibria can exist between phases are shown graphically in a phase diagram. Three equilibrium lines intersect at the triple point. The liquid–gas line terminates at the critical point. Above the critical point, a liquid phase cannot be formed; the single phase that exists is a supercritical fluid. The equilibrium lines also divide a phase diagram into temperature– pressure regions in which a substance exists in just a single phase. Water is different from most substances in that its melting point decreases with increasing pressure, albeit very slightly.

Order in Solids

Approximating atoms as spheres allows us to determine their possible close-packed arrangements. A

hexagonal arrangement is more. The efficient than a square arrangement for a single layer of spheres. Additional layers may be added to give either an ABABAB or ABCABC arrangement, depending on how the additional atoms are arranged relative to the original layer. The former is called a hexagonal close-packed (hcp) arrangement and the latter is a cubic close-packed (ccp) arrangement. Both are called close-packed structures as they fill 74% of the space, which is the maximum possible for identical spheres.

The overall structure of any crystalline solid can be described in terms of a repeating three-dimensional array of lattice points, which is called a lattice. The simplest portion of a lattice is its unit cell. Many structures can be described by the same lattice by changing the contents and dimensions of the unit cell. Three possible cubic unit cells are: primitive cubic, face-centred cubic and body-centred cubic. In a lattice of spheres, the spaces between the spheres are called interstitial holes.

Sodium chloride and many other alkali metal halides crystallise in a face-centred cubic arrangement, which contains four NaCl units per unit cell. The relative sizes of the cations and anions in ionic crystals determine the structure adopted; hence CsCl, in which the cations and anions are nearly the same size, crystallises in a primitive cubic structure. The ratio of cations to anions is also important; for example, CaF_2 adopts a structure in which the Ca^{2+} ions are arranged in a face-centred cubic array, with the F^- ions filling all the tetrahedral holes.

X-ray Diffraction

X-ray diffraction can be used to determine the structure of crystal-line solids. The diffraction of X-rays from a crystalline solid results in constructive interference of the X-rays in particular directions as determined by the Bragg equation. This gives a diffraction pattern, which can be analysed to allow the calculation of the structure of the solid.

Amorphous Solids

Some solids, when formed by rapid cooling, do not crystallise with their constituent atoms, molecules or ions in a regular arrangement. These are known as amorphous solids. The most important example is glass, a family of amorphous solids based on silica. Rapid cooling of molten SiO_2 gives an amorphous solid glass, while the addition of compounds such as Na_2O, B_2O_3 and CaO gives different glasses with particular physical and chemical properties.

Crystal Imperfections

Crystalline defects can significantly alter the properties of a solid. The introduction of small impurity ‘defects’ can change the electrical conductivity of a solid, and even its colour. Substitutional impurities arise from the replacement of one atom with another of a different type, while interstitial impurities result from the placement of atoms in interstitial holes.

Modern Ceramics

Ceramics are composed of inorganic components such as metal oxides or nitrides that have been heat-treated. Most ceramics have high melting points and are very hard. This is a result of significant covalent bonding, which gives rise to network-type solids. Modern ceramics are used in such diverse areas as coatings, filters, cosmetics and bullet-proof vests. Piezoelectric ceramics can deform in response to an electric potential and can be used in smart materials. High-temperature superconductors are ceramics and are used in rapid maglev trains.

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KEY CONCEPTS AND EQUATIONS

Boiling points of substances *(section 7.1)*

The strengths of intermolecular forces in substances can be compared based on their boiling points.

Phase diagram *(section 7.3)*

We use a phase diagram to identify temperatures and pressures at which equilibrium can exist between phases of a substance and to identify conditions under which only a single phase can exist.

Unit cell *(section 7.4)*

A unit cell shows how the constituent atoms, molecules or ions are arranged in three dimensions in a crystalline solid. It is the smallest repeating unit of a crystalline structure.

The Bragg equation *(section 7.5)*

The Bragg equation relates λ, θ and the distance between the planes of atoms, *d*, and allows the determination of the structures of solids from X-ray diffraction patterns.

$$n\lambda = 2d \sin\theta$$

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REVIEW QUESTIONS

Liquids

7.1 Pentane is a C_5 hydrocarbon, gasoline contains mostly C_8hydrocarbons, and fuel oil contains hydrocarbons in the C_{12} range. List these three hydrocarbons in order of increasing viscosity, and explain what molecular feature accounts for the variation.

7.2 Aluminium tubing has a thin surface layer of aluminium oxide. What shape meniscus would you expect to find for water and for mercury inside aluminium tubing? Explain your answers in terms of intermolecular forces.

7.3 Water forms 'beads' on the surface of a freshly waxed car, but forms a film on the clean windscreen. Why is this?

7.4 For each of the following pairs of liquids, choose which has the lower vapour pressure at room temperature and explain your reasoning.

(a) water, H_2O, or methanol, CH_3OH

(b) pentan-1-ol, $C_5H_{12}OH$, or hexan-1-ol, $C_6H_{13}OH$

(c) chloromethane, CH_3Cl, or chloroform, $CHCl_3$

Solids

7.5 Classify each of the following as an ionic, network, molecular or metallic solid: Sn, S_8, Se, SiO_2 and Na_2SO_4.

7.6 Describe the differences between molecular and ionic solids in relation to:

(a) interparticle forces and

(b) macroscopic properties.

7.7 Indicate which type of solid (ionic, network, metallic or molecular/atomic) each of the following forms on solidification.

(a) Br_2

(b) KBr

(c) Ba

(d) SiO_2

(e) CO_2

Phase changes

7.8 From table 7.2, determine which of each of the following pairs has the higher value. Use intermolecular forces to explain the data.

(a) enthalpies of vaporisation of methane and ethane

(b) enthalpies of vaporisation of ethanol and diethyl ether

(c) enthalpies of fusion of argon and methane

7.9 Sketch the approximate phase diagram for Br_2 from the following information: normal melting point is 265.9 K, normal boiling point is 331.9 K, triple point is at $p = 5.87 \times 10^3$ Pa and $T = 265.7$ K. Label the axes and the area where each phase is stable.

7.10 Using the phase diagram from question 7.9, describe what happens to a sample of Br_2 as the following processes take place. Draw lines on the phase diagram showing each process.

(a) A sample at $T = 400$ K is cooled to 250 K at constant $p = 1.013 \times 10^5$ Pa.

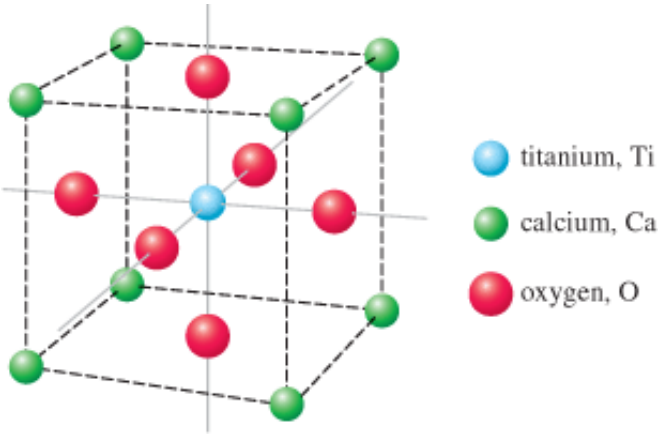
(b)

A sample is compressed from $p = 1.013 \times 10^2$ Pa to $p = 1.013 \times 10^8$ Pa at constant $T = 265.8$ K.

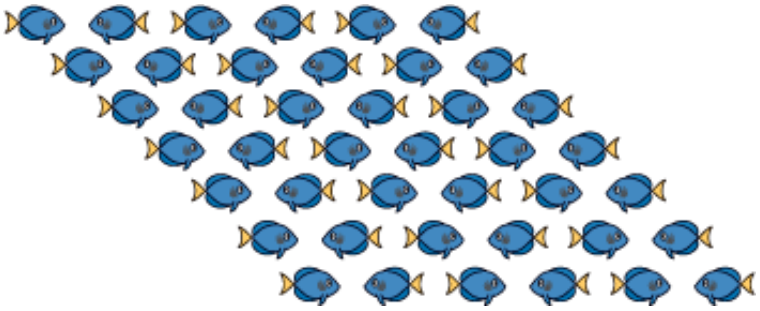
(c) A sample is heated from 250 K to 400 K at constant $p = 2.026 \times 10^3$ Pa.

Order in Solids

7.11 The unit cell of the mineral perovskite is shown below. What is the formula of perovskite?



7.12 For the pattern shown below, draw a tile that represents a unit cell for the pattern and contains only complete fish. Draw a second tile that is a unit cell but contains no complete fish.



7.13 In the unit cell of calcium oxide, the oxide ions adopt a face-centred cubic arrangement. The calcium ions are in the holes within the face-centred cubic unit cell. How many complete calcium ions must be packed within each face-centred cube for the unit cell to be charge-neutral?

X-ray Diffraction

7.14 Write the Bragg equation and define the symbols used.

7.15 Explain in general terms how an X-ray diffraction pattern of a crystal and the Bragg equation provide information that allows chemists to determine the structures of molecules.

Amorphous Solids

7.16 What does the word ‘amorphous’ mean?

7.17 What is an amorphous solid? Compare what happens when crystalline and amorphous solids are broken into pieces.

7.18 Amorphous silica has a density of around 2.3 g mL^{-1} and crystalline quartz has a density of 2.65 g mL^{-1}. Describe the bonding features that cause these two forms of the same substance to have different densities.

Crystal Imperfections

7.19 What are ‘substitutional impurities’?

7.20 What are ‘interstitial impurities’?

Modern Ceramics

7.21 What are ‘ceramics’?

7.22 What are two physical properties that make ceramics useful materials?

7.23 What are ‘refractories’? Give two uses for refractories.

7.24 What are ‘superconductors’? Why is it very expensive to use typical superconductors in practical applications?

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REVIEW PROBLEMS

7.25 List the different kinds of forces that must be overcome to convert each of the following compounds from a liquid to a gas.

(a) NH_3

(b) $CHCl_3$

(c) CCl_4

(d) CO_2

7.26 List all the intermolecular forces that stabilise the liquid phase of each of the following.

(a) Xe

(b) SF_4

(c) CF_4

(d) CH_3COOH (acetic acid)

7.27 Manganese forms crystals in either body-centred cubic or face-centred cubic geometry. Which geometry has the higher density? Explain your choice.

7.28 Beryllium forms crystals in either body-centred cubic or hexagonal close-packed geometry. Which solid phase has the higher density? Explain your choice.

7.29 For each of the following pairs, identify which has the higher boiling point, and identify the type of force that is responsible.

(a) H_3COCH_3 and CH_3OH

(b) SO_2 and SiO_2

(c) HF and HCl

(d) Br_2 and I_2

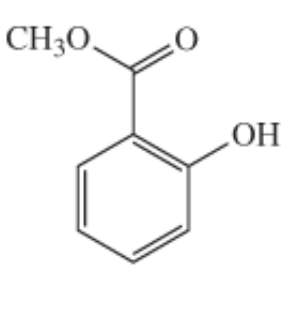
7.30 Refer to figure 7.21. Describe in detail what occurs when each of the following processes is carried out.

(a) A sample of CO_2 gas is compressed from 1.013×10^5 Pa to 5.065×10^6 Pa at $T = 298$ K.

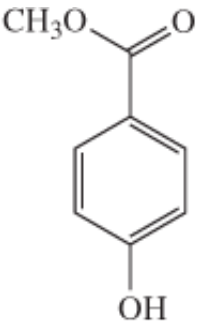
(b) Dry ice at 195 K is heated to 350 K at $p = 6.078 \times 10^5$ Pa.

(c) A sample of CO_2 gas at $p = 1.013 \times 10^5$ Pa is cooled from 298 K to 50 K.

7.31 Why do the two isomers shown below have very different melting points?



$C_8H_8O_3$
methyl 2-hydroxybenzoate
(oil of wintergreen)
mp = −8 °C



$C_8H_8O_3$
methyl 4-hydroxybenzoate
mp = 127 °C

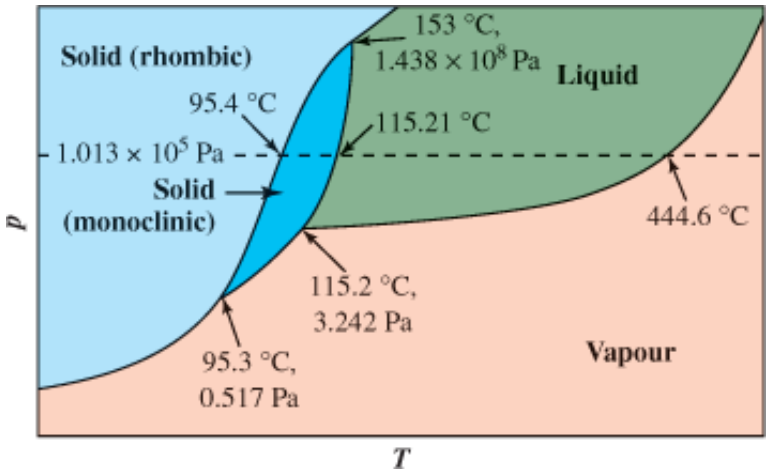
7.32 With reference to figure 7.22, describe what happens to silica as it is slowly heated from room

temperature to 2000 °C at atmospheric pressure (1.013×10^5 Pa).

7.33 How many triple points appear on the phase diagram in figure 7.22? For each one, describe the conditions and name the three phases that coexist under these conditions.

7.34 Solid sodium metal can exist in two different crystalline forms, body-centred cubic and hexagonal. One is stable only below 5 K at relatively low pressure; the other is stable under all other conditions. Draw atomic pictures of both phases, identify the phase that is stable only at low temperature and pressure, and explain your choice.

7.35 The figure below shows the phase diagram for elemental sulfur (not to scale). Use it to answer the following questions.



(a) Under what conditions does rhombic sulfur melt?

(b) Under what conditions does rhombic sulfur convert to monoclinic sulfur?

(c) Under what conditions does rhombic sulfur sublime?

7.36 Use the figure in question 7.35 to answer the following.

(a) How many triple points are there in the diagram?

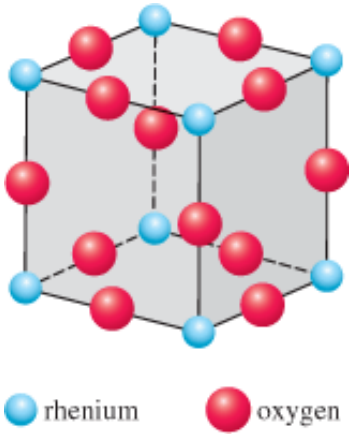
(b) Which phases coexist at each triple point?

(c) If sulfur is at the triple point at 153 °C, what happens if the pressure is reduced?

7.37 Sketch the phase diagram for a substance that has a triple point at -15.0 °C and 0.30×10^5 Pa, melts at –10.0 °C at 1×10^5 Pa, and has a normal boiling point of 90 °C.

7.38 Based on the phase diagram in question 7.37, below what pressure will the substance undergo sublimation? How does the density of the liquid compare with the density of the solid?

7.39 The unit cell of rhenium oxide appears in the figure below.

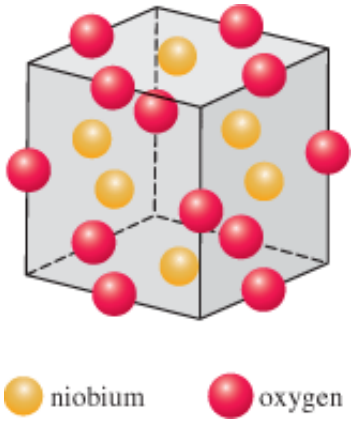


(a) Name the cubic lattice compatible with this arrangement of the atoms.

(b) Calculate the number of rhenium and oxygen atoms in the unit cell and identify the

formula of rhenium oxide (the chemical symbol for rhenium is Re).

7.40 One form of niobium oxide crystallises in the unit cell shown below. Calculate the number of niobium and oxygen atoms in the unit cell, and identify the formula of niobium oxide (the chemical symbol for niobium is Nb).



7.41 Tungsten does not melt even when heated to incandescence. How do interatomic forces in tungsten compare with those in more typical metals such as gold or nickel?

7.42 Silver forms face-centred cubic crystals. The atomic radius of a silver atom is 144 pm. Draw the face of a unit cell with the nuclei of the silver atoms at the lattice points. The atoms are in contact along the diagonal. Calculate the length of an edge of this unit cell.

7.43 The atomic radius of nickel is 124 pm. Nickel crystallises in a face-centred cubic lattice. What is the length of the edge of the unit cell expressed in picometres?

7.44 Potassium ions have a radius of 133 pm, and bromide ions have a radius of 195 pm. The crystal structure of potassium bromide is the same as sodium chloride. Estimate the length of the edge of the unit cell in potassium bromide.

7.45 The unit cell in sodium chloride has an edge length of 564.0 pm. The sodium ion has a radius of 95 pm. What is the diameter of a chloride ion?

7.46 Caesium chloride, CsCl, crystallises with a cubic unit cell of edge length 412.3 pm. The density of CsCl is 3.99 g mL^{-1}. Show that the unit cell cannot be body-centred cubic or face-centred cubic.

7.47 Tin(IV) chloride, $SnCl_4$, has soft crystals with a melting point of –30.2 °C. The liquid is nonconducting. What type of solid (ionic, molecular, covalent or metallic) is formed by $SnCl_4$?

7.48 Elemental boron is a semiconductor, is very hard and has a melting point of about 2250 °C. What type of solid is formed by boron?

7.49 Gallium crystals are shiny and conduct electricity. Gallium melts at 29.8 °C. What type of solid does gallium form?

7.50 Titanium(IV) bromide forms soft orange-yellow crystals that melt at 39 °C to give a liquid that does not conduct electricity. The liquid boils at 230 °C. What type of solid does $TiBr_4$ form?

7.51 Titanium(IV) bromide forms soft orange-yellow crystals that melt at 39 °C to give a liquid that does not conduct electricity. The liquid boils at 230 °C. What type of solid does $TiBr_4$ form?

The element niobium is shiny, soft and ductile. It melts at 2468 °C and the solid conducts electricity. What type of solid does it form?

7.52 Elemental phosphorus consists of soft, white, ‘waxy’ crystals that are easily crushed and melt at 44 °C. The solid does not conduct electricity. What type of solid does phosphorus form?

7.53 Indicate which type of solid each of the following would form when it solidifies:

(a) Br_2,

(b) LiF,

(c) MgO,

(d) Mo,

(e) Si,

(f) PH_3,

(g) NaOH.

7.54 Indicate which type of solid each of the following would form when it solidifies:

(a) O_2,

(b) H_2S,

(c) Pt,

(d) KCl,

(e) Ge,

(f) $Al_2(SO_4)_3$,

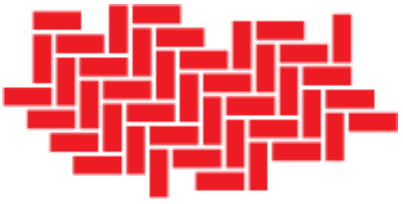
(g) Ne.

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7.55 Molecular hydrogen and atomic helium both have two electrons, but He boils at 4.2 K, whereas H_2 boils at 20 K. Neon boils at 27.1 K, whereas methane, which has the same number of electrons, boils at 114 K. Explain why molecular substances boil at a higher temperature than atomic substances with the same number of electrons.

7.56 Draw the unit cell of the NaCl crystal and determine the number of nearest neighbours of opposite charge for each ion in this unit cell.

7.57 Below is an illustration of a 'herringbone' pattern for patio pavers. Identify the unit cell for this pattern.



7.58 Construct a qualitative graph similar to the one in figure 7.16 that summarises the energy changes that accompany the following process: A sample of water at 35 °C is placed in a freezer until the temperature reaches –25 °C. Plot temperature along the *y*-axis and kilojoules of heat removed along the *x*-axis.

7.59 As a gas, acetic acid, CH_3COOH, exists as a mixture of individual molecules and pairs of molecules held together by hydrogen bonds.

(a) Draw a Lewis structure that shows how two acetic acid molecules can form a pair by hydrogen bonding.

(b) Does the fraction of paired acetic acid molecules increase or decrease as the temperature rises? Explain.

7.60 Gold crystallises in a face-centred cubic lattice. The edge of the unit cell has a length of 407.86 pm. The density of gold is 19.31 g mL^{-1}.

(a) Use these data and the atomic mass of gold to calculate the value of the Avogadro constant.

(b) Calculate the atomic radius of gold in units of picometres.

7.61 Silver has an atomic radius of 144 pm. What would the density of silver be in g mL^{-1} if it were to crystallise in:

(a) a simple cubic lattice

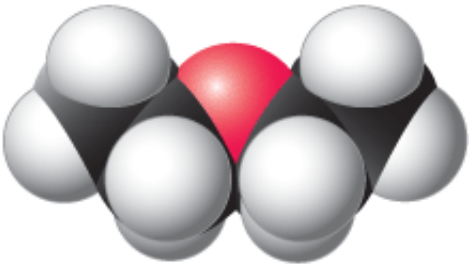
(b) a body-centred cubic lattice

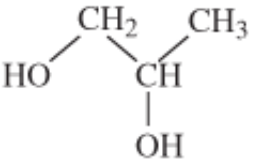
(c) a face-centred cubic lattice?

The actual density of silver is 10.6 g mL^{-1}. Which cubic lattice does silver have?

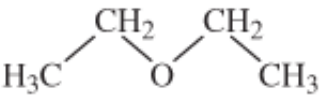
7.62 Which of the following molecules would you expect to wet a greasy glass surface more effectively?







propylene glycol (propane-1,2-diol)



diethyl ether

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KEY TERMS

amorphous
body-centred cubic lattice (bcc)
Bragg equation
capillary action
ceramics
close-packed structures
critical point
critical pressure
critical temperature (T_c)
crystal lattice
crystalline defects
crystalline solid
cubic close-packed (ccp)
deposition
diffraction pattern
face-centred cubic structure (fcc)
glass
hexagonal close-packed (hcp)
interstitial hole
ionic solid
lattice
lattice point
meniscus
metallic solid
molar enthalpy of fusion ($\Delta_{fus}H$)
molar enthalpy of sublimation ($\Delta_{sub}H$)
molar enthalpy of vaporisation ($\Delta_{vap}H$)
molecular solid
network solid
phase change
phase diagram
primitive cubic structure
refractory
sublimation
superconductor
supercritical fluid
surface tension
triple point
unit cell
vapour pressure
viscosity

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CHAPTER

8 Chemical Thermodynamics

The reaction of hydrogen, H_2, with oxygen, O_2, is spontaneous — once the gas is ignited, it reacts to form water, H_2O, giving out a large amount of heat in the process. Yet we cannot carry out this reaction in reverse — in other words, H_2O under the same conditions does not give spontaneous formation of H_2 and O_2. Why do chemical reactions proceed in one direction only, and what determines the direction in which they proceed? In this chapter, we will study chemical thermodynamics and we will find that a function called Gibbs energy is central to determining the spontaneity of a particular chemical reaction or physical process under precisely defined conditions. We will also learn about enthalpy and entropy, two functions that are intimately linked to Gibbs energy. Chemical thermodynamics is crucial to understanding chemical equilibria and forms the basis of this chapter and chapters 9, 10, 11 and 12. It is an essential part not only of chemistry, but also of life itself.



KEY TOPICS

8.1 Introduction to chemical thermodynamics
8.2 Thermodynamic definitions
8.3 The first law of thermodynamics
8.4 Enthalpy
8.5 Entropy

8.5 Entropy
8.6 The second law of thermodynamics
8.7 The third law of thermodynamics
8.8 Gibbs energy and reaction spontaneity

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8.1 Introduction to Chemical Thermodynamics

When a lump of solid sodium metal is placed in water, a vigorous chemical reaction occurs that forms hydrogen gas and aqueous sodium hydroxide (figure 8.1):

$$Na(s) + H_2O(l) \rightarrow NaOH(aq) + \frac{1}{2}H_2(g)$$

However, if we try to carry out the reverse reaction by bubbling hydrogen gas through an aqueous solution of sodium hydroxide, no chemical reaction is observed:

$$NaOH(aq) + \frac{1}{2}H_2(g) \rightarrow \text{no reaction}$$



FIGURE 8.1 Metallic sodium reacts violently with water. In the reaction, sodium is converted to Na^+, and water gives hydrogen gas and hydroxide ions. When the reaction is over, the solution contains sodium hydroxide.

Similarly, if a block of ice is left at room temperature and atmospheric pressure, it will eventually melt to give liquid water:

$$H_2O(s, 25\ ^\circ C, 1.013 \times 10^5\ Pa) \rightarrow H_2O(l, 25\ ^\circ C, 1.013 \times 10^5\ Pa)$$

but liquid water under the same conditions will never solidify into ice:

$$H_2O(l, 25\ ^\circ C, 1.013 \times 10^5\ Pa) \rightarrow \text{no change}$$

These examples show that both chemical reactions and physical changes occur in one particular direction only under particular conditions of temperature and pressure, and we say that such changes are **spontaneous**; in other words, once started they proceed without the involvement of any outside factors. The reaction of sodium with water and the melting of ice described above are examples of spontaneous processes that proceed to completion. However, many spontaneous chemical reactions do not give complete conversion of reactants to products. An example of a spontaneous reaction that does not go to completion is the reaction of N_2O (laughing gas) with oxygen at room temperature and atmospheric pressure to give $NO_2(g)$. Although we can write the balanced chemical equation for this reaction as:

$$2N_2O(g) + 3O_2(g) \rightarrow 4NO_2(g)$$

this does not mean that, if we mixed 2 moles of $N_2O(g)$ with 3 moles of $O_2(g)$ in a container at room temperature and pressure, we would obtain 4 moles of $NO_2(g)$. In fact, we would find that, no matter how

long we waited, no more than about 2 moles of $NO_2(g)$ would form and there would always be significant amounts of the starting materials present in the reaction mixture. It is important for you to appreciate that *a balanced chemical equation tells us nothing about whether or not a particular reaction proceeds to completion; it simply tells us the mole ratios in which reactants react to give products.*

We can force nonspontaneous reactions to proceed provided that we couple them to a spontaneous process. For example, water does not spontaneously decompose into hydrogen gas and oxygen gas, but, by passing an electric current (a spontaneous flow of electrons) through water, we can force the reaction:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

to proceed (figure 8.2). This process is called electrolysis. Production of hydrogen and oxygen will continue, however, only as long as the electric current is maintained. As soon as the supply of electricity is cut off, the decomposition ceases. This example demonstrates the difference between spontaneous and nonspontaneous changes. Once a spontaneous event begins, it tends to continue until it stops of its own accord (figure 8.3). A nonspontaneous event, on the other hand, can continue only as long as it receives some sort of outside assistance. You should also note that the electrolysis of water requires some sort of spontaneous mechanical or chemical change to generate the needed electricity. In short, *all nonspontaneous events occur at the expense of spontaneous ones.* Everything that happens can be traced, either directly or indirectly, to spontaneous changes.

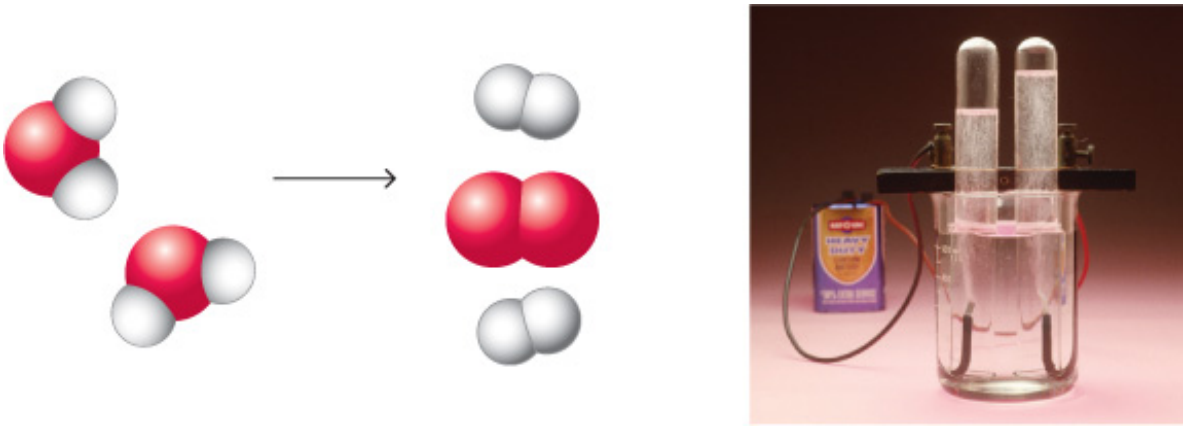


FIGURE 8.2 The electrolysis of water produces H_2 and O_2 gases. It is a nonspontaneous change that continues only as long as electricity is supplied.



FIGURE 8.3 Three common spontaneous events — iron rusts, fuel burns and an ice cube melts at room temperature.

As chemists, we are interested in predicting whether a reaction is spontaneous under our conditions of interest, and, if it is, how far it will proceed towards completion under those conditions. The science of **chemical thermodynamics** allows us to predict both the direction and extent of spontaneous chemical and physical change under particular conditions. We do this using a property called Gibbs energy, *G*. We can liken a spontaneous change to a ball at the top of a hill — once pushed, it will roll spontaneously down the hill until it reaches the bottom, the point of minimum energy. In the same way, we will see that chemical reactions proceed in the direction that leads to a decrease in the Gibbs energy of the system. We will also see that overall chemical and physical change will cease once the Gibbs energy of the system is minimised, and that, under these conditions, the system is at equilibrium.

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8.2 Thermodynamic Definitions

Before we begin our study of chemical thermodynamics, we need to define some important thermodynamic terms.

Heat and Temperature

Arguably the most important and indeed most familiar thermodynamic term, **heat**, is perhaps the most conceptually difficult. Heat is a transfer of energy due to a temperature difference. If two bodies having different temperatures are brought into direct contact, there will be heat flow from the hotter to the colder body, until both are at the same temperature. As we will see, we cannot actually measure heat directly. The definition of temperature also follows from the above; two bodies have the same temperature if they are in thermal equilibrium; i.e. there is no heat flow between them when they are in direct contact. It is important to note that the **thermodynamic temperature** (sometimes called the absolute temperature) scale is used in nearly all thermodynamic calculations. The thermodynamic temperature is measured in kelvin (K), and a thermodynamic temperature can be converted to a temperature in degrees Celsius by subtracting 273.15. You should note that a temperature *difference* of 1 K is numerically equal to a temperature difference of 1 °C, so, for calculations involving a temperature *change*, the numerical value of this change will be the same, regardless of whether the individual temperatures are expressed in K or °C.

System, Surroundings and Universe

We will use the word **system** to refer to the particular part of the universe (generally one or more chemical species) that we are studying, while every-thing else is the **surroundings**. Together, the system and surroundings constitute the **universe** (figure 8.4). As we are usually interested in heat flow between the system and surroundings, it is very important to specify the **boundary** across which heat flows. The boundary might be visible (such as the walls of a beaker) or invisible (such as the boundary that separates warm air from cold air along a weather front). Three types of system are possible, depending on whether matter or energy can cross the boundary.

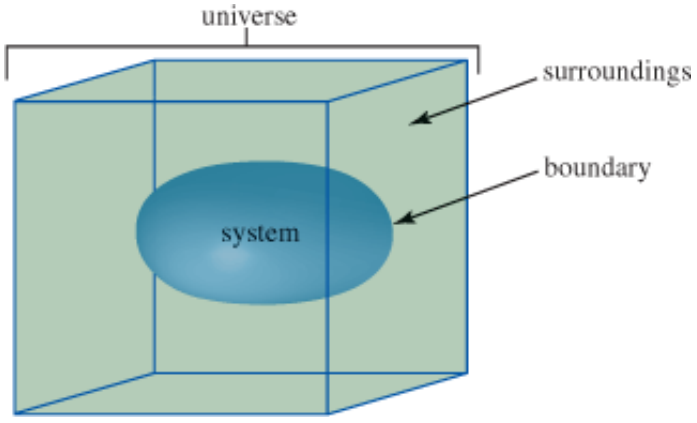


FIGURE 8.4 In thermodynamics, it is important to define the system, surroundings, universe and the boundary.

- ***Open systems.*** can gain or lose mass and energy across their boundaries. The human body is an example of an open system.
- ***Closed systems.*** can absorb or release energy, but not mass, across the boundary. The mass of a

closed system is constant, no matter what happens inside. A light bulb is an example of a closed system as it can release energy as both heat and light, but its mass is constant.

- ***Isolated systems.*** cannot exchange matter or energy with their surroundings. Because energy cannot be created or destroyed, the energy of an isolated system is constant, no matter what happens inside. A stoppered vacuum flask is a good approximation of an isolated system. Processes that occur within an isolated system with no heat transfer to the surroundings are called *adiabatic*, from the Greek words *a* and *diabatos* meaning 'not passable'.

Units

We must be aware of the units used in chemical thermodynamics. The SI unit of energy, work (motion against an opposing force) and heat is the **joule (J)**. Recall that the joule is a derived unit (table 8.2, p. 25) and can be expressed in terms of SI base units as:

$$1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}}$$

A joule is the amount of kinetic energy possessed by a 2-kilogram object moving at a speed of 1 metre per second, or, to use another example, 1 joule is approximately the energy of a single human heartbeat. The joule is actually a rather small amount of energy and in most cases we will use the larger unit, the **kilojoule (kJ)**:

$$1\ \mathrm{kJ} = 10^3\ \mathrm{J}$$

Thermodynamic Functions

There are four important thermodynamic functions which we will study in detail: internal energy (*U*, section 8.3), enthalpy (*H*, section 8.4), entropy (*S*, section 8.5) and Gibbs energy (*G*, section 8.8). Very brief definitions of these are as follows.

- ***Internal energy (U)*** is the sum of all the nuclear, electronic, vibrational, rotational, translational and interaction energies of all of the individual particles in a sample of matter.
- ***Enthalpy (H)*** is a function related to the heat absorbed or evolved by a chemical system and may be determined by measuring the temperature change that occurs during a chemical reaction or physical change under conditions of constant pressure.
- ***Entropy (S)*** is a measure of the number of ways energy is distributed throughout a chemical system. Its value is related to the enthalpy of the system at a particular temperature *T*.
- ***Gibbs energy (G)*****,** named after the American mathematical physicist Josiah Willard Gibbs (1839–1903), is defined as:

  $$G = H - TS$$

  where *T* is the thermodynamic temperature. As we will see, the Gibbs energy of a chemical system may be thought of as the energy that is available to do work.

We will look at these in greater detail, and provide exact definitions, in the appropriate sections of this chapter.

Δ *X*: the change in *X*

We are generally interested in the *change* in the values of U, H, S and G as the result of either a chemical reaction or a change in phase, rather than their absolute values. We denote such a change using Δ (the uppercase Greek letter Δ delta). Therefore, for any thermodynamic quantity X:

$$\Delta X = \text{final value of } X - \text{initial value of } X$$

We often use the Δ terminology when discussing changes in temperature. Thus, any change in temperature, ΔT, is defined as:

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

Note that, if T_{final} is less than T_{initial}, ΔT is then, by definition, negative.

The thermodynamic functions ΔU, ΔH, ΔS and ΔG, can refer to both chemical and physical changes. Chemical changes generally occur as a result of chemical reactions; in these, the reactants and products are chemically different, as the result of the making and/or breaking of chemical bonds, or the transfer of electrons. Physical changes refer primarily to changes of phase. Here, the chemical identities of the reactants and products are the same, but their physical states are different: e.g. liquid water freezing to give ice, and solid iodine subliming to give gaseous iodine. On the occasions when we are referring to the values of these thermodynamic functions *specifically* for chemical reactions, we denote this using the symbols $\Delta_r U$, $\Delta_r H$, $\Delta_r S$ and $\Delta_r G$.

State Functions

As we will see, ΔU, ΔH, ΔS and ΔG are all examples of a **state function**. This means that the value of each depends only on the current state of the system and it does not matter how the system came to be in its current state or how the system will behave in the future. We can usually define the state of a chemical system by specifying the amount and type of substances present in the system, and the pressure, temperature and volume of the system. When we then change the state of the system by changing one or more of the above variables, the change in the value of any state function X of the system is given by:

$$\Delta X = X_{\text{final}} - X_{\text{initial}}$$

and *depends only on the initial and final states of the system* and not on the path taken during the change in the state of the system. This concept is illustrated in figure 8.5.

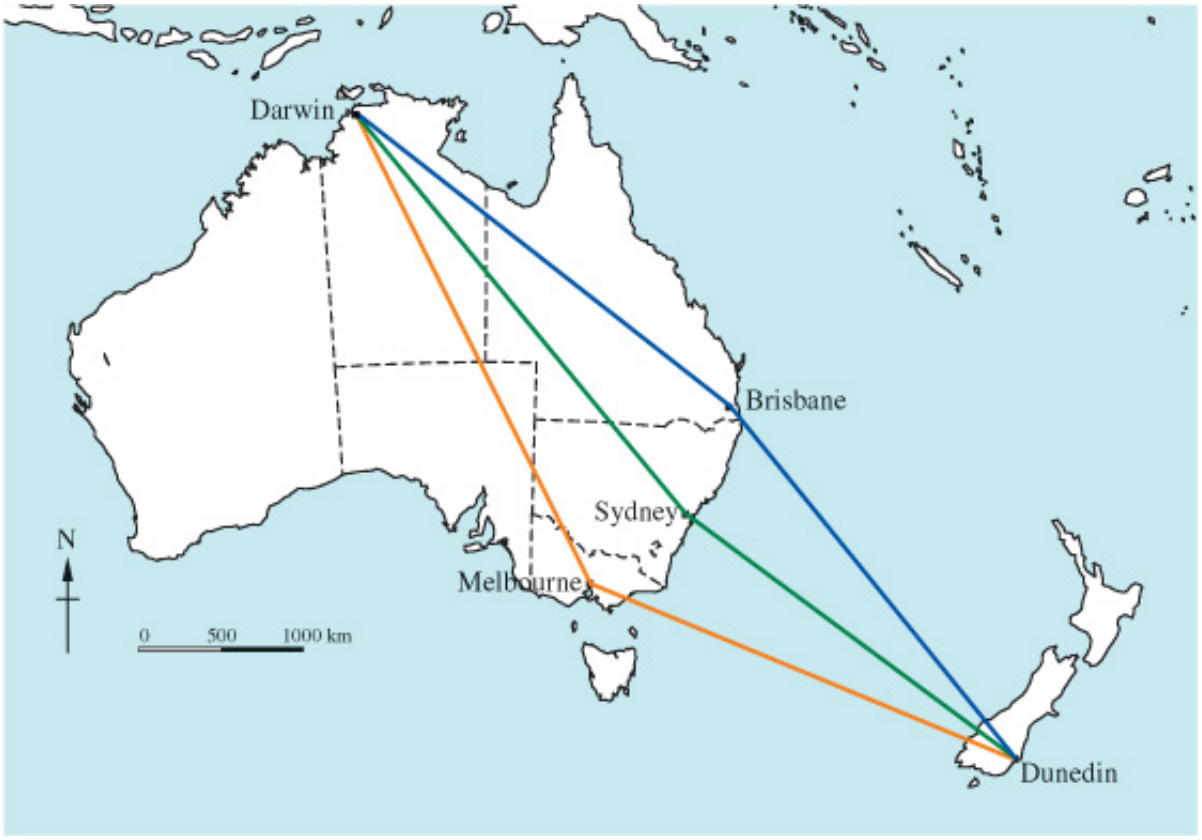


FIGURE 8.5 The latitude of Darwin airport is 12°24'S, while that of Dunedin airport is 45°55'S. As there are no direct flights between Darwin and Dunedin, if we wish to travel between them, we must fly via Brisbane (blue line, a total of 5401 km), Sydney (green line, 5244 km) or Melbourne (orange line, 5410 km). The actual distance travelled is different in each case, and is therefore not a state function as it depends on the path taken. However, the change in latitude that occurs, 33°31', is the same, regardless of which route we take, and is therefore a state function.

As we will see later, the advantage of recognising that a particular property is a state function is that many calculations become much easier.

ΔG and Spontaneity

The primary aim of this chapter is to show that the spontaneity of a chemical or physical process at constant temperature and pressure can be predicted from the sign of the Gibbs energy change for the process (ΔG), which itself depends on the values of ΔH and ΔS via the equation:

$$\Delta G = \Delta H - T\Delta S$$

This is one of the most important equations in all of chemistry. A negative value of ΔG means that the products are of lower G than the reactants; the process must proceed in the direction of decreasing G so it is spontaneous. Conversely, if ΔG is positive, the products are of higher G than the reactants; the process will not be spontaneous as it has to proceed in the direction of increasing G (figure 8.6).

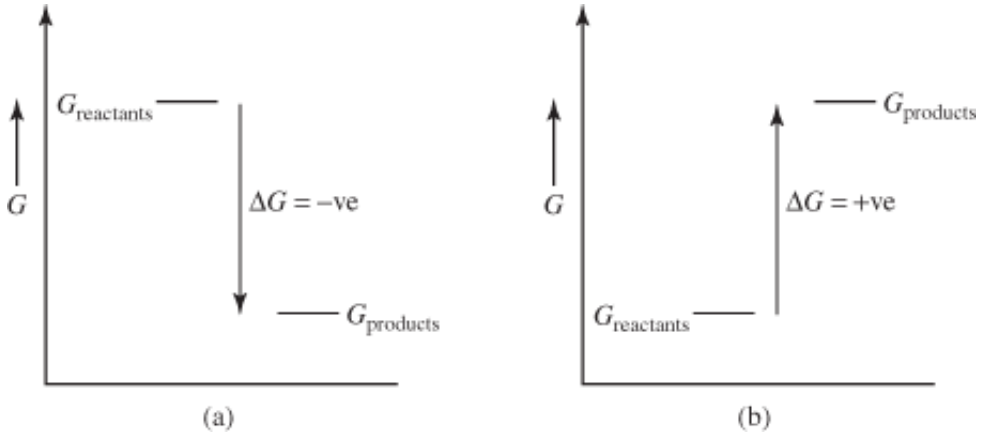


FIGURE 8.6 Diagrams showing the origin of the sign of ΔG. **(a)** $G_{products}$ is less than $G_{reactants}$, so ΔG (= $G_{products}$ - $G_{reactants}$) is negative, and the process reactants → products is spontaneous in the direction of decreasing G. **(b)** Conversely, when $G_{products}$ is greater than $G_{reactants}$ (right-hand diagram), ΔG is positive, and the process reactants → products is not spontaneous as it involves an increase in G.

If $\Delta G = 0$, the system is at equilibrium, a state in which no overall chemical or physical change is observed. In short, we can say that, for a process occurring at constant temperature and pressure:

- if $\Delta G < 0$, the process is spontaneous
- if $\Delta G > 0$, the process is nonspontaneous
- if $\Delta G = 0$, the system is at equilibrium.

The magnitude of ΔG under precisely defined conditions is also important in telling us how far a reaction goes towards completion, as we will see in chapter 9. Obviously, to determine the value of ΔG, we need to know the values of both ΔH and ΔS. We will define the former by way of the first law of thermodynamics. In so doing, we will introduce the concepts of heat q, work and internal energy.

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8.3 The First Law of Thermodynamics

We stated earlier that the equation for Gibbs energy contained terms involving both enthalpy and entropy. In this section, we will investigate what is meant by the term ‘enthalpy’. In doing this, we will introduce some new concepts: internal energy (U), work (w) and heat (q), as well as the first law of thermodynamics.

If you have ever dissolved a large amount of sodium chloride, NaCl, in water, you will have noticed that the resulting solution gets colder as the salt dissolves. However, if you dissolve the chemically similar salt lithium chloride, LiCl, in water, you will find that the resulting solution becomes surprisingly hot. The first process absorbs heat from its surroundings while the second gives out heat to its surroundings.

The energy that is transferred as heat comes from an object's internal energy. Internal energy is the sum of energies for all of the individual particles in a sample of matter and is given the symbol U. In studying both chemical and physical changes, we are interested in the *change* in internal energy (ΔU) that accompanies the particular process:

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

For a chemical reaction, U_{final} corresponds to the internal energy of the products, so we will write it as U_{products}. Similarly, we will use the symbol $U_{\text{reactants}}$ for U_{initial}. So for a chemical reaction the change in internal energy is given by:

$$\Delta_r U = U_{\text{products}} - U_{\text{reactants}}$$

Thus, when we dissolve sodium chloride in water, the system *absorbs* energy from its surroundings; its final energy is therefore greater than its initial energy, so $\Delta_r U$ is positive. Conversely, when we dissolve lithium chloride in water, the system gives out energy to its surroundings; its final energy is therefore less than its initial energy, so $\Delta_r U$ is negative.

A chemical system can exchange energy with its surroundings in two ways. The first, as we have seen above, is by either absorbing heat from or emitting heat to the surroundings. The second is by doing work on the surroundings, or having the surroundings do work on it. **Work** may be defined simply as motion against an opposing force. For example, lifting a weight against the force of gravity is work, as is stretching or compressing a spring. While there are a number of different types of work possible in chemical systems (such as electrical work and osmotic work), we will consider only the work associated with the compression or expansion of a gas to illustrate a number of important thermodynamic concepts. This type of work is often called pressure–volume or pV work, as it involves a change in pressure and volume of a gas sample. When a gas is compressed at constant temperature, the surroundings are doing work on the system, while the expansion of a gas at constant temperature is an example of a system doing work on the surroundings (figure 8.7).

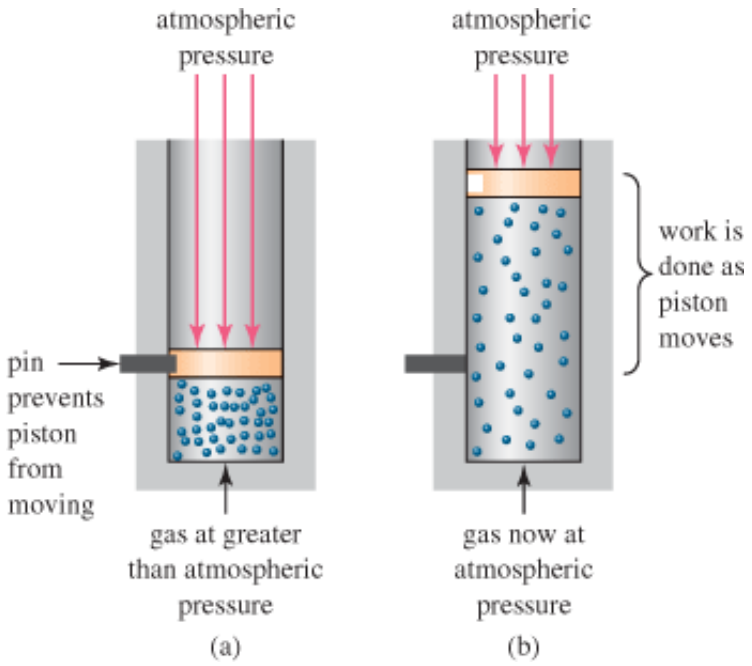


FIGURE 8.7 Pressure–volume work:

(a) A gas is confined under pressure in a cylinder fitted with a piston that is held in place by a sliding pin.

(b) When the piston is released, the gas inside the cylinder expands and pushes the piston upwards against the opposing pressure of the atmosphere. As it does so, the gas does some pressure–volume work on the surroundings.

The magnitude of the work done during a volume change, ΔV, against an opposing pressure, p, is given by the equation:

$$w = -p\Delta V$$

As ΔV (V_{final} - $V_{initial}$) is positive for the expansion of a gas, work is negative for this process at constant temperature, while similar reasoning shows that work is positive for the compression of a gas.

As heat and work are the only ways by which a closed chemical system can exchange energy with its surroundings, it follows that the change in internal energy of a chemical system during a chemi cal or physical change must be equal to the sum of the heat absorbed or emitted by the system and the work done on or by the system. In mathematical terms, this becomes:

$$\Delta U = q + w$$

where q = heat and w = work. This equation is known as the **first law of thermodynamics**. In simple terms, it means that energy can be transferred between a system and its surroundings as either heat or work, but it can never be created or destroyed. An alternative statement of the first law of thermodynamics is that the energy of an isolated system is constant. Both formulations are essentially alternative versions of the law of conservation of energy, which says that energy cannot be created or destroyed. As with H, S and G, we are not interested in the absolute value of U, but rather the change in U (ΔU) that occurs as the result of a chemical or physical change.

While ΔU is a state function, the values of q and w depend on what happens between the initial and final states of any change; in other words, q and w are not state functions. For example, consider the discharge of a car battery by two different paths (figure 8.8). Both paths take us between the same two states, one being the fully charged state and the other the fully discharged state. Because ΔU is a state function and because both paths have the same initial and final states, ΔU must be the same for both paths. But what about q and w?

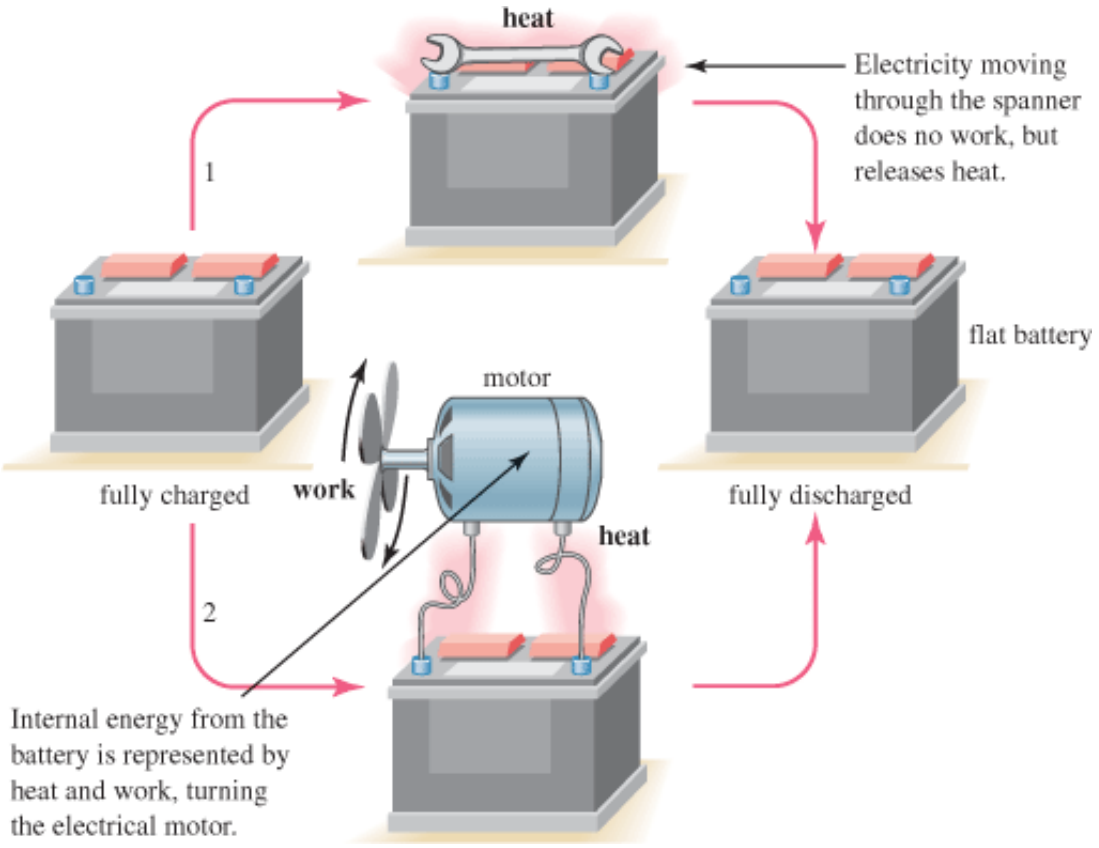


FIGURE 8.8 Internal energy, heat and work. The complete discharge of a battery along two different paths yields the same total amount of internal energy, ΔU. However, if the battery is simply short-circuited with a heavy spanner, as shown in path 1, this energy appears entirely as heat. Path 2 gives part of the total internal energy as heat, but most of the internal energy appears as work done by the motor.

In path 1 of figure 8.8, we simply short-circuit the battery by placing a heavy spanner across the terminals. If you have ever done this, even by accident, you know how violent the result can be. Sparks fly and the spanner becomes very hot as the battery quickly discharges. Lots of heat is given off, but *the system does no work* ($w = 0$). All of ΔU is transferred to the surroundings as heat.

In path 2, we discharge the battery more slowly by using it to operate a motor. Along this path, most of the energy represented by ΔU appears as work (running the motor) and only a relatively small amount appears as heat (from the friction within the motor and the electrical resistance of the wires).

Therefore, neither q nor w is a state function. Their values depend *entirely* on the path between the initial and final states.

Heat Capacity

It is important to realise that heat and temperature are not the same thing. If we take two objects that are initially at different temperatures and bring them into contact, both objects will eventually come to the same temperature, provided we wait long enough. This comes about through the transfer of heat from the hotter object to the colder object, so we can say that *heat is a transfer of energy due to a temperature difference*. We cannot measure heat directly, but we can calculate it using the temperature change that occurs when heat flows from one body to another. There is, in fact, a linear relationship between heat and temperature change given by the equation:

$$q = C\Delta T$$

where q is heat and C is the **heat capacity** of the object in question. The units of heat capacity (J K^{-1})

help us to understand what it is; it can be thought of as the amount of heat required to increase the temperature of an object by a particular amount, in this case 1 K.

WORKED EXAMPLE 8.1

Experimental determination of heat Capacity

Central processing chips in computers generate a tremendous amount of heat — enough to damage themselves permanently if the chip is not cooled somehow. Aluminium 'heat sinks' are often attached to the chips to carry away excess heat. We can measure the heat capacity of such heat sinks by placing them (hot) into a known volume of water and measuring the temperature rise of the water. Suppose that a heat sink at 71.3 °C is dropped into a styrofoam cup containing 100.0 g of water at 25.0 °C. The temperature of the water rises to 27.4 °C. Given that it takes 4.18 J to raise the temperature of 1 g of water by 1 K, what is the heat capacity of the heat sink?

Analysis

We want to find the heat capacity, *C*. We can solve $q = \Delta CT$ for *C* by dividing both sides by the temperature change, ΔT:

$$C = \frac{q}{\Delta T}$$

We must find the temperature change of the heat sink and the amount of heat, *q*, that it exchanges with the water in the cup.

Solution

To find *q*, we can assume that the heat lost by the heat sink will be gained by the much cooler water, so we start by calculating the heat gained by the water:

$$\text{heat lost by heat sink} = -\text{heat gain a ed by the water}$$

The temperature of the water rises from 25.0 °C to 27.4 °C, a rise of 2.4 K (recall that a temperature *difference* has the same numerical value in both K and °C). It would take 2.4 K × 4.18 J K^{-1} = 1.0 × 10^1 J of heat to raise the temperature of each gram of water by 2.4 K, so it would take 100.0 × 1.0 × 10^1 J = 1.0 × 10^3 J to raise the temperature of 100.0 g of water by 2.4 K.

The temperature of the heat sink drops from 71.3 °C to 27.4 °C, so:

$$\begin{aligned} \Delta T &= T_{\text{final}} - T_{\text{initial}} \\ &= 27.4\ °C - 71.3\ °C \\ &= -43.9\ °C \\ &= -43.9\ K \end{aligned}$$

The heat gained by the water is 1.0 × 10^3 J. The heat lost by the heat sink will be - 1.0 ×10^3 J (notice that the negative sign means heat was lost by the object). The heat capacity is:

$$C = \frac{q}{\Delta T}$$
$$= \frac{-1.0 \times 10^3 \text{ J}}{-43.9 \text{ K}}$$
$$= 23 \text{ J K}^{-1}$$

Is our answer reasonable?

In any calculation involving energy transfer, we first check to see that all quantities have the correct signs. The water gained about 1000 J and warmed up by 2.4 K, so the water's heat capacity is 1000 J/2.4 K, or about 400 J K^{-1}. This is about 20 times the calculated heat capacity of the heat sink. We would expect, then, the temperature rise of the water to be about 1/20 of the temperature drop of the heat sink, since it absorbs 20 times as much heat as the heat sink before its temperature will rise 1 degree. The temperature of the heat sink dropped by 43.9 K, and the temperature of the water rose by 2.4 K, which agree with this prediction.

PRACTICE EXERCISE 8.1

A ball bearing at 220 °C is dropped into a styrofoam cup containing 250 g of water. The water warms from 25.0 to 30.0 °C. What is the heat capacity of the ball bearing, in J K^{-1}?

Heat capacity depends on the size of the sample. If it takes 4.184 J to raise the temperature of 1 g of water by 1 K, it will take twice that amount of energy (8.368 J) to obtain the same temperature rise in 2 g of water. Any property with a value that depends on the size of the sample is called an **extensive property**, while one with a value that is the same regardless of the size of the sample is called an **intensive property**. For example, the volume of a system is an extensive property, whereas its temperature is an intensive property. We can turn heat capacity, an extensive property, into a new intensive property called **specific heat capacity** by dividing by the mass of the sample. Specific heat capacity (often called **specific heat**) is simply the heat capacity per gram of substance. It has the symbol *c* and is defined as:

$$c = \frac{C}{m}$$

giving *c* the units of J g^{-1} K^{-1}. The advantage of using the intensive property specific heat is that we can easily compare values for the same mass of different substances by inspection. As we can see in table 8.1, the specific heat of water is approximately nine times that of iron, meaning that it takes nine times as much heat to raise the temperature of water by a specified amount as it does for the same mass of iron. The heat required to raise the temperature of 1 mole of a substance by 1 K is called the **molar heat capacity** and has units of J mol^{-1} K^{-1}.

TABLE 8.1 Specific Heats of Selected Substances at 25 °C

Substance	Specific heat (J $g^{-1}K^{-1}$)	Molar heat capacity (J $mol^{-1}K^{-1}$)
lead	0.128	26.5
gold	0.129	25.4

silver	0.235	25.4
copper	0.387	24.6
iron	0.4498	25.1
carbon (graphite)	0.711	8.5
oxygen (gas)	0.920	29.4
neon (gas)	1.03	20.8
nitrogen (gas)	1.04	29.1
ethanol	2.45	113
water (liquid)	4.18	75.3

We can calculate the heat absorbed or emitted by an object given its mass (m), temperature change (ΔT) and specific heat (c) by:

$$q = cm\Delta T$$

WORKED EXAMPLE 8.2

Calculating Heat from a Temperature Change, Mass and Specific Heat

If a gold ring with a mass of 5.50 g changes in temperature from 25.0 to 28.0 °C, how much heat has it absorbed?

Analysis

The question asks us to connect the heat absorbed by the ring with its temperature change, ΔT. We don't know the heat capacity of the ring. We do know the mass of the ring and that it is made of gold, so we can look up the specific heat. We will use the value of the specific heat of gold given for 25 °C in table 8.1, that is, 0.129 J g^{-1} K^{-1}.

Solution

The mass, m, of the ring is 5.50 g, the specific heat, c, is 0.129 J g^{-1} K^{-1}, and the temperature increases from 25.0 to 28.0 °C, so ΔT is 3.0 °C. Using these values gives:

$$\begin{aligned} q &= cm\Delta T \\ &= (0.129\ \text{J g}^{-1}\ \text{K}^{-1}) \times (5.50\ \text{g}) \times (3.0\ \text{K}) \\ &= 2.1\ \text{J} \end{aligned}$$

Thus, just 2.1 J raises the temperature of 5.50 g of gold by 3.0 °C. Because ΔT is positive, so is the heat, 2.1 J. Thus, the *sign* of q signifies that the ring *absorbs* heat.

Is our answer reasonable?

If the ring had a mass of only 1 g and its temperature increased by 1 °C, we'd know from the

specific heat of gold (let's round it to 0.13 J g^{-1} K^{-1}) that the ring would absorb 0.13 J. For a 3-degree temperature increase, the answer would be three times as much, or 0.39 J, nearly 0.4 J. For a ring a little heavier than 5 g, the heat absorbed would be five times as much, or about 2.0 J. So our answer (2.1 J) is clearly reasonable. Notice also that analysis of units can be very helpful in problems like these. We want our final answer in joules, and there is only one possible way of combining heat capacity (J g^{-1} K^{-1}), mass (g) and ΔT (K) to give this unit — namely multiplying them together. If you cannot remember the form of the equation, you can always figure it out using units (see section 2.2).

PRACTICE EXERCISE 8.2

The temperature of 250 g of water was changed from 25.0 to 30.0 °C. How much heat was transferred into the water?

The determination of heat

Now that we know the relationship between temperature change and heat, we can use this to determine the heat lost or gained in a chemical reaction or physical process. We carry out the re action or process in a **calorimeter**, which is a piece of apparatus especially designed to minimise heat loss between the system and surroundings. There are two main types of calorimeter — those that operate under conditions such that the system remains at constant volume and those that contain the system at constant pressure. While the distinction may appear small, we will see that there are important implications. Let us first consider **combustion reactions** where a substance undergoes reaction with oxygen in a constant volume **bomb calorimeter**, an example of which is shown in figure 8.9. Because the volume of the system cannot change during the reaction, ΔV for the system will be 0. This means that $p\Delta V$ must also be 0. Remember that $w = -p\Delta V$; therefore, no work can be done by or on the system. Recall that:

$$\Delta U = q + w$$

so, for a reaction carried out under constant volume conditions in a bomb calorimeter, it follows that:

$$\Delta_r U = q_v$$

where q_v is the **heat of reaction at constant volume**.

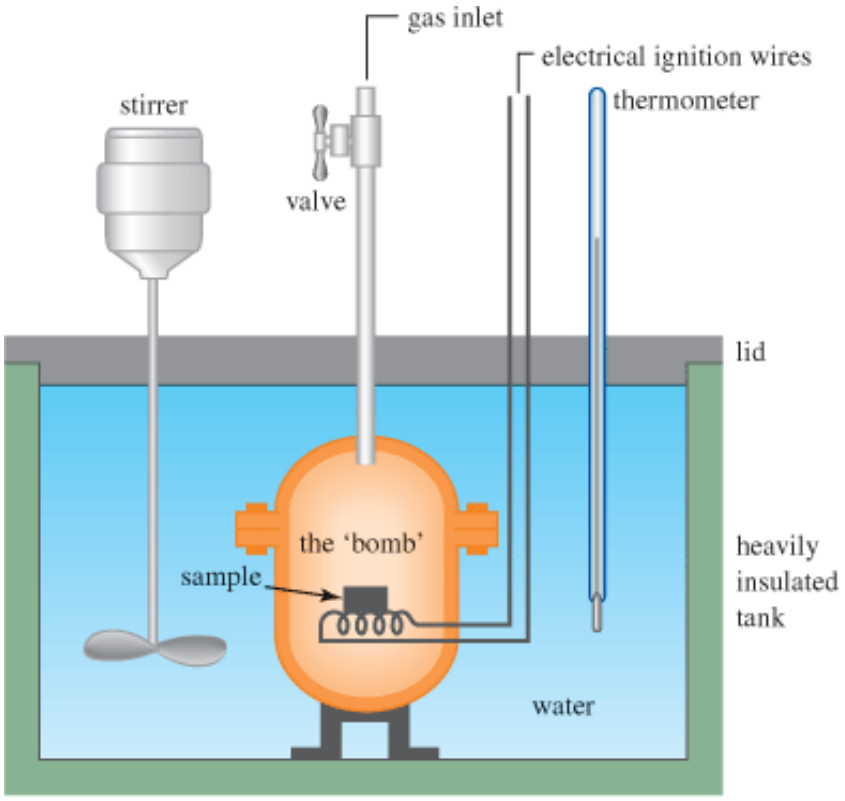


FIGURE 8.9 A bomb calorimeter. The sample is placed in the steel bomb which is then filled with $O_2(g)$. The initial temperature of the stirred water is measured, and the combustion reaction is then initiated electrically. The reaction gives out heat, which is absorbed by the steel calorimeter and the surrounding water. Measurement of the temperature rise of the water, together with knowledge of the heat capacities of the bomb calorimeter and the water, allow the heat of reaction at constant volume, q_V, and therefore the internal energy of the reaction, $\Delta_r U$, to be calculated.

Food scientists determine the internal energy of foods and food ingredients by burning them in a bomb calorimeter. The reactions that break down foods in the body are complex, but they produce the same products as the combustion reaction for the food.

It is important that you use the correct sign of the heat change in any calculations based on calorimetric measurements. Consider, for example, a combustion reaction carried out in a bomb calorimeter of the type shown in figure 8.9. The heat given out by the chemical reaction is absorbed by the calorimeter and the surrounding water, leading to a measured temperature rise of the water. In simple terms, the chemical reaction gives out an amount of heat (q_{reaction}), which is gained by the calorimeter and its surroundings ($q_{\text{calorimeter}}$). These two amounts of heat are numerically equal, but opposite in sign. It is always true that:

$$q_{\text{calorimeter}} = -q_{\text{reaction}}$$

regardless of whether the reaction gives out, or takes in, heat.

WORKED EXAMPLE 8.3

Bomb Calorimetry

(a) When 1.000 g of olive oil is completely burned in pure oxygen in a bomb calorimeter like the one shown in figure 8.9, the temperature of the water bath increases from 22.000 °C to 22.241 °C. The heat capacity of the calorimeter is 9.032 kJ K^{-1}. How

much heat is produced on burning 1.000 g of olive oil?

(b) Olive oil is almost pure glyceryl trioleate, $C_{57}H_{104}O_6$. The equation for the combustion of glyceryl trioleate is:

$$C_{57}H_{104}O_6(1) + 80O_2(g) \rightarrow 57CO_2(g) + 52H_2O(1)$$

What is the change in internal energy, $\Delta_r U$, in kJ for the combustion of 1 mole of glyceryl trioleate? Assume the olive oil burned in (a) was pure glyceryl trioleate.

Analysis

In (a), we are given the heat capacity of the calorimeter and its temperature change and we are asked for the heat produced by burning 1.000 g of olive oil. The calorimeter absorbs the heat released by the burning olive oil. We can calculate the heat absorbed by the calorimeter ($q_{\text{calorimeter}}$) from its temperature change and heat capacity, and the heat released by the oil (q_{reaction}) will be the negative of this. Since the heat capacity is in kJ K^{-1}, the heat released will be in kJ.

In (b), we are asked for the change in internal energy, $\Delta_r U$. Bomb calorimetry measures heat at constant volume, which is equal to the internal energy change for the reaction. Thus, the heat calculated in (a) is equal to $\Delta_r U$ for 1 g of glyceryl trioleate. We can use the molar mass of glyceryl trioleate to convert $\Delta_r U$ per gram to $\Delta_r U$ per mole.

Solution

(a) We calculate the heat absorbed by the calorimeter when 1.000 g of olive oil is burned using:

$$\begin{aligned} q_{\text{calorimeter}} &= C\Delta T \\ &= 9.032\ \text{kJ K}^{-1} \times (22.241 - 22.000)\text{K} \\ &= 9.032\ \text{kJ K}^{-1} \times 0.241\ \text{K} \\ &= 2.18\ \text{kJ} \end{aligned}$$

The heat absorbed by the calorimeter comes from the combustion of the olive oil; i.e. $q_{\text{calorimeter}} = -q_{\text{reaction}}$. Therefore, q_{reaction} for burning 1.000 g of olive oil is - 2.18 kJ, and the energy content of the olive oil on a mass basis is thus -2.18 kJ g^{-1}.

(b) We convert the heat produced per gram to the heat produced per mole, using the molar mass of $C_{57}H_{104}O_6$, 885.4 g mol^{-1}:

$$-2.18\ \text{kJ g}^{-1} \times 885.4\ \text{g mol}^{-1} = -1.93 \times 10^3\ \text{kJ mol}^{-1}$$

Since this is heat at constant volume, we have $\Delta_r U = q_v$ = -1.93 × 10^3 KJ for combustion of 1 mole of $C_{57}H_{104}O_6$.

Is our answer reasonable?

Always check the signs of calculated heats in calorimetry. The combustion reaction releases heat, so the sign must be negative. We appear to have done the numerical calculations correctly, so we can assume our answer is correct.

PRACTICE EXERCISE 8.3

A 1.50 g sample of carbon is burned in a bomb calorimeter with a heat capacity of 8.930 kJ K^{-1}. The temperature of the water jacket rises from 20.00 °C to 25.51 °C. What is $\Delta_r U$ for the combustion of 1 mole of carbon?

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8.4 Enthalpy

In chemistry, we are most often concerned with reactions that occur in solution, and it is more convenient to carry out such reactions in a beaker, flask or test tube open to the atmosphere than inside a metal 'bomb'. In these cases, we are working under conditions of constant atmospheric pressure. Hence, the system is free to expand or contract and this means that it can potentially do work. Thus we can see that we will not be able to make the same simplifications as we did under constant volume conditions. As we have already seen, when a system expands against a constant pressure, p, the work done is given by:

$$w = -p\Delta V$$

where:

$$\Delta V = V_{\text{finial}} - V_{\text{initial}}$$

Under conditions where the system expands, ΔV is positive and so w is negative, meaning that the system has done work on the surroundings and consequently lowered its internal energy. The opposite is true if the system is compressed. We now rewrite:

$$\Delta U = q + w$$

under conditions of constant pressure as:

$$\Delta U = q_p - p\Delta V$$

where q_p is the **heat of reaction at constant pressure**. However, this equation is inconvenient as we need to know the value of ΔV if we wish to calculate ΔU. At this point, we define a new thermodynamic function called enthalpy, which has the symbol H, as:

$$H = U + pV$$

Thus, under conditions of constant pressure:

$$\Delta H = \Delta U + p\Delta V$$

Substituting $\Delta U = q_p - p\,\Delta V$ into this gives:

$$\Delta H = q_p - p\Delta V + p\Delta V$$

so:

$$\Delta H = q_p$$

Thus, the heat of reaction at constant pressure is equal to $\Delta_r H$, in the same way that the heat of reaction at constant volume is equal to $\Delta_r U$. Like $\Delta_r U$, $\Delta_r H$ is a state function, meaning that the enthalpy change for a reaction depends only on the initial and final states of the system. If the final enthalpy of the system is greater than the initial, the system has absorbed heat from its surroundings, so $\Delta_r H$ will be positive and the reaction is said to be **endothermic**. Conversely, if the system has lost heat to the surroundings, the enthalpy of the system has decreased, so $\Delta_r H$ will be negative and the reaction is said to be **exothermic**.

The difference between the enthalpy change and the internal energy change for a reaction is $p\Delta V$. The difference between $\Delta_r U$ and $\Delta_r H$ can be very large for reactions that produce or consume gases, because these reactions can have very large volume changes. If a reaction involves only solids and liquids, though, the values of ΔV are tiny, so $\Delta_r U$ and $\Delta_r H$ for these reactions are nearly identical.

A very simple constant pressure calorimeter, dubbed the coffee cup calorimeter, comprises two nested and capped cups made of styrofoam, a very good insulator (figure 8.10). A reaction occurring in such a calorimeter exchanges very little heat with the surroundings, particularly if the reaction is fast, under which conditions the temperature change is rapid and easily measured. We can find the heat of reaction if we have determined the heat capacity of the calorimeter and its contents before the reaction. The styrofoam cup and the thermometer absorb only a tiny amount of heat, and we can usually ignore them in our calculations.

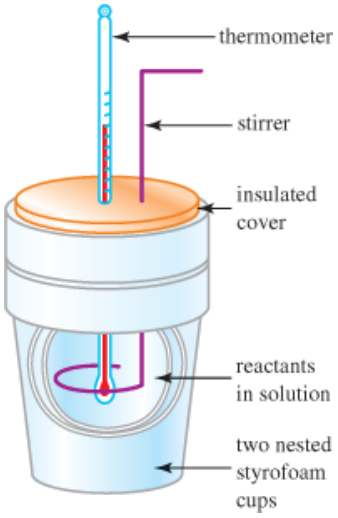


FIGURE 8.10 A coffee cup calorimeter used to measure heats of reaction at constant pressure.

Constant Pressure Calorimetry

The reaction of hydrochloric acid and sodium hydroxide is very rapid and exothermic. The balanced chemical equation is:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

In one experiment, 50.0 mL of 1.00 M HCl at 25.5 °C was placed in a coffee cup calorimeter. To this was added 50.0 mL of 1.00 M NaOH solution, also at 25.5 °C. The mixture was stirred, and the temperature quickly increased to a maximum of 32.2 °C. The density of 1.00 M HCl is 1.02 g mL^{-1} and that of 1.00 M NaOH is 1.04 g mL^{-1}. What is the heat evolved in joules per mole of HCl? Assume that the specific heats of the solutions are the same as that of water, 4.18 J g^{-1} K^{-1}. (We will neglect the heat lost to the styrofoam, the thermometer and the surrounding air.)

Analysis

Before we can use $q = cm\Delta T$ to find the heat evolved, we have to calculate the system's total mass and the temperature change. The mass here refers to the *total* mass of the combined solutions, but we were given volumes. So we have to use their densities to calculate their masses, using the equation:

$$\text{mass} = \text{density} \times \text{volume (table 2.2, p . 25)}$$

For the HCl solution, the density is 1.02 g mL^{-1} so:

$$\text{mass}_{HCl} = 1.02\ \text{g mL}^{-1} \times 50.0\ \text{mL} = 51.0\ \text{g}$$

For the NaOH solution, the density is 1.04 g mL^{-1} so:

$$\text{mass}_{NaOH} = 1.04\ \text{g mL}^{-1} \times 50.0\ \text{mL} = 52.0\ \text{g}$$

The mass of the final solution is thus the sum, 103.0 g.

Solution

The reaction changes the temperature of the calorimeter by T_{final} - $T_{initial}$, so:

$$\Delta T = (32.2 - 25.5)\text{K} = 6.7\ \text{K}$$

Now we can calculate the heat absorbed by the calorimeter, $q_{calorimeter}$:

$$\begin{aligned} q_{calorimeter} &= cm\Delta T \\ &= 4.18\ \text{J g}^{-1}\ \text{K}^{-1} \times 103.0\ \text{g} \times 6.7\ \text{K} \\ &= 2.9 \times 10^3\ \text{J} \end{aligned}$$

Knowing that $q_{reaction} = -q_{calorimeter}$, we obtain $q_{reaction} = -2.9 \times 10^3$ J.

This is the heat evolved for the specific mixture prepared. However, the problem calls for joules *per mole of HCl*. We calculate the amount of HCl using the equation:

$$\begin{aligned} n_{HCl} &= cV \\ &= 1.00\ \text{mol L}^{-1} \times 0.0500\ \text{L} \\ &= 0.0500\ \text{mol} \end{aligned}$$

Neutralising 0.0500 mol of acid gave $q_{reaction} = -2.9 \times 10^3$ J. So, on a per mole basis:

$$\begin{aligned} \text{heat evolved} &= \frac{-2.9 \times 10^3\ \text{J}}{0.0500\ \text{mol}} \\ &= -58 \times 10^3\ \text{J mol}^{-1} = -58\ \text{kJ mol}^{-1} \end{aligned}$$

Thus, the enthalpy change for this reaction is –58 kJ mol^{-1}. (The negative sign shows that the reaction is exothermic.)

Is our answer reasonable?

Let's first review the logic of the steps we used. *Notice how the logic is driven by defi-nitions, which carry specific units.* Working backwards, knowing that we want units of joules per mole in the answer, we must calculate separately the amount of acid neutralised and the amount of heat evolved. The latter will emerge when we multiply the solution's mass (g) and specific heat (J g^{-1} K^{-1}) by the temperature increase (K).

The step in the calculation that involves the mass of the final sample is straightforward. Because the densities are close to 1 g mL^{-1}, the combined masses are about 50 g per solution or a total of 100 g.

The specific heat is around 4.2 J g^{-1} K^{-1}, which means that, if the final solution weighed 1 g, its heat capacity would be 4.2 J K^{-1}. If the mass is 100 g, the heat capacity is 100 times as much, or 420 J K^{-1}.

The temperature increased by about 7 K so, when we multiply 420 J K^{-1} by 7, we get the heat absorbed by the calorimeter, about 2940 J or 2.9 × 10^3 J, which is the same as 2.9 kJ; $q_{reaction}$ is the negative of this.

This much heat is associated with neutralising 0.0500 mol HCl, so the heat per mole is -2.9 kJ divided by 0.0500 mol, or -58 kJ mol^{-1}.

PRACTICE EXERCISE 8.4

When pure sulfuric acid dissolves in water, a large amount of heat is given off. To measure it, 175 g of water was placed in a coffee cup calorimeter and chilled to 10.0 °C. Then 4.90 g of sulfuric acid, H_2SO_4, also at 10.0 °C, was added, and the mixture was quickly stirred with a thermometer. The temperature rose rapidly to 14.9 °C. Assume that the value of the specific heat of the solution is 4.18 J g^{-1} K^{-1} and that the solution absorbs all the heat evolved. Calculate the heat evolved in kilojoules on formation of this solution. (Remember to use the *total* mass of the solution: the water plus the solute.) Calculate also the heat evolved *per mole* of sulfuric acid.

Standard enthalpy change

The amount of heat a reaction produces or absorbs depends on the amounts of reactants we combine. It makes sense that, if we burn 2 moles of carbon, we will get twice as much heat as if we had burned 1 mole. For heats of reaction to have meaning, we must describe the system completely. Our description must include amounts and concentrations of reactants, amounts and concentrations of products, temperature and pressure, because all of these things can influence heats of reaction.

Chemists have agreed on a set of **standard states** to make it easier to report and compare heats of reaction. Most thermochemical equations are written for reactants and products at a pressure of 10^5 Pa or, for substances in aqueous solution, a concentration of 1 M. A temperature of 25 °C (298 K) is often specified as well, although temperature is not part of the definition of standard states in thermochemistry. The use of standard states is denoted by the superscript symbol $\text{symbol}^{\ominus}$.

The **standard enthalpy of reaction** $\left(\Delta_r H^{\ominus}\right)$ at temperature *T* is the value of Δ*H* for a reaction in which the pure, separated reactants in their standard states are converted to the pure separated products in their standard states, all at temperature *T*, and in which the stoichiometric coefficients in the balanced chemical equation refer to actual numbers of moles. While the SI unit of $\Delta_r H^{\ominus}$ is J mol^{-1}, values are usually quoted in kJ mol^{-1}.

To illustrate clearly what we mean by $\Delta_r H^{\ominus}$, let us use the reaction between gaseous nitrogen and hydrogen that produces gaseous ammonia:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

When 1.000 mol of N_2(g) and 3.000 mol of H_2(g) react to form 2.000 mol of NH_3(g) at 25 °C and 10^5 Pa, the reaction releases 92.38 kJ. Hence, for the reaction as given by the preceding equation, $\Delta_r H^{\ominus} = -92.38\ \text{kJ mol}^{-1}$. Often, the enthalpy change is given immediately after the equation, for example:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta_r H^{\ominus} = -92.38\ \text{kJ mol}^{-1}$$

An equation that also shows the value of $\Delta_r H^{\ominus}$ is called a **thermochemical equation**. It always gives the physical states of the reactants and products, and its associated $\Delta_r H^{\ominus}$ value is true only when the coefficients of the reactants and products are numerically equal to the amounts of the corresponding substances. The equation above, for example, shows a release of 92.38 kJ if 2 moles of NH_3 form. If we were to make twice as much, or 4.000 mol, of NH_3 (from 2.000 mol of N_2 and 6.000 mol of H_2), then twice as much heat (184.8 kJ) would be released. On the other hand, if only 0.5000 mol of N_2 and 1.500 mol of H_2 were to react to form just 1.000 mol of NH_3, then only half as much heat (46.19 kJ) would be released. For the various reactions just described, for example, we would

have the following thermochemical equations:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta_r H^\ominus = -92.38\ \text{kJ mol}^{-1}$$
$$2N_2(g) + 6H_2(g) \rightarrow 4NH_3(g) \quad \Delta_r H^\ominus = -184.8\ \text{kJ mol}^{-1}$$
$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g) \quad \Delta_r H^\ominus = -46.19\ \text{kJ mol}^{-1}$$

Because the coefficients of a thermochemical equation always mean *moles*, not molecules, we may use fractional coefficients.

You must write down physical states for all reactants and products in thermochemical equations. The combustion of 1 mole of methane, for example, has different values of $\Delta_r H^\ominus$ if the water produced is in its liquid or its gaseous state:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta_r H^\ominus = -890.5\ \text{kJ mol}^{-1}$$
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta_r H^\ominus = -802.3\ \text{kJ mol}^{-1}$$

The difference in $\Delta_r H^\ominus$ values for these two reactions is the quantity of energy that would be released by the physical change of 2 moles of water vapour at 25 °C to 2 moles of liquid water at 25 °C.

WORKED EXAMPLE 8.5

Writing a Thermochemical Equation

The following thermochemical equation is that for the exothermic reaction of hydrogen and oxygen that produces water (see figure 8.11):

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta_r H^\ominus = -483.6\ \text{kJ mol}^{-1}$$

What is the thermochemical equation for this reaction when it is carried out to produce 1.000 mol H_2O?

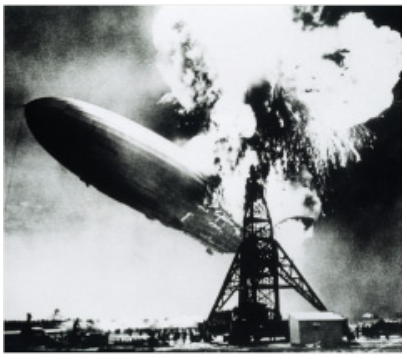


FIGURE 8.11 The airship *Hindenburg* used hydrogen, a gas that is lighter than air but also flammable, to provide lift. On 6 May 1937, at Lakehurst, New Jersey, USA, it caught fire while mooring, probably as a result of build-up of static electricity, and the explosive reaction of hydrogen with oxygen destroyed the airship in minutes.

Analysis

The given equation is for the production of 2.000 mol of H_2O, and any changes in the coefficient for water must be made identically to all other coefficients, as well as to the value of $\Delta_r H^\ominus$.

Solution

We divide everything by 2 to obtain:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \quad \Delta_r H^\ominus = -241.8\ \text{kJ mol}^{-1}$$

Is our answer reasonable?

Compare the equation just found with the initial equation to see that the coefficients and the value of $\Delta_r H^\ominus$ are all divided by 2.

PRACTICE EXERCISE 8.5

What is the thermochemical equation for the formation of 2.500 mol of H_2O in worked example 8.5?

Once we have the thermochemical equation for a given reaction, we can write the equation for the reverse reaction, regardless of how hard it might actually be to make it happen. For example, the thermochemical equation for the combustion of carbon in oxygen to give carbon dioxide is:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta_r H^\ominus = -393.5 \text{ kJ mol}^{-1}$$

The reverse reaction, which is extremely difficult to carry out, would be the decomposition of carbon dioxide to carbon and oxygen:

$$CO_2(g) \longrightarrow C(s) + O_2(g) \quad \Delta_r H^\ominus = ?$$

Despite how hard it would be to carry out this reaction, we can still determine its value of $\Delta_r H^\ominus$. It must be +393.5 kJ mol^{-1}, that is, equal in size but opposite in sign to $\Delta_r H^\ominus$ for the reaction written in the opposite direction. The law of conservation of energy requires this remarkable result. If the values of $\Delta_r H^\ominus$ for the forward and the reverse reactions were not equal but opposite in sign, then perpetual-motion machines would be possible. (Despite numerous claims, such machines will always be an unattainable dream.) Thus, regardless of the difficulty of directly decomposing CO_2 into its elements, we can still write a thermochemical equation for it:

$$CO_2(g) \longrightarrow C(s) + O_2(g) \quad \Delta_r H^\ominus = +393.5 \text{ kJ mol}^{1}$$

To repeat, if we know $\Delta_r H^\ominus$ for a given reaction, then we also know $\Delta_r H^\ominus$ for the reverse re action; it has the same numerical value, but the opposite algebraic sign. This extremely useful fact makes thermochemical data available that would otherwise be impossible to measure.

Hess's Law

Hess's law is a method for combining known thermochemical equations in a way that allows us to calculate $\Delta_r H^\ominus$ for another reaction. This requires experience in other kinds of manipulations of equations. We will illustrate this using the combustion of carbon.

We can imagine two paths leading from 1 mole each of carbon and oxygen to 1 mole of carbon dioxide.

One-step path

Let C and O_2 react to give CO_2 directly:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta_r H^\ominus = -393.5 \text{ kJ mol}^{-1}$$

Two-step path

Let C and O_2 react to give CO, and then let CO react with O_2 to give CO_2:

Step 1:

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \quad \Delta_r H^\ominus = -110.5 \text{ kJ mol}^{-1}$$

Step 2:

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta_r H^\ominus = -283.0 \text{ kJ mol}^{-1}$$

Overall, the two-step path consumes 1 mole each of C and O_2 to make 1 mole of CO_2, just like the one-step path. The initial and final states for the two routes to CO_2 are identical.

If $\Delta_r H^\ominus$ is a state function dependent only on the initial and final states and independent of path, the values of $\Delta_r H^\ominus$ for both routes should be identical. We can see that this is true simply by adding the equations for the two-step path and comparing the result with the equation for the one-step path:

$$\begin{array}{lll}
\textit{Step 1:} & C(s) + \tfrac{1}{2}O_2(g) \longrightarrow \cancel{CO(g)} & \Delta_r H^\ominus = -110.5 \text{ kJ mol}^{-1} \\
\textit{Step 2:} & \cancel{CO(g)} + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) & \Delta_r H^\ominus = -283.0 \text{ kJ mol}^{-1} \\
\hline
 & C(s) + O_2(g) \longrightarrow CO_2(g) & \Delta_r H^\ominus = -110.5 \text{ kJ mol}^{-1} + (-283.0 \text{ kJ mol}^{-1}) \\
 & & = -393.5 \text{ kJ mol}^{-1}
\end{array}$$

Note that we can cancel CO(g) as it appears *identically* on opposite sides of the arrow in steps 1 and 2. Such a cancellation is permitted only when both the formula and the physical state of a species are identical on opposite sides of the arrow. The net thermochemical equation for the two-step process, therefore, is:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta_r H^\ominus = -393.5\ \text{kJ mol}^{-1}$$

The results, chemically and thermochemically, are identical for both routes to CO_2, demon-strating that $\Delta_r H^\ominus$ is a state function. The above example is a manifestation of **Hess's law**, which states that *the overall enthalpy change for any chemical reaction is constant, regardless of how the reaction is carried out.*

The chief use of Hess's law is to calculate the enthalpy change for a reaction for which such data cannot be determined experimentally or are otherwise unavailable. Because this requires that we manipulate equations, let's restate the few rules that govern these operations.

Rules for Manipulating Thermochemical Equations

1. When an equation is reversed — written in the opposite direction — the sign of $\Delta_r H^\ominus$ must also be reversed. To illustrate, the reverse of the equation:

   $$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta_r H^\ominus = -393.5\ \text{kJ mol}^{-1}$$

   is the following equation:

   $$CO_2(g) \longrightarrow C(s) + O_2(g) \quad \Delta_r H^\ominus = +393.5\ \text{kJ mol}^{-1}$$

2. Substances can be cancelled from both sides of an equation only if the substance is in an identical physical state.
3. If all the coefficients of an equation are multiplied or divided by the same factor, the value of $\Delta_r H^\ominus$ must likewise be multiplied or divided by that factor.

WORKED EXAMPLE 8.6

Using Hess's Law

Carbon monoxide is often used in metallurgy to remove oxygen from metal oxides to give the free metal. The thermochemical equation for the reaction of CO with iron(III) oxide, Fe_2O_3, is:

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g) \quad \Delta_r H^\ominus = -26.7\ \text{kJ mol}^{-1}$$

Use this equation and the equation for the combustion of CO:

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta_r H^\ominus = -283.0\ \text{kJ mol}^{-1}$$

to calculate the value of $\Delta_r H^\ominus$ for the following reaction:

$$2Fe(s) + \tfrac{3}{2}O_2(g) \rightarrow Fe_2O_3(s)$$

Analysis

We cannot simply add the two given equations, because this will not produce the equation we want. We first have to manipulate these equations so that when we add them we will obtain the target equation.

Solution

We can manipulate the two given equations as follows:

Step 1: We begin with the iron atoms. The target equation must have 2Fe on the left, but the first equation in this worked example has 2Fe to the right of the arrow. To move it to the left, we must reverse the entire equation, remembering also to reverse the sign of $\Delta_r H^\ominus$. This puts Fe_2O_3 to the right of the arrow, which is where it has to be after we add our adjusted equations. After these manipulations, and reversing the sign of $\Delta_r H^\ominus$, we have:

$$2Fe(s) + 3CO_2(g) \longrightarrow Fe_2O_3(s) + 3CO(g) \quad \Delta_r H^\ominus = +26.7\ \text{kJ mol}^{-1}$$

Step 2: There must be $\tfrac{3}{2}O_2$ on the left, and we must be able to cancel 3CO and $3CO_2$ when the equations are added. If

we multiply the second equation in this worked example by 3, we will obtain the necessary coefficients. We must also multiply the value of $\Delta_r H^\ominus$ for this equation by 3, because three times the amount of substances are now involved in the reaction. When we have done this, we have:

$$3CO(g) + \frac{3}{2}O_2(g) \longrightarrow 3CO_2(g) \quad \Delta_r H^\ominus = 3 \times (-283.0\ kJ) = -849.0\ kJ\ mol^{-1}$$

We now put our two equations together and find the answer:

$$\begin{array}{lll} & 2Fe(s) + \cancel{3CO_2(g)} \longrightarrow Fe_2O_3(s) + \cancel{3CO(g)} & \Delta_r H^\ominus = +26.7\ kJ\ mol^{-1} \\ & \cancel{3CO(g)} + \frac{3}{2}O_2(g) \longrightarrow \cancel{3CO_2(g)} & \Delta_r H^\ominus = -849.0\ kJ\ mol^{-1} \\ \hline \text{Sum:} & 2Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s) & \Delta_r H^\ominus = -822.3\ kJ\ mol^{-1} \end{array}$$

Thus, the value of $\Delta_r H^\ominus$ for the oxidation of 2 mol Fe(s) to 1 mol $Fe_2O_3(s)$ is -822.3 kJ mol^{-1}. (The reaction is *very* exothermic.)

Is our answer reasonable?

There is no shortcut to check that we are right. But, for each step, double-check that you have followed the rules for manipulating thermochemical equations.

PRACTICE EXERCISE 8.6

Ethanol, C_2H_5OH, is made industrially by the reaction of water with ethene, C_2H_4. Calculate the value of $\Delta_r H^\ominus$ for the reaction:

$$C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$$

given the following thermochemical equations:

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l) \quad \Delta_r H^\ominus = -1411.1\ kJ\ mol^{-1}$$

$$C_2H_5OH(1) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta_r H^\ominus = -1367.1\ kJ\ mol^{-1}$$

Standard Enthalpy of Formation

Enormous databases of thermochemical equations have been compiled to allow the calculation of any enthalpy of reaction using Hess's law. The most frequently tabulated data are those for formation reactions.

The **standard enthalpy of formation** $\left(\Delta_f H^\ominus\right)$ of a substance is the enthalpy change when 1 mole of the substance is formed at 10^5 Pa and the specified temperature from its elements in their standard states. An element is in its standard state when it is in its most stable form and physical state (solid, liquid or gas) at 10^5 Pa and the specified temperature. Oxygen, for example, is in its standard state at a temperature of 25 °C only as a gas at 10^5 Pa and only as O_2 molecules, not as O atoms or O_3 (ozone) molecules. Carbon must be in the form of graphite, not diamond, to be in its standard state at a temperature of 25 °C because the graphite form of carbon is the most stable form at this temperature under standard con ditions (10^5 Pa).

Standard enthalpies of formation for a variety of substances are given in table 8.2, and a more extensive table can be found in appendix A. Notice in particular that all values of $\Delta_f H^\ominus$ for the elements in their standard states are 0; forming an element from itself, of course, would yield no change in enthalpy. For this reason, values of $\Delta_f H^\ominus$ for the elements are generally not included in tables.

TABLE 8.2 Standard Enthalpies of Formation of Selected Substances at 25 °C

Substance	$\Delta_f H^\ominus$ (kJ mol^{-1})
Ag(s)	0
AgBr(s)	-100.4
AgCl(s)	-127.0
Al(s)	0
	–1669.8

$Al_2O_3(s)$	
C(s, C_{60})	2320
C(s, diamond)	1.9
C(s, graphite)	0
$CH_3Cl(g)$	-82.0
$CH_3I(g)$	14.2
$CH_3OH(l)$	-238.6
$CH_3COOH(l)$	–487.0
$CH_4(g)$	-74.848
$C_2H_2(g)$	226.75
$C_2H_4(g)$	52.284
$C_2H_6(g)$	–84.667
$C_2H_5OH(l)$	-277.63
CO(g)	-110.5
$CO_2(g)$	-393.5
$CO(NH_2)_2(s)$	–333.19
Ca(s)	0
$CaBr_2(s)$	-682.8
$CaCO_3(s)$	-1207
$CaCl_2(s)$	–795.0
CaO(s)	-635.5
$Ca(OH)_2(s)$	-986.59
$CaSO_4(s)$	-1432.7
$CaSO_4 \cdot \frac{1}{2}H_2O(s)$	-1575.2
$CaSO_4 \cdot 2H_2O(s)$	-2021.1
$Cl_2(g)$	0
Fe(s)	0
$Fe_2O_3(s)$	-822.3
$H_2O(g)$	-241.8
$H_2O(l)$	-285.9
$H_2(g)$	0
$H_2O_2(l)$	-187.6
HBr(g)	-36
HCl(g)	-92.30
HI(g)	26.6
$HNO_3(l)$	-173.2
$H_2SO_4(l)$	–811.32
Hg(l)	0
Hg(g)	60.84
$I_2(s)$	0
K(s)	0

KCl(s)	-435.89
K_2SO_4(s)	-1433.7
N_2(g)	0
NH_3(g)	-46.19
NH_4Cl(s)	-315.4
NO(g)	90.37
NO_2(g)	33.8
N_2O(g)	81.57
N_2O_4(g)	9.67
N_2O_5(g)	11
Na(s)	0
$NaHCO_3$(s)	-947.7
Na_2CO_3(s)	-1131
NaCl(s)	-411.0
NaOH(s)	-426.8
Na_2SO_4(s)	-1384.5
O_2(g)	0
Pb(s)	0
PbO(s)	-219.2
S(s, rhombic)	0
SO_2(g)	-296.9
SO_3(g)	–395.2

It is important to remember the meaning of the subscript f in the symbol $\Delta_f H^\ominus$. It is applied only when *1 mole* of the substance is formed *from its elements in their standard states*. Consider, for example, the following four thermochemical equations and their corresponding values of $\Delta H^\ominus$:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta_f H^\ominus = -285.9\ \text{kJ mol}^{-1}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta_r H^\ominus = -571.8\ \text{kJ mol}^{-1}$$

$$H_2O(g) \rightarrow H_2O(l) \quad \Delta_r H^\ominus = -44.1\ \text{kJ mol}^{-1}$$

$$2H(g) + O(g) \rightarrow H_2O(l) \quad \Delta_r H^\ominus = -971.1\ \text{kJ mol}^{-1}$$

Only in the first equation is $\Delta H^\ominus$ given the subscript f. It is the only reaction that satisfies both of the conditions specified for standard enthalpies of formation. The second equation shows the formation of 2 moles of water, rather than 1 mole. The third involves a compound as the reactant. The fourth involves the elements as atoms, which are not standard states for these elements. We can obtain $\Delta_r H^\ominus$ for the second equation simply by multiplying the $\Delta_f H^\ominus$ value of the first equation by 2.

WORKED EXAMPLE 8.7

Writing an Equation for a Standard Enthalpy of Formation

Write the equation to which $\Delta_f H^\ominus_{HNO_3(l)}$ refers.

Analysis

The equation must show only 1 mole of the product. We begin with its formula and take whatever fractions of moles of the elements are needed to make it. We also remember to include the physical states. Table 8.2 gives the value of $\Delta_f H^\ominus$ for $HNO_3(l)$ as -173.2 kJ mol^{-1}.

Solution

The three elements, H, N and O, all occur as diatomic molecules in the gaseous state, so the following fractions of moles supply exactly enough to make 1 mole of HNO_3:

$$\frac{1}{2}H_2(g) + \frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) \longrightarrow HNO_3(l) \quad \Delta_f H^\ominus = -173.2\ \text{kJ mol}^{-1}$$

Is our answer reasonable?

The answer correctly shows only 1 mole of HNO_3, and this governs the coefficients for the reactants. So simply check that the equation is balanced.

PRACTICE EXERCISE 8.7

Write the thermochemical equation that would be used to represent the standard enthalpy of formation of sodium bicarbonate, $NaHCO_3(s)$.

Standard enthalpies of formation are useful because they provide a convenient method for applying Hess's law without having to manipulate thermochemical equations. This is possible because, as we will demonstrate, $\Delta_r H^\ominus$ for a reaction equals the sum of the standard enthalpies of formation of the products minus the sum of the standard enthalpies of formation of the reactants, with each $\Delta_f H^\ominus$ value multiplied by the appropriate stoichiometric coefficient given by the thermochemical equation. In other words, for the reaction:

$$aA + bB \rightarrow cC + dD$$

$$\Delta_r H^\ominus = c\Delta_f H^\ominus_C + d\Delta_f H^\ominus_D - (a\Delta_f H^\ominus_A + b\Delta_f H^\ominus_B)$$

or, in more general terms:

$$\Delta_r H^\ominus = \sum_i^{\text{products}} \nu_i \Delta_f H^\ominus_i - \sum_j^{\text{reactants}} \nu_j \Delta_f H^\ominus_j$$

where Σ means 'the sum over' and ν_i and ν_j are the stoichiometric coefficients for the products and reactants, respectively, in the balanced chemical equation for the reaction.

Although the two expressions above for $\Delta_r H^\ominus$ look very different, they are merely alternative formulations of the Hess's law equation. While both are given in terms of standard enthalpies of formation, $\Delta_f H^\ominus$, they also apply to standard enthalpies of combustion, $\Delta_c H^\ominus$ (see p. 313). However, you need to ensure you use only either standard enthalpies of formation or standard enthalpies of combustion when calculating $\Delta_r H^\ominus$ using the above equations — you must never mix them.

We will now demonstrate that the Hess's law equation works. Consider the reaction given by the following equation:

$$SO_3(g) \longrightarrow SO_2(g) + \frac{1}{2}O_2(g) \quad \Delta_r H^\ominus = ?$$

We wish to calculate the enthalpy of reaction using standard enthalpies of formation.

If we use the first method we learned, namely, the manipulation of thermochemical equations, we would need to imagine a path from the reactant to the products that involves first decomposing $SO_3(g)$ into its elements in their standard states and then recombining the elements to form the products. This path is shown in figure 8.12. The first step with the enthalpy change indicated as $\Delta_r H^\ominus_1$, corresponds to the decomposition of $SO_3(g)$ into sulfur and oxygen. This is just the reverse of the equation for the formation of $SO_3(g)$, so we can write:

$$\Delta_r H^\ominus_1 = -\Delta_f H^\ominus$$

We use a negative sign because, when we reverse a process, we change the sign of its $\Delta_r H$.

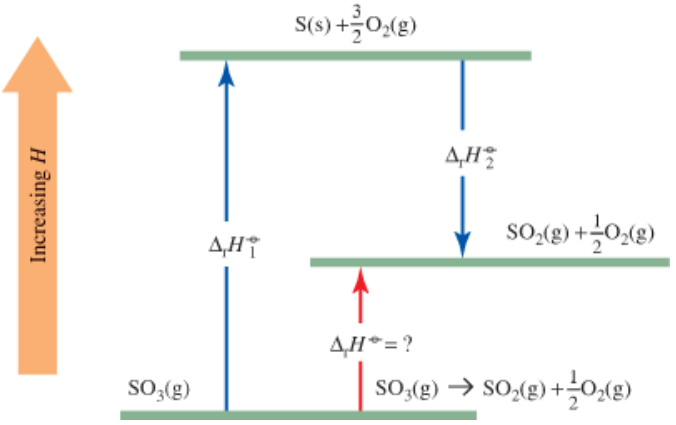


FIGURE 8.12 Enthalpy diagram for the reaction:

$$SO_3(g) \rightarrow SO_2(g) + \frac{1}{2}O_2(g)$$

The path of the reaction in this diagram involves the reactant being decomposed into its elements in their standard states (red arrow), and then the elements being recombined to form the products (downward blue arrow). The difference in the lengths of these two arrows is proportional to the net enthalpy change (upward blue arrow).

The second step in figure 8.12, with the enthalpy change indicated as $\Delta_r H_2^\ominus$, is the for mation of $SO_2(g)$ plus $\frac{1}{2}$ mole of $O_2(g)$ from sulfur and oxygen. Therefore, we can write:

$$\Delta_r H_2^\ominus = \Delta_f H_{SO_2(g)}^\ominus + \frac{1}{2}\Delta_f H_{O_2(g)}^\ominus$$

The sum of these two steps gives the net change we want, so the sum of $\Delta_r H_1^\ominus$ and $\Delta_r H_2^\ominus$ must equal the desired $\Delta_r H^\ominus$:

$$\Delta_r H^\ominus = \Delta_r H_1^\ominus + \Delta_r H_2^\ominus$$

By substitution:

$$\Delta_r H^\ominus = (-\Delta_f H_{SO_3(g)}^\ominus) + (\Delta_f H_{SO_2(g)}^\ominus + \frac{1}{2}\Delta_f H_{O_2(g)}^\ominus)$$

This can be rewritten as:

$$\Delta_r H^\ominus = (\Delta_f H_{SO_2(g)}^\ominus + \frac{1}{2}\Delta_f H_{O_2(g)}^\ominus) + (-\Delta_f H_{SO_3(g)}^\ominus)$$

The change of sign gives:

$$\Delta_r H^\ominus = (\Delta_f H_{SO_2(g)}^\ominus + \frac{1}{2}\Delta_f H_{O_2(g)}^\ominus) - (\Delta_f H_{SO_3(g)}^\ominus)$$

Notice carefully the net result. $\Delta_r H^\ominus$ for the reaction equals the sum of the enthalpies of formation of the products minus the enthalpy of formation of the reactant, each multiplied by the appropriate coefficient. So, we could have obtained the identical result by using the Hess's law equation directly, instead of by the more laborious method of manipulating thermochemical equations.

WORKED EXAMPLE 8.8

Using Hess's Law and Standard Enthalpies of Formation

Some chefs keep baking soda, $NaHCO_3$, handy to put out fat and oil fires. When thrown on the fire, baking soda partly smothers the fire and the heat decomposes it to give CO_2, which further smothers the flame. The equation for the decomposition of $NaHCO_3$ is:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

Use the data in table 8.2 to calculate $\Delta_r H^\ominus$ for this reaction.

Analysis

The Hess's law equation is now our basic tool for calculating values of $\Delta_r H^\ominus$. So we calculate the sum of the $\Delta_f H^\ominus$ values for the products (table 8.2), each multiplied by the appropriate stoichiometric coefficient, and do the same for the reactants. Then we subtract the latter from the former to calculate $\Delta_r H^\ominus$.

Solution

The Hess's law equation gives us:

$$\Delta_r H^\ominus = (1 \times \Delta_f H^\ominus_{Na_2CO_3(s)}) + (1 \times \Delta_f H^\ominus_{H_2O(g)}) + (1 \times \Delta_f H^\ominus_{CO_2O(g)}) - (2 \times \Delta_f H^\ominus_{NaHCO_3O(s)})$$

We now use table 8.2 to find the values of $\Delta_f H^\ominus$ for each substance in its proper physical state.

$$\begin{aligned} \Delta_r H^\ominus &= 1 \times (-1131\ \text{kJ mol}^{-1}) + 1 \times (-241.8\ \text{kJ mol}^{-1}) + 1 \times (-393.5\ \text{kJ mol}^{-1}) - 2 \times (-947.7\ \text{kJ mol}^{-1}) \\ &= (-1766\ \text{kJ mol}^{-1}) - (-1895\ \text{kJ mol}^{-1}) \\ &= +129\ \text{kJ mol}^{-1} \end{aligned}$$

Thus, under standard conditions, the reaction is endothermic by 129 kJ mol^{-1}. (Notice that we did not have to manipulate any equations.)

Is our answer reasonable?

Double-check that all of the coefficients found in the given equation are correctly applied as multipliers in the solution. Be sure that the signs of the values of $\Delta_r H^\ominus$ have all been carefully used. Have you used the order of subtracting specified in the Hess's law equation? Keeping track of negative signs requires particular care.

PRACTICE EXERCISE 8.8

Calculate $\Delta_r H^\ominus$ for the following reactions:

(a) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

(b) $NaOH(s) + HCl(g) \rightarrow NaCl(s) + H_2O(l)$

Standard Enthalpy of Combustion

The **standard enthalpy of combustion** $\Delta_c H^\ominus$ of a substance at temperature *T* is the enthalpy change when 1 mole of the substance is completely burned in pure oxygen gas, with all reactants and products brought to temperature *T* and 10^5 Pa pressure. All carbon in the substance becomes carbon dioxide gas, and all hydrogen becomes liquid water. *Combustion reactions are always exothermic*, so $\Delta_c H^\ominus$ is always negative. The units of $\Delta_c H^\ominus$ are usually kJ mol^{-1}.

WORKED EXAMPLE 8.9

Writing an Equation for a Standard Enthalpy of Combustion

What amount of carbon dioxide gas is produced by a gas-fired power plant for every 1.0 MJ (megajoule) of energy it produces? The plant burns methane, $CH_4(g)$, for which $\Delta_c H^\ominus$ is -890 kJ mol^{-1}.

Analysis

We need to link the amount of carbon dioxide with the amount of heat produced. To do this, we require a balanced thermochemical equation. As this is a combustion reaction, the reactants will be the fuel, $CH_4(g)$, and oxygen, $O_2(g)$, and the products will be carbon dioxide gas (because the fuel contains carbon) and liquid water (because the fuel contains hydrogen). We must therefore balance the following equation for combustion of 1 mole of $CH_4(g)$:

$$CH_4(g) + ?\,O_2(g) \longrightarrow ?\,CO_2(g) + ?\,H_2O(l) \quad \Delta_c H^{\ominus} = -890\ \text{kJ mol}^{-1}$$

The coefficient in front of $CO_2(g)$ will be the amount of CO_2 produced when 890 kJ of heat is released. Using this, we can then obtain a conversion factor to relate megajoules of heat to the amount of $CO_2(g)$. To link megajoules with kilojoules, we'll need to remember the meanings of the SI prefixes *kilo* and *mega:*

$$1\ \text{kJ} = 10^3\ \text{J}$$
$$1\ \text{MJ} = 10^6\ \text{J}$$

These three relations are all we need to link megajoules of heat with the amount of $CO_2(g)$.

Solution

We balance the equation for 1 mole of CH_4 as follows:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta_c H^{\ominus} = -890\text{kJ mol}^{-1}$$

so 1 mol CO_2 is released for every 890 kJ of heat released. Knowing that 1 MJ = 1000 kJ, the amount of CO_2 produced when 1 MJ of heat is released is:

$$\frac{1.0 \times 10^3\ \text{kJ}}{890\ \text{kJ mol}^{-1}} = 1.1\ \text{mol}\ CO_2$$

Is our answer reasonable?

We can see that the equation has been correctly balanced for 1 mol CH_4; each side has one C atom, four H atoms and four O atoms. We can also see that it makes sense that only slightly more than 1 mole of CO_2 is produced with 1 MJ (1000 kJ) of heat, because 1000 kJ is only slightly more than 890 kJ, the amount of heat produced on formation of 1 mole of CO_2.

PRACTICE EXERCISE 8.9

A 60-litre car fuel tank can hold about 507 moles of *n*-octane, $C_8H_{18}(l)$, which has a standard enthalpy of combustion of 5450.5 kJ mol^{-1}. How much heat could be produced by burning a full tank of *n*-octane?

Bond Enthalpies

Chemical reactions generally involve the breaking of chemical bonds in the reactants and the making of chemical bonds in the products. The observed enthalpy change for any chemical reaction is predominantly a result of these bond-breaking and bond-making processes; energy is required to break a chemical bond and energy is liberated on formation of a chemical bond. Therefore, a knowledge of individual bond energies can provide us with a means to estimate the overall enthalpy change in a chemical reaction.

A **bond enthalpy** is the enthalpy change on breaking 1 mole of a particular chemical bond to give electrically neutral fragments in the gas phase at temperature *T*. You should appreciate that the bond energies we have encountered in previous chapters are associated with ΔU and refer to conditions of constant volume. Bond enthalpies are useful in rationalising chemical reactivity, as they provide a measure of the ease with which a particular chemical bond can be broken. Elemental nitrogen, for example, has a very low degree of reactivity, which is generally attributed to the very strong triple bond in N_2. Reactions that involve breaking this bond in a single step simply do not occur. When N_2 does react, it is by a stepwise breaking of its three bonds, one at a time.

Bond Enthalpies and Hess's Law

The bond enthalpies of simple diatomic molecules such as H_2, O_2 and Cl_2 are usually measured spectroscopically, using techniques similar to those we discussed in chapter 4 (p. 123). An electric discharge is used to excite the molecules, causing them to emit light. An analysis of the spectrum of the emitted light allows calculation of the amount of energy needed to break the bond.

For more complex molecules, thermochemical data can be used to calculate bond enthalpies using Hess's law. We will use the standard enthalpy of formation of methane to illustrate how this is accomplished. However, before we can attempt such a calculation, we must first define a thermochemical quantity called the **atomisation enthalpy ($\Delta_{at}H$)**. This is the enthalpy change that occurs on rupturing all the chemical bonds in 1 mole of gaseous molecules to give gaseous atoms as products. For example, the equation for the atomisation of methane is:

$$CH_4(g) \rightarrow C(g) + 4H(g)$$

and the enthalpy change for the process is $\Delta_{at}H^{\ominus}$ under standard conditions. For this particular molecule, $\Delta_{at}H^{\ominus}$ corresponds to the total enthalpy change on breaking all the C—H bonds in 1 mole of CH_4 under standard conditions; therefore, division of $\Delta_{at}H^{\ominus}$ by 4 would give the average C—H bond enthalpy in methane.

Figure 8.13 shows how we can use the standard enthalpy of formation, $\Delta_f H^{\ominus}$, to calculate the atomisation enthalpy. Across the bottom we have the chemical equation for the formation of 1 mole of CH_4 from its elements in their standard states. The enthalpy change for this reaction is $\Delta_f H^{\ominus}$. In this figure, we also can see an alternative three-step path that leads to $CH_4(g)$. One step is the breaking of H—H bonds in the H_2 molecules to give gaseous hydrogen atoms; another is the vaporisation of carbon to give a gaseous carbon atom, and the third is the combination of the gaseous atoms to form a CH_4 molecule. These changes are labelled 1, 2 and 3 in the figure.

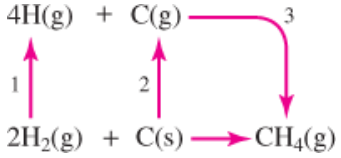


FIGURE 8.13 Two paths (equations) for the formation of methane from its elements in their standard states. As described in the text, steps 1, 2 and 3 of the upper path are the formation of gaseous atoms of the elements and then the formation of the bonds in CH_4. The lower path is the direct combination of the elements in their standard states to give CH_4. Because ΔH is a state function, the sum of the enthalpy changes along the upper path must equal the enthalpy change for the lower path, $\Delta_f H^{\ominus}$

Since enthalpy is a state function, the net enthalpy change from one state to another is the same regardless of the path that we follow. This means that the sum of the enthalpy changes along the upper path must be the same as the enthalpy change along the lower path, $\Delta_f H^{\ominus}$. Perhaps this can be seen more easily in Hess's law terms if we write the changes along the upper path in the form of thermochemical equations.

Steps 1 and 2 have enthalpy changes that are standard enthalpies of formation of gaseous atoms. Values for these quantities have been measured for many of the elements, and some are given in table 8.3. Step 3 is the opposite of atomisation, and its enthalpy change will, therefore, be the negative of $\Delta_{at}H^{\ominus}$ (recall that if we reverse a reaction, we change the sign of its ΔH).

TABLE 8.3 Standard Enthalpies of Formation of Selected Gaseous Atoms from the Elements in their Standard States at 25 °C

Atom	$\Delta_f H^{\ominus}$ (kJ mol^{-1})[a]
B	560
Be	324.3
Li	161.5
Br	112.38
C	716.67
Cl	121.47
F	79.14
H	217.89
I	107.48
N	472.68
O	249.17
P	332.2
S	276.98
Si	450

All values are positive because formation of the gaseous atoms from the elements involves bond breaking, which requires an input of energy.

Step 1:	$2H_2(g) \longrightarrow 4H(g)$	$\Delta_r H^{\ominus}_1 = 4\Delta_f H^{\ominus}_{H(g)}$
Step 2:	$C(s) \longrightarrow C(g)$	$\Delta_r H^{\ominus}_2 = \Delta_f H^{\ominus}_{C(g)}$
Step 3:	$4H(g) + C(g) \longrightarrow CH_4(g)$	$\Delta_r H^{\ominus}_3 = -\Delta_{at} H^{\ominus}$
	$2H_2(g) + C(s) \longrightarrow CH_4(g)$	$\Delta_r H^{\ominus} = \Delta_f H^{\ominus}_{CH_4(g)}$

Notice that, by adding the first three equations, we get the equation for the formation of CH_4 from its elements in their standard states. This means that adding the $\Delta_r H^\ominus$ values of the first three equations should give $\Delta_f H^\ominus$ for CH_4:

$$\Delta_r H_1^\ominus + \Delta_r H_2^\ominus + \Delta_r H_3^\ominus = \Delta_f H^\ominus_{CH_4(g)}$$

We will substitute for $\Delta_r H_1^\ominus$, $\Delta_r H_2^\ominus$, $\Delta_r H_3^\ominus$, and then solve for $\Delta_{at} H^\ominus$. First, we substitute for the $\Delta_r H^\ominus$ quantities:

$$4\Delta_f H^\ominus_{H(g)} + \Delta_f H^\ominus_{C(g)} + (-\Delta_{at} H^\ominus) = \Delta_f H^\ominus_{CH_4(g)}$$

Next, we solve for $(-\Delta_{at} H^\ominus)$:

$$-\Delta_{at} H^\ominus = \Delta_f H^\ominus_{CH_4(g)} - 4\Delta_f H^\ominus_{H(g)} - \Delta_f H^\ominus_{C(g)}$$

Changing signs and rearranging the right-hand side of the equation gives:

$$\Delta_{at} H^\ominus = 4\Delta_f H^\ominus_{H(g)} + \Delta_f H^\ominus_{C(g)} - \Delta_f H^\ominus_{CH_4(g)}$$

Now all we need are the $\Delta_f H^\ominus$ values on the right-hand side. We obtain $\Delta_f H^\ominus_{H(g)}$ and $\Delta_f H^\ominus_{C(g)}$ from table 8.3 and $\Delta_f H^\ominus_{CH_4(g)}$ from table 8.2 and round these to the nearest 0.1 kJ mol^{-1}:

$$\begin{aligned} \Delta_f H^\ominus_{H(g)} &= +217.9\ \text{kJ mol}^{-1} \\ \Delta_f H^\ominus_{C(g)} &= +716.7\ \text{kJ mol}^{-1} \\ \Delta_f H^\ominus_{CH_4(g)} &= -74.8\ \text{kJ mol}^{-1} \end{aligned}$$

Substituting these values gives:

$$\Delta_{at} H^\circ = 1663.1\ \text{kJ mol}^{-1}$$

Given that each CH_4 molecule contains four C—H bonds, division by 4 gives an estimate of the average C—H bond enthalpy in this molecule:

$$\begin{aligned} \text{bond enthalpy} &= \frac{1663.1\ \text{kJ mol}^{-1}}{4} \\ &= 415.8\ \text{kilojoules per mole of C—H bonds} \end{aligned}$$

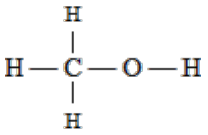
This value is quite close to the one in table 8.4, which is an average of the C—H bond enthalpies in many different compounds. The other bond enthalpies in table 8.4 are also based on thermo-chemical data and were obtained by similar calculations.

TABLE 8.4 Some Average Bond Enthalpies at 25 °C

Bond	Bond enthalpy (kJ mol^{-1})	Bond	Bond enthalpy (kJ mol^{-1})	Bond	Bond enthalpy (kJ mol^{-1})
C—C	348	C—F	484	H—H	436
C═C	612	C—Cl	338	H—F	565
C≡C	960	C—Br	276	H—Cl	431
C—H	412	C—I	238	H—Br	366
C—N	305			H—I	299
C═N	613			H—N	388
C≡N	890			H—O	463
C—O	360			H—S	338
C═O	743			H—Si	376

A remarkable thing about many covalent bond enthalpies is that they are very nearly the same in many different compounds. This suggests, for example, that a C—H bond is very nearly the same in CH_4 as it is in a large number of other compounds that contain this kind of bond. Also note that, in general, triple bond enthalpies (e.g. C≡C) are greater than double bond enthalpies (C═C), which in turn are greater than single bond enthalpies (C—C).

Because the bond enthalpy does not vary much from compound to compound, we can use tabulated bond enthalpies to estimate the enthalpies of formation of substances. We will illustrate this by calculating the standard enthalpy of formation of methanol vapour, $CH_3OH(g)$. The structural formula for methanol is:



To carry out this calculation, we set up two paths from the elements to the compound, as shown in figure 8.14. The lower path has an enthalpy change corresponding to $\Delta_f H^{\ominus}_{CH_3OH(g)}$ while the upper path takes us to the gaseous elements and then through the enthalpy change when the bonds in the molecule are formed. This latter enthalpy can be calculated from the bond enthalpies in table 8.4. As before, the sum of the enthalpy changes along the upper path must be the same as the enthalpy change along the lower path, and this allows us to determine $\Delta_f H^{\ominus}_{CH_3OH(g)}$.

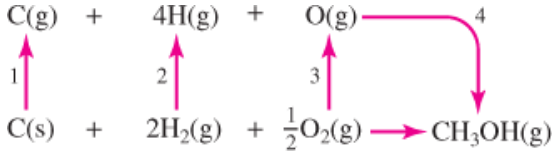


FIGURE 8.14 Two paths for the formation of methanol vapour from its elements in their standard states. The numbered steps are discussed in the text.

Steps 1, 2 and 3 in figure 8.14 involve the formation of the gaseous atoms from the elements, and their enthalpy changes are obtained from table 8.3:

$$\Delta_r H^{\ominus}_1 = \Delta_f H^{\ominus}_{C(g)} = 1 \times 716.7\ \text{kJ mol}^{-1} = 716.7\ \text{kJ mol}^{-1}$$

$$\Delta_r H^{\ominus}_2 = 4\Delta_f H^{\ominus}_{H(g)} = 4 \times 217.9\ \text{kJmol}^{-1} = 871.6\ \text{kJ mol}^{-1}$$

$$\Delta_r H^{\ominus}_3 = \Delta_f H^{\ominus}_{O(g)} = 1 \times 249.2\ \text{kJ mol}^{-1} = 249.2\ \text{kJ mol}^{-1}$$

The sum of these values, +1837.5 kJ mol^{-1}, is the net $\Delta_r H^{\ominus}$ for the first three steps.

The formation of the CH_3OH molecule from the gaseous atoms is exothermic because energy is always released when atoms become joined by covalent bonds. In this molecule, we can count three C—H bonds, one C—O bond and one O—H bond. Their formation releases energy equal to the sum of their bond enthalpies, which we obtain from table 8.4.

Bond	Bond enthalpy (kJ mol^{-1})
3(C—H)	3 × 412 = 1236
C—O	360
O—H	463

Adding these gives a total of 2059 kJ mol^{-1}. Therefore, $\Delta_r H^{\ominus}_4$ is -2059 kJ mol^{-1} because it involves bond formation, and so it is exothermic. Now we can calculate the total enthalpy change for the upper path.

$$\Delta_r H^{\ominus} = (+1837.5\ \text{kJ mol}^{-1}) + (-2059\ \text{kJ mol}^{-1})$$
$$= -222\ \text{kJ mol}^{-1}$$

The value just calculated should be equal to $\Delta_f H^{\ominus}$ for $CH_3OH(g)$. For comparison, it has been found experimentally that $\Delta_f H^{\ominus}$ for this molecule (in the vapour state) is -201 kJ mol^{-1}. At first glance, the agreement does not seem very good, but on a relative basis the calculated value (-222 kJ) differs from the experimental value by only about 10%.

Lattice Enthalpies and Hess's Law

Hess's law can be used in combination with particular thermodynamic data to calculate the values of lattice enthalpies for ionic solids. We will illustrate this using NaCl(s). Recall from chapter 5 (p. 170) that the lattice enthalpy (or, as we called it then, lattice energy) of an ionic solid is the enthalpy change for the conversion of 1 mole of the ionic solid into its constituent gaseous ions. For NaCl(s) we would represent this process by the equation:

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \quad \Delta_r H = \text{lattice enthalpy}$$

We can break this process into smaller steps, each with an associated enthalpy change, as shown in figure 8.15.

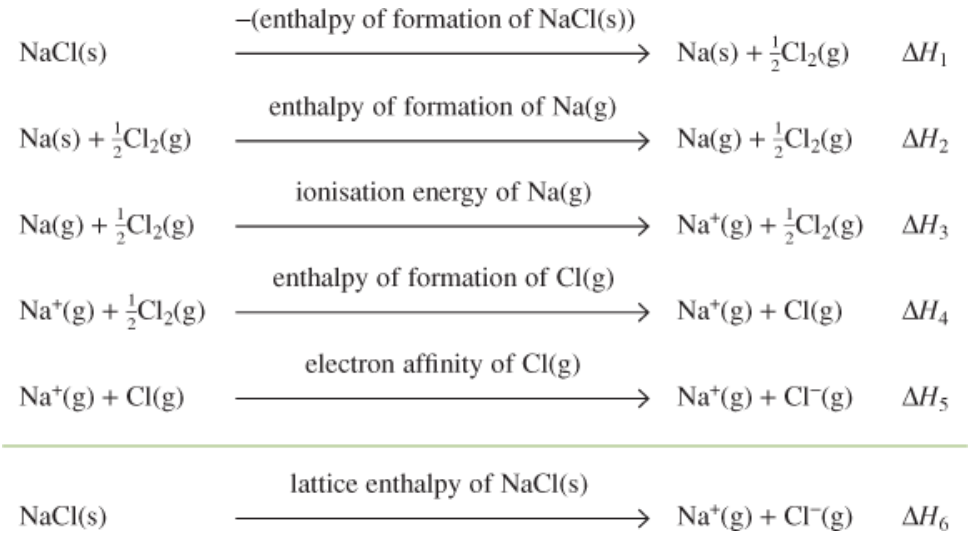


FIGURE 8.15 An enthalpy diagram that can be used to calculate the lattice enthalpy of NaCl(s). Note that the enthalpy changes are not drawn to scale.

The unknown lattice enthalpy, ΔH_6, is shown at the bottom of figure 8.15. This is an endothermic process that requires energy to turn NaCl(s) into its gaseous ions $Na^+(g)$ and $Cl^-(g)$. From Hess's law, we know that $\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$. As each of ΔH_1 to ΔH_5 is a tabulated thermodynamic quantity, we can calculate ΔH_6, the lattice enthalpy of NaCl(s). Notice that we have defined ΔH_1 as the enthalpy change for the process:

$$\mathrm{NaCl(s)} \rightarrow \mathrm{Na(s)} + \frac{1}{2}\mathrm{Cl_2(g)}$$

This is the reverse of the equation defining the enthalpy of formation of NaCl(s):

$$\mathrm{Na(s)} + \frac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{NaCl(s)}$$

so we must use the *negative* of the enthalpy of formation of NaCl(s) in our calculations.

The calculation is then:

$$\begin{aligned}\Delta H_6 &= -\Delta_f H^\ominus_{\mathrm{NaCl(g)}} + \Delta_f H^\ominus_{\mathrm{Na(g)}} + E_{\mathrm{il\ Na(g)}} + \Delta_f H^\ominus_{\mathrm{Cl(g)}} + E_{\mathrm{EA\ Cl(g)}} \\ &= 411\,\mathrm{kJ\,mol^{-1}} + 107\,\mathrm{kJ\,mol^{-1}} + 496\,\mathrm{kJ\,mol^{-1}} + 121\,\mathrm{kJ\,mol^{-1}} + \left(-349\,\mathrm{kJ\,mol^{-1}}\right) \\ &= 786\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

The lattice enthalpy of NaCl(s) is thus 786 kJ mol^{-1}.

This approach gives values close to the experimentally measured lattice enthalpies for ionic solids containing relatively small ions. As the sizes of the ions increase, the values become less accurate because the bonding in such solids is no longer purely ionic.

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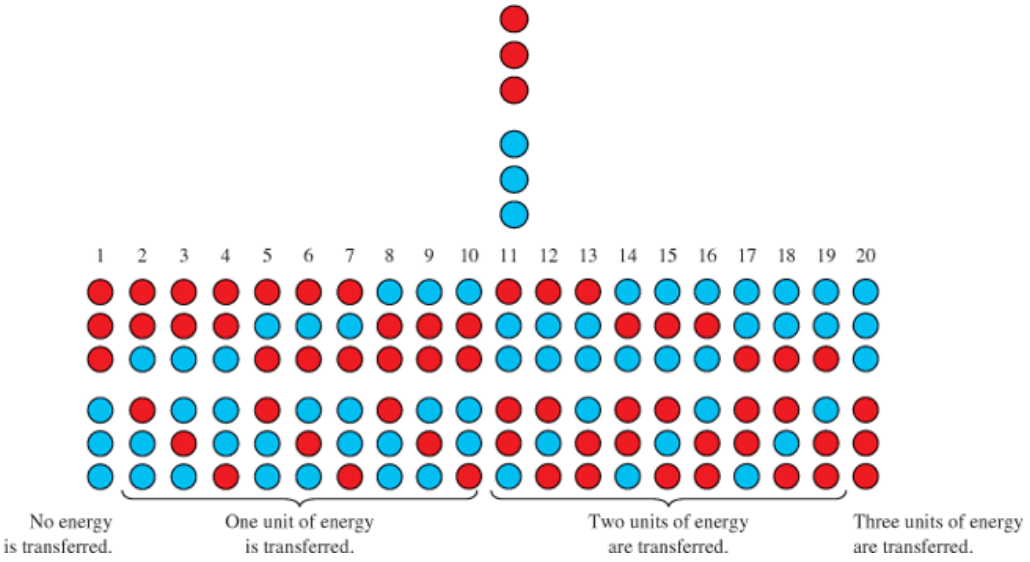
8.5 Entropy

In the previous section, we defined enthalpy, showing how it is related to heat. We will now discuss the thermodynamic function entropy. While there are many different textbook definitions of entropy, here we will concentrate on its statistical basis.

Entropy and probability

Earlier in this chapter, you learned that, when a hot object is placed in contact with a colder one, heat will flow spontaneously from the hot object to the colder one. But why? Energy will be conserved no matter what the direction of the heat flow is. And if we believe that the lowering of energy is the driving force behind spontaneous change, we might wonder why the lowering of the energy of the hot object is favoured over the gain in energy that results for the colder one.

We will build a simple model to explain the direction of heat flow. Imagine that we have two objects made of molecules that have a low-energy ground state and a high-energy excited state. They will actually have many different excited states, but we will keep things simple and assume that the molecules can be either 'low energy' in the ground state or 'high energy' in just one excited state. We will use a blue dot to represent a low-energy cold molecule, and a red dot to represent a high-energy hot molecule. If we place three high-energy molecules in contact with three low-energy molecules, we initially have a configuration like the one shown on the right. Where the three molecules on the left represent an object that is 'hot' and the three on the right represent a 'cold' object. After the objects are placed in contact, energy can be transferred between molecules in the two objects. The total energy of the two objects must be the same before and after contact. Because our molecules can have only high-energy (red) or low-energy (blue) states, the total number of red molecules must be the same before and after contact. Here are all possible distributions of energy among the six molecules after the objects have been placed into contact:



We can see four possible outcomes; 0, 1, 2 or 3 units of energy can be transferred from the hot body to the colder one. Which is most likely to occur?

Notice that some of the outcomes can be produced in a number of different ways. For example, arrangements 2 to 10 represent ways energy can be distributed among the molecules after 1 unit of energy is transferred. The more ways that a state can be produced, the more likely it is to occur. We can use this fact to estimate the probability of the state occurring. There are 20 possible arrangements of energy among the particles after the hot and cold objects are brought into contact. Let's assume that all of these arrangements are equally probable. The probability of a particular outcome can be calculated as:

$$\text{probability of an outcome} = \frac{\text{number of wayes the outcome can be produced}}{\text{total number of ways all outcomes can be produced}}$$

For example, there are nine arrangements that correspond to a transfer of 1 energy unit and 20 arrangements in all, so the probability that 1 energy unit will be transferred is 9/20 = 0.45 or 45%.

Units of energy transferred	Number of equivalent ways to produce the energy transfer	Probability of energy transfer
0	1	1/ 20 = 5%
1	9	9/ 20 = 45%
2	9	9/ 20 = 45%
3	1	1/ 20 = 5%

In this model system, there is a 19/20 or 95% chance that some amount of energy transfer will occur. This agrees with our expectation that heat should flow spontaneously from the hot object to the colder one.

To show the importance of probability in determining the direction of heat flow, consider the possible outcomes if the initial state of the system was given by arrangement 2 on the previous page, as shown on the right. Here, the hot object contains two high-energy molecules and one low-energy molecule, while the cold object contains two low-energy molecules and one high-energy molecule. If we bring the objects into contact, the final possible states are still given by arrangements 1 to 20 on the previous page. Notice though that, if the final state of the system is arrangement 1, as shown below right, then this formally involves the 'hot' object getting hotter and the 'cold' object getting colder,

something alien to our everyday experience. However, as this is only one of 20 possible final arrangements, the probability of this occurring is only 5%. If we repeat this analysis with objects that contain more and more particles, the probability of energy transfer becomes so high that we can be quite certain that heat will flow from a hot object to a colder one. If we are dealing with hot and cold objects that contain moles of particles, the chance that no energy transfer would occur once they were placed into contact is negligible.



Although our model for heat transfer is very simple, it demonstrates the role of probability in determining the direction of a spontaneous process. *Spontaneous processes tend to proceed from states of low probability to states of higher probability*. The higher probability states are those that allow more options for distributing energy among the molecules, so we can also say that *spontaneous processes tend to disperse energy*.

Entropy and entropy change

Because statistical probability is so important in determining the outcome of chemical and physical events, thermodynamics defines a quantity, called entropy (*S*), that describes the number of equivalent ways that energy can be distributed in the system. The larger the value of the entropy, the more energetically equivalent versions there are of the system and, therefore, the higher is its statistical probability. In mathematical terms:

$$S = K \ln W$$

where W is the number of ways of dispersing a fixed amount of energy in a system of fixed size, and k is the Boltzmann constant ($1.380\ 65 \times 10^{-23}$ J K^{-1}).

In chemistry, we usually deal with systems that contain very large numbers of particles. It is usually impractical to count the number of ways that the particles can be arranged to produce a system with a particular energy, as we did in our simple model for energy flow between a hot and cold object. Fortunately, we do not need to do so. The entropy of a system can be related to experimental heat and temperature measurements. We can also recognise increases and decreases in entropy without explicitly counting the number of ways the system can be realised.

Like enthalpy, entropy is a state function. It depends only on the state of the system, so a change in entropy, ΔS, is independent of the path from start to finish. As with other thermodynamic quantities, ΔS is defined as 'final minus initial' or 'products minus reactants'. Thus:

$$\Delta S = S_{\text{finial}} - S_{\text{initial}}$$

or, for a chemical reaction:

$$\Delta_r S = S_{\text{products}} - S_{\text{reactants}}$$

The units of $\Delta_r S$ are J mol^{-1} K^{-1}.

As you can see, when S_{final} is larger than S_{initial} (or when S_{products} is larger than $S_{\text{reactants}}$), the value of ΔS is positive. A positive value for ΔS

means an increase in the number of energy-equivalent ways the system can be produced; we have seen that this kind of change tends to be spontaneous (see figure 8.16). This leads to a general statement about entropy: *Any event that is accompanied by an increase in the entropy of an isolated system has a tendency to occur spontaneously.*

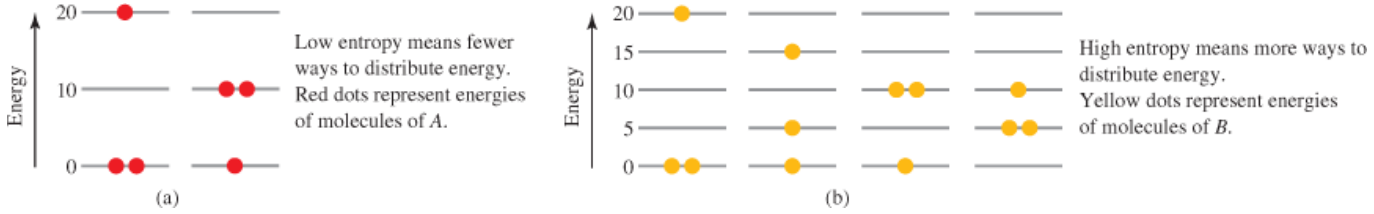


FIGURE 8.16 A positive value for $\Delta_r S$ means an increase in the number of ways energy can be distributed among a system's molecules. Consider the reaction $3A \rightarrow 3B$, where *A* molecules can take on energies that are multiples of 10 energy units, and *B* molecules can take on energies that are multiples of 5 units. Suppose that the total energy of the reacting mixture is 20 units.

(a) There are two ways to distribute 20 units of energy among three molecules of *A*.

(b) There are four ways to distribute 20 units of energy among three molecules of *B*. The entropy of *B* is higher than the entropy of *A* because there are more ways to distribute the same amount of energy in *B* than in *A*. The reaction $3A \rightarrow 3B$ is therefore spontaneous.

Factors that Affect Entropy

It is often possible to predict whether ΔS is positive or negative for a particular change. This is because several factors influence the magnitude of the entropy in predictable ways.

Volume

For gases, the entropy increases with increasing volume, as illustrated in figure 8.17. At the left we see a gas confined to one side of a container, separated from a vacuum by a removable partition. let's suppose the partition could be pulled away in an instant, as shown in figure 8.17a. Now we find a situation in which all the molecules of the gas are at one end of a larger container. There are many more possible ways that the total kinetic energy can be distributed if we give the molecules greater freedom of movement and spread them throughout the larger volume. That makes the configuration in figure 8.17b extremely unlikely. Therefore, the gas expands spontaneously to achieve a more probable (higher entropy) particle distribution (figure 8.17c).

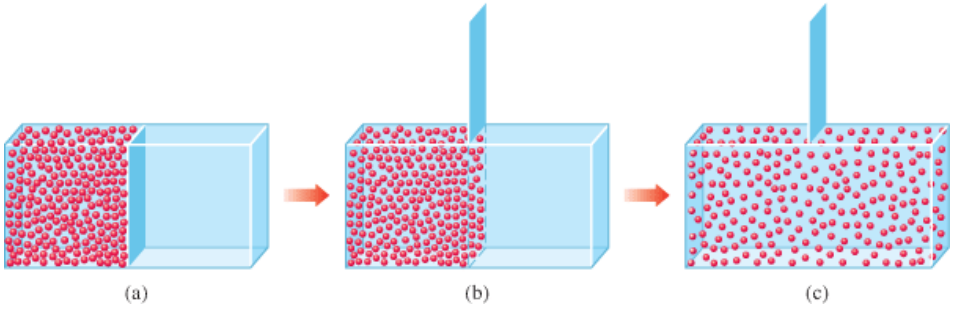


FIGURE 8.17 The expansion of a gas into a vacuum:

(a) a gas in a container separated from a vacuum by a partition and

(b) the gas at the moment the partition is removed.

(c) The gas expands to achieve a more probable (higher entropy) particle distribution.

Temperature

Entropy is affected by temperature: the higher the temperature, the higher the entropy. For example, when a substance is a solid at temperatures close to absolute zero, its particles are essentially motionless. There is relatively little kinetic energy; with few ways to distribute kinetic energy among the particles, the entropy of the solid is relatively low (figure 8.18a). If some heat is added to the solid, the kinetic energy of the particles increases along with the temperature. This causes the particles to vibrate within the crystal, so at a particular moment (figure 8.18b) the particles are not found exactly at their equilibrium lattice sites. There is more kinetic energy and more freedom of movement, so there are more ways to distribute the energy among the molecules. At a still higher temperature, there is more kinetic energy and more possible ways to distribute it, so the solid has a still higher entropy (figure 8.18c).

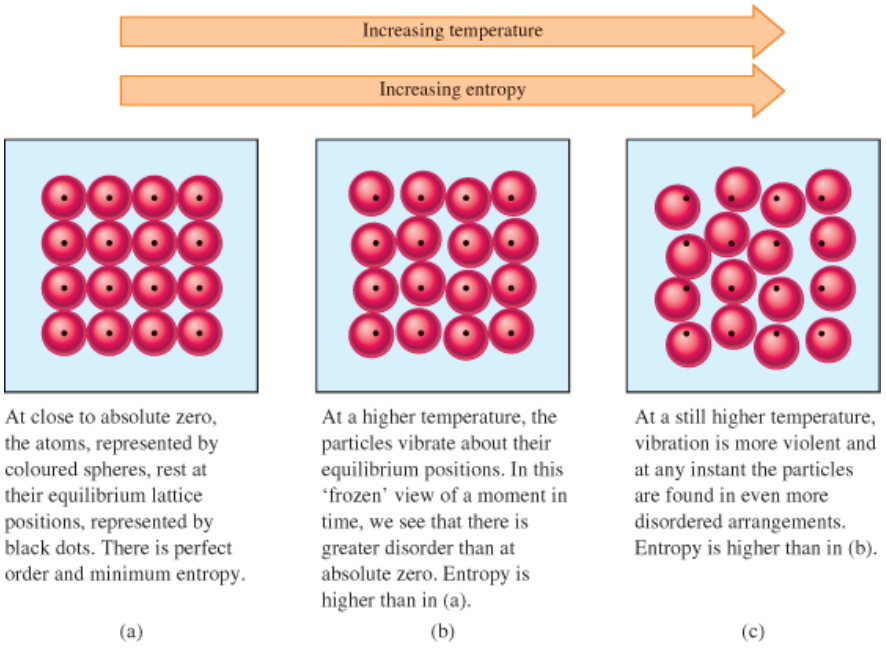


FIGURE 8.18 Variation of entropy with temperature.

Physical state

One of the major factors that affects the entropy of a system is its physical state, which is demonstrated in figure 8.19. Suppose that the contents of the three containers are ice, liquid water and water vapour at the same temperature. There is greater freedom of molecular movement in liquid water than in ice at the same temperature, and so there are more ways to distribute kinetic energy among the molecules of liquid water than there are in ice. Water vapour molecules are free to move through the entire container, so there are many more possible ways to distribute the kinetic energy among the gas molecules than there are in liquid or solid water. In fact, any gas has such a large entropy compared with a liquid or solid that changes which produce gases from liquids or solids are almost always accompanied by increases in entropy.

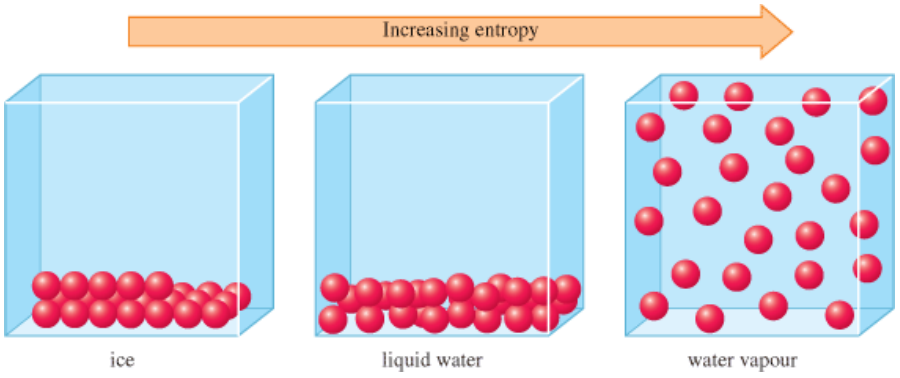


FIGURE 8.19 Comparison of the entropies of the solid, liquid, and gaseous states of water. The crystalline solid has a very low entropy. The liquid has a higher entropy because its molecules can move more freely and, therefore, there are more ways to distribute kinetic energy among them. All the molecules are still found at the bottom of the container. The gas has the highest entropy because the molecules are randomly distributed throughout the entire container, so there are many ways to distribute the kinetic energy.

For reactions that involve gases, we can simply calculate the change in the amount of gas, Δn_{gas}, on going from reactants to products.

$$\Delta n_{gas} = n_{\text{gaseous products}} - n_{\text{geseous reactants}}$$

When Δn_{gas} is positive, so is the entropy change.

When a chemical reaction produces or consumes gases, the sign of its entropy change is usually easy to predict. This is because the entropy of a gas is so much larger than that of either a liquid or solid. For example, the thermal decomposition of sodium bicarbonate produces two gases, CO_2 and H_2O:

$$2NaHCO_3(s) \xrightarrow{\text{heat}} Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Because the amount of gaseous products is larger than the amount of gaseous reactants, we can predict that the entropy change for the reaction is positive. On the other hand, the reaction:

$$CaO(s) + SO_2(g) \rightarrow CaSO_3(s)$$

which can be used to remove sulfur dioxide, an atmospheric pollutant, from a gas mixture, has a negative entropy change as $\Delta n_{gas} < 0$.

Number of particles

For chemical reactions, another major factor that affects the sign of $\Delta_r S$ is an increase in the total number of molecules as the reaction proceeds. When more molecules are produced during a reaction, more ways of distributing the energy among the molecules are possible. *When all other things are equal, reactions that increase the number of particles in the system tend to have a positive entropy change*, as shown in figure 8.20. This is particularly true when the products are gases, owing to their inherently large, positive entropies.

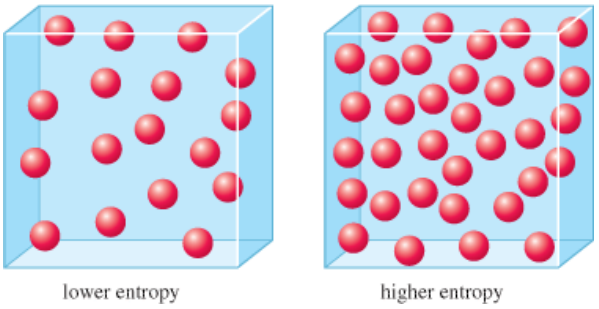


FIGURE 8.20 Entropy is affected by the number of particles. Adding particles to a system increases the number of ways that energy can be distributed in the system so, with all other things being equal, a reaction that produces more particles has a positive value of $\Delta_r S$.

WORKED EXAMPLE 8.10

Predicting the Sign of $\Delta_r S$

Predict the algebraic sign of $\Delta_r S$ for the reactions:

(a) $2NO_2(g) \rightarrow N_2O_4(g)$

(b) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

(c) $CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$

Analysis

As we examine the equations, we look for changes in the number of molecules of gas and changes in the number of particles on going from reactants to products.

Solution

In reaction (a), we are forming one N_2O_4 molecule from the two NO_2 molecules. Since we are forming fewer molecules, there are fewer ways to distribute energy among them, which means that the entropy must be decreasing. Therefore, $\Delta_r S$ must be negative.

For reaction (b), we can count the number of molecules on both sides. On the left of the equation we have six molecules; on the right there are seven. There are more ways to distribute kinetic energy among seven molecules than among six, so for reaction (b) we expect $\Delta_r S$ to be positive.

For reaction (c), there is the same number of molecules on both sides. We cannot there-fore predict the sign of $\Delta_r S$ with confidence, but we expect its magnitude to be small.

Is our answer reasonable?

We reach the same conclusion by counting the number of moles of gas on both sides of the equation. In reaction (a), 1 mole of gaseous product is formed from 2 moles of gaseous reactant. When there is a decrease in the number of moles of gas, the reaction tends to have a negative $\Delta_r S$. In reaction (b), there are 6 moles of gas on the reactant side of the equation and 7 moles of gas on the product side. Because the number of moles of gas is increasing, we expect $\Delta_r S$ to be positive.

In reaction (c), there is the same number of moles of gas on both sides, so we cannot predict the sign of $\Delta_r S$.

PRACTICE EXERCISE 8.10

Predict the sign of the entropy change for (a) the condensation of steam to liquid water and(b) the sublimation of a solid.

PRACTICE EXERCISE 8.11

Predict the sign of $\Delta_r S$ for the following reactions.

(a) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

(b) $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$

PRACTICE EXERCISE 8.12

What is the expected sign of $\Delta_r S$ for the following reactions? Justify your answers.

(a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

(b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(c) $$Ca(OH)_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2OH^-(aq)$$

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8.6 The Second Law of Thermodynamics

The **second law of thermodynamics** can help us appreciate the importance of entropy. This law states that, *whenever a spontaneous event takes place in our universe, the total entropy of the universe increases* ($\Delta S_{total} > 0$). Notice that the increase in entropy referred to here is for the total entropy of the universe (system plus surroundings), not just the system alone. This means that the entropy of a system can decrease, as long as there is a larger increase in the entropy of the surroundings so that the overall entropy change is positive. The consequence of this is that we cannot use the entropy change of the system alone as a criterion for spontaneity of a particular chemical reaction. Because everything that happens relies on spontaneous changes of some sort, the entropy of the universe is constantly rising.

Now let's examine more closely the entropy change for the universe. As we have suggested, this quantity equals the sum of the entropy change for the system plus the entropy change for the surroundings:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

It can be shown that the entropy change for the surroundings is equal to the heat transferred *to* the surroundings *from* the system, $q_{\text{surroundings}}$, divided by the thermodynamic temperature, T, at which it is transferred:

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T}$$

The law of conservation of energy requires that the heat gained by the surroundings equals the negative of the heat lost by the system, so we can write:

$$q_{\text{surroundings}} = -q_{\text{system}}$$

In our study of the first law of thermodynamics we saw that, for changes at constant temperature and pressure, $q_{\text{system}} = \Delta H$ for the system. By substitution, therefore, we arrive at the relationship:

$$\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$$

and our expression for total entropy change therefore becomes:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

Multiplying through by T gives:

$$T\Delta S_{\text{total}} = T\Delta S_{\text{system}} - \Delta H_{\text{system}}$$

or:

$$T\Delta S_{\text{total}} = -(\Delta H_{\text{system}} - T\Delta S_{\text{system}})$$

We stated above that ΔS_{total} is > 0 for a spontaneous process, and, because T is always positive, the left-hand side of this equation will be positive. To make the right-hand side of this equation positive requires that the quantity in parentheses is negative. In other words, for a spontaneous process:

$$\Delta H_{\text{system}} - T\Delta S_{\text{system}} < 0$$

We now formally define the thermodynamic function Gibbs energy (G) as:

$$G = H - TS$$

For changes at constant T and p, we can therefore write:

$$\Delta G = \Delta H - T\Delta S$$

where $\Delta G = G_{\text{final}} - G\text{initial}$

We showed on the previous page that $\Delta H_{\text{system}} - T\Delta S_{\text{system}} < 0$ for a spontaneous process. As $\Delta G = \Delta H - T\Delta S$, it follows from this that, if $\Delta G < 0$ for a chemical process in a system at constant T and p, that

process will be spontaneous. We will investigate this concept further in section 8.8.

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8.7 The Third Law of Thermodynamics

Earlier we described how the entropy of a substance depends on temperature, and we noted that at temperatures approaching absolute zero the order within a crystal increases and the entropy decreases. The **third law of thermodynamics** goes one step further by stating that, *at absolute zero, the entropy of a perfectly ordered pure crystalline substance is zero*.

$$S = 0 \quad \text{at} \quad T = 0\,\text{K}$$

Because we know the point at which entropy has a value of 0, it is possible by *experimental measurement* and calculation to determine the entropy of a substance at temperatures above 0 K. If the entropy of 1 mole of a substance is determined under standard conditions, we call it the **standard entropy** $\left(S^\circ\right)$. Table 8.5 lists the standard entropies of a number of substances at 25 °C.

TABLE 8.5 Standard Entropies of Selected Substances at 25 °C

Substance	$S^\circ\,(\text{J mol}^{-1}\text{K}^{-1})$
Ag(s)	42.55
AgCl(s)	96.2
Al(s)	28.3
$Al_2O_3(s)$	51.00
C(s, diamond)	2.4
C(s, graphite)	5.69
$CH_3Cl(g)$	234.2
$CH_3OH(l)$	126.8
$CH_3COOH(l)$	160
$CH_4(g)$	186.2
$C_2H_2(g)$	200.8
$C_2H_4(g)$	219.8
$C_2H_6(g)$	229.5
$C_2H_5OH(l)$	161
$C_8H_{18}(l)$	466.9
CO(g)	197.9
$CO_2(g)$	213.6
$CO(NH_2)_2(s)$	104.6
Ca(s)	41.4
$CaCO_3(s)$	92.9
$CaCl_2(s)$	114
CaO(s)	40
$Ca(OH)_2(s)$	76.1
$CaSO_4(s)$	107
$CaSO_4 \cdot \frac{1}{2}H_2O(s)$	131
$CaSO_4 \cdot 2H_2O(s)$	194.0
Cl(g)	223.0

$Cl_2(g)$	223.0
Fe(s)	27
$Fe_2O_3(s)$	90.0
$H_2(g)$	130.6
$H_2O(g)$	188.7
$H_2O(l)$	69.96
HCl(g)	186.7
$HNO_3(l)$	155.6
$H_2SO_4(l)$	157
Hg(l)	76.1
Hg(g)	175
K(s)	64.18
KCl(s)	82.59
$K_2SO_4(s)$	176
$N_2(g)$	191.5
$NH_3(g)$	192.5
$NH_4Cl(s)$	94.6
NO(g)	210.6
$NO_2(g)$	240.5
$N_2O(g)$	220.0
$N_2O_4(g)$	304
Na(s)	51.0
$Na_2CO_3(s)$	136
$NaHCO_3(s)$	102
NaCl(s)	72.38
NaOH(s)	64.18
$Na_2SO_4(s)$	149.4
$O_2(g)$	205.0
PbO(s)	67.8
S(s, rhombic)	31.9
$SO_2(g)$	248.5
$SO_3(g)$	256.2

Once we have the entropies of a variety of substances, we can calculate the **standard entropy of reaction** $\left(\Delta_r S^\ominus\right)$ for chemical reactions in much the same way as we calculated $\Delta_r H^\ominus$ earlier. For the reaction:

$$aA + bB \rightarrow cC + dD$$

$$\Delta_r S^\ominus = cS^\ominus_C + dS^\ominus_D - (aS^\ominus_A + bS^\ominus_B)$$

or:

$$\Delta_r S^\ominus = \sum_i^{\text{products}} \nu_i S^\ominus_i - \sum_j^{\text{reactants}} \nu_j S^\ominus_j$$

If the reaction we are working with happens to correspond to the formation of 1 mole of a compound from its elements, the $\Delta_r S^\ominus$ that we calculate can be referred to as the **standard entropy of formation $\Delta_f S^\ominus$. Values of $\Delta_r S^\ominus$** are not tabulated, however; if we need them for some purpose, we can calculate them from tabulated values of $S^\ominus$.

WORKED EXAMPLE 8.11

Calculating $\Delta_r S^\ominus$ from standard entropies

Urea (a compound found in urine) is manufactured commercially from CO_2 and NH_3. One of its uses is as a fertiliser, where it reacts slowly with water in the soil to produce ammonia and carbon dioxide:

$$\underset{\text{urea}}{CO(NH_2)_2(s)} + H_2O(l) \rightarrow CO_2(g) + 2NH_3(g)$$

The ammonia provides nitrogen for growing plants. What is the standard entropy of reaction when 1 mole of urea reacts with water at 298 K?

Analysis

We can calculate the standard entropy of reaction for the reaction using the standard entropies, $S^\ominus$, of each reactant and product. The data we need can be found in table 8.5 and are listed below.

Substance	$S^\ominus$ (J mol^{-1}K^{-1})
$CO(NH_2)_2(s)$	104.6
$H_2O(l)$	69.96
$CO_2(g)$	213.6
$NH_3(g)$	192.5

Solution

The standard entropy of reaction can be calculated from the equation:

$$\begin{aligned}
\Delta S^\ominus &= (S^\ominus_{CO_2(g)} + 2S^\ominus_{NH_3(g)}) - (S^\ominus_{CO(NH_2)_2(s)} + S^\ominus_{H_2O(l)}) \\
&= (1 \times 213.6\,\text{J mol}^{-1}\text{K}^{-1}) + (2 \times 192.5\,\text{J mol}^{-1}\text{K}^{-1}) \\
&\quad -[(1 \times 104.6\,\text{J mol}^{-1}\text{K}^{-1}) + (1 \times 69.96\,\text{J mol}^{-1}\text{K}^{-1})] \\
&= (598.6\,\text{J mol}^{-1}\text{K}^{-1}) - (174.6\,\text{J mol}^{-1}\text{K}^{-1}) \\
&= 424.0\,\text{J mol}^{-1}\text{K}^{-1}
\end{aligned}$$

Thus, the standard entropy of reaction for this reaction is +424.0 J mol^{-1} K^{-1}.

Is our answer reasonable?

In the reaction, gases are formed from liquid reactants. Since gases have much larger entropies than liquids, we expect $\Delta_r S^\ominus$ to be positive, which agrees with our answer.

PRACTICE EXERCISE 8.13

Calculate the standard entropy of reaction, $\Delta_r S^\ominus$, for each of the following reactions.

(a) $CaO(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2O(l)$

(b) $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

As there is no standard temperature, the temperature is specified as a subscript on the symbol for standard thermodynamic quantities: for example, $\Delta S^\ominus_{298k}$. As you will see later, there are times when it is desirable to indicate the temperature explicitly.

Chemical Connections

Airconditioning and the Second Law of Thermodynamics

Regardless of where you live, Queensland, Queenstown or beyond, chances are it will be either too hot or too cold inside your house at some stage of the day or night. While it is easy to heat the interior of a house using central heating or a radiant heater, cooling it presents us with a more difficult problem — somehow we need to get rid of unwanted heat, and this is diffi-cult when it's hotter outside than inside. Of course, we all know that the interior of a house can be cooled by using an airconditioner (figure 8.21), but let's stop and think about what actually happens when we do this.



FIGURE 8.21 Airconditioners use electrical energy to compress and expand a fluid that carries heat from the

inside of a building to the outside. In doing so, the airconditioner provides an entropy contribution to the system, and the overall entropy of the universe increases.

Let's assume that it's a scorching 45 °C outside while the inside temperature of our house is a tropical 35 °C. The normal direction of heat flow will be from the outside to the inside; if we were to open all the windows, the inside temperature would increase and eventually become the same as that outside, a spontaneous process precisely in accord with what we have learned in this chapter. The reverse process, heat flowing from the 35 °C interior of the house (the system) to the 45 °C exterior (the surroundings), is nonspontaneous, and we must therefore use an airconditioner to drive this. In terms of entropy, we can show, from the equation $\Delta S = \frac{\Delta H}{T}$, that adding heat to, or removing heat from, a cool system gives a greater entropy change than the analogous process with a hotter system. This means that cooling the house will lower the entropy of the inside by more than it will increase the entropy of the outside; it may therefore appear that the overall process leads to a *decrease* in entropy of the universe, violating the second law of thermodynamics. Of course, this is not the case, as we have neglected to include the airconditioner itself in this discussion. It uses electrical energy to do work by compressing and expanding a fluid that carries the heat from the inside to the outside. In so doing, the airconditioner itself provides an entropy contribution, and the sum of this and the entropy increase of the surroundings is greater than the entropy decrease of the system, thereby ensuring that the overall entropy of the universe increases and that the second law of thermodynamics remains intact.

Heat pumps operate on the same principle but in the opposite direction, taking heat from the chilly outside and delivering it to the warmer inside, and the same arguments concerning the total entropy change apply.

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8.8 Gibbs Energy and Reaction Spontaneity

Now that we have defined enthalpy and entropy, we are ready to look in detail at Gibbs energy. In section 8.2, we stated that a process is spontaneous if ΔG for the process is negative at constant temperature and pressure. We will begin by looking at the factors that determine the sign of ΔG.

The sign of ΔG

We might naively expect, as did a number of nineteenth-century scientists, that any chemical process that evolves heat will be spontaneous, as it will lead to a lowering in energy. However, we can show that this is not the case by considering the melting of ice under standard conditions at 25.0 °C, a process that is spontaneous. $\Delta H^{\ominus}$ for this process is approximately 6 kJ mol^{-1}, meaning it is endothermic. Recalling our expression for $\Delta G^{\ominus}$:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

and remembering that $\Delta G^{\ominus}$ must be negative for the process to be spontaneous, we can see that, in this case, if $\Delta H^{\ominus}$ is positive, the product of T and $\Delta S^{\ominus}$ must be *more* positive to ensure that $\Delta G^{\ominus}$ is negative. As T is always positive, $\Delta S^{\ominus}$ *must* be positive for the melting of ice to be spontaneous. (We have seen in section 8.5 that liquids generally have larger entropies than solids, so we would expect $\Delta S^{\ominus}$ for the melting of ice to be positive.) You can see from this example that the signs of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are crucial in determining the spontaneity of physical and chemical processes under standard conditions.

The combustion of octane, like all combustion reactions (p. 313), is exothermic. There is also a large increase in entropy since the number of particles in the system increases. For this change, ΔH is negative and ΔS is positive, both of which favour spontaneity:

$$\Delta \text{His negative } (-\text{ve}) .$$
$$\Delta \text{S is positive} (+\text{ve}) .$$

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ &= (-\text{ve}) - (+\text{ve}) \\ &= (-\text{ve}) \end{aligned}$$

Notice that, regardless of the thermodynamic temperature, which must have a positive value, ΔG will be negative. This means that such a change must be spontaneous at any temperature. In fact, once started, fires continue to consume all available fuel or oxygen because combustion reactions are always spontaneous (see figure 8.22a).



FIGURE 8.22 Process spontaneity can be predicted if ΔH, ΔS and T are known.

(a) When ΔH is negative and ΔS is positive, as in any combustion reaction, the reaction is spontaneous at any temperature.

(b) When ΔH is positive and ΔS is negative, the process is not spontaneous. Wood does not

spontaneously re-form from ash, carbon dioxide and water.

(c) When ΔH and ΔS have the same sign, temperature determines whether the process is spontaneous. Water spontaneously becomes ice below 0 °C, and ice spontaneously melts into liquid water above 0 °C.

When a change is endothermic and is accompanied by a lowering of the entropy, both factors work against spontaneity:

$$\Delta H \text{ is positive } (+\text{ve}).$$
$$\Delta S \text{ is negative} (-\text{ve}).$$

$$\begin{aligned} \Delta G &= \Delta H + T\Delta S \\ &= (+\text{ve}) - (-\text{ve}) \\ &= (+\text{ve}) \end{aligned}$$

Now, no matter what the temperature is, ΔG will be positive and the change must be nonspontaneous. An example would be carbon dioxide and water recombining to form wood and oxygen after a fire. If you saw such a thing happen on a film, experience would tell you that the film was being played backwards.

When ΔH and ΔS have the same algebraic sign, the temperature becomes the determining factor in controlling spontaneity. If ΔH and ΔS are both positive:

$$\begin{aligned} \Delta G &= (+\text{ve}) - (+\text{ve}) \\ &= (+\text{ve}) \text{ or } (-\text{ve}) \end{aligned}$$

ΔG is the difference between two positive quantities, ΔH and $T\Delta S$. This difference will be negative only if the term $T\Delta S$ is larger than ΔH, and this will be true only when the temperature is high. (Note: We assume that the values of ΔH and ΔS change negligibly with change in temperature.) In other words, when ΔH and ΔS are both positive, the change will be spontaneous at high temperature but not at low temperature. An example we have already seen is the melting of ice:

$$H_2O(s) \rightarrow H_2O(l)$$

This is an endothermic change that is accompanied by an increase in entropy. We know that at high temperature (above 0 °C) melting is spontaneous, but at low temperature (below 0 °C) it is not.

For similar reasons, when ΔH and ΔS are both negative, ΔG will be negative (and the change spontaneous) only at low temperature:

$$\begin{aligned} \Delta G &= (-\text{ve}) - (-\text{ve}) \\ &= (-\text{ve}) \text{ or } (+\text{ve}) \end{aligned}$$

Only when the negative value of ΔH is larger than the negative value of $T\Delta S$ will ΔG be negative. Such a change is spontaneous only at low temperature. An example is the freezing of water:

$$H_2O(l) \rightarrow H_2O(s)$$

This is an exothermic change that is accompanied by a decrease in entropy; it is spontaneous only at low temperatures (below 0 °C).

Figure 8.23 summarises the effects of the signs of ΔH and ΔS on ΔG, and hence on the spontaneity of physical and chemical events.

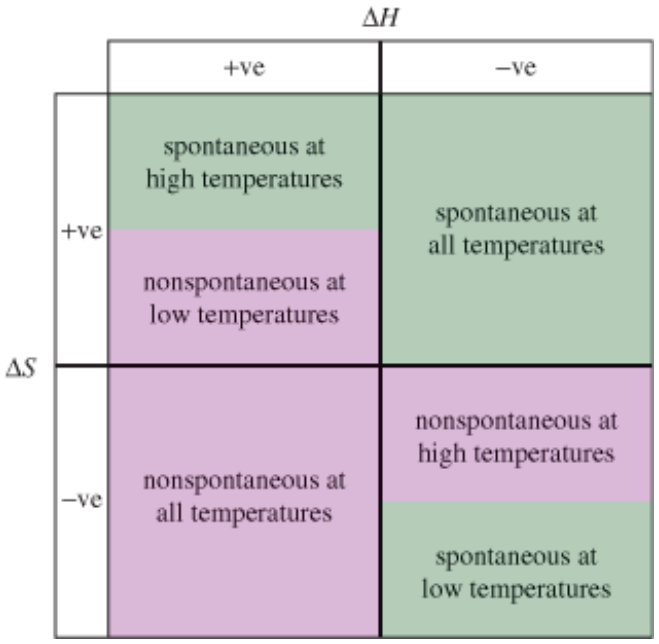


FIGURE 8.23 Summary of the effects of the signs of ΔH and ΔS on spontaneity.

Standard Gibbs Energy Change

When ΔG is determined at 10^5 Pa, we call it the **standard Gibbs energy change** $\left(\Delta G^{\ominus}\right)$. There are several ways of obtaining $\Delta_r G^{\ominus}$ for a reaction. One is to calculate $\Delta_r G^{\ominus}$ from $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$:

$$\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$$

WORKED EXAMPLE 8.12

Calculating $\Delta_r G^{\ominus}$ from $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$

Calculate $\Delta_r G^{\ominus}$ for the reaction of urea with water at 25.0 °C from values of $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ at this temperature:

$$CO(NH_2)_2(s) + H_2O(l) \rightarrow CO_2(g) + 2NH_3(g)$$

Analysis

We can calculate $\Delta_r G^{\ominus}$ using the equation:

$$\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$$

The data needed to calculate $\Delta_r H^{\ominus}$ come from table 8.2 and require a Hess's law calculation. To obtain $\Delta_r S^{\ominus}$, we would normally need to do a similar calculation with data from table 8.5. However, we already calculated this in worked example 8.11.

Solution

First we calculate $\Delta_r H^\ominus$ from data in table 8.2:

$$\begin{aligned}\Delta H^\ominus &= (\Delta_f H^\ominus_{CO_2(g)} + 2\Delta_f H^\ominus_{NH_3(g)}) - (\Delta_f H^\ominus_{CO(NH_2)_2(s)} + \Delta_f H^\ominus_{H_2O(l)}) \\ &= [1 \times (-393.5\,kJ\,mol^{-1}) + 2 \times (-46.19\,kJ\,mol^{-1})] \\ &\quad -[1 \times (-333.19\,kJ\,mol^{-1}) + 1 \times (-285.9\,kJ\,mol^{-1})] \\ &= (-485.9\,kJ\,mol^{-1}) - (-619.1\,kJ\,mol^{-1}) \\ &= +133.2\,kJ\,mol^{-1}\end{aligned}$$

In worked example 8.11, we found $\Delta_r S^\ominus$ to be +424.0 J mol^{-1} K^{-1}. To calculate $\Delta_r G^\ominus$, we also need to express 25.0 °C as a thermodynamic temperature by adding 273 K. Thus, 25.0 °C = 298 K. Also, we must be careful to express $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ in the same energy units, so we change the units of the enthalpy change to J mol^{-1} to give $\Delta_r H^\ominus = +133.2 \times 10^3$ J mol^{-1}. Substituting into the equation for $\Delta_r G^\ominus$:

$$\begin{aligned}\Delta G^\ominus &= +133.2 \times 10^3\,J\,mol^{-1} - [298K \times (+424.0 Jmol^{-1}\,K^{-1})] \\ &= +133.2 \times 10^3\,J\,mol^{-1} - 126 \times 10^3\,J\,mol^{-1} \\ &= +7.2 \times 10^3\,J\,mol^{-1} = 7.2\,kJ\,mol^{-1}\end{aligned}$$

Therefore, for this reaction, $\Delta_r G^\ominus = +7.2$ kJ mol^{-1}.

Is our answer reasonable?

There's not much we can do to check the reasonableness of the answer. We just need to be sure we've done the calculations correctly and that the units are consistent. Note that, instead of changing the units of $\Delta_r H^\ominus$ to J mol^{-1}, we could also have changed the units of $\Delta S^\ominus$ to kJ mol^{-1} K^{-1} by dividing by 10^3. The most common mistake made in calculations like this is forgetting to change the units of either $\Delta_r H^\ominus$ or $\Delta_r S^\ominus$ to ensure the units are consistent.

PRACTICE EXERCISE 8.14

Use the data in tables 8.2 and 8.5 to calculate $\Delta_r G^\ominus$ for the formation of iron(III) oxide (the iron oxide in rust). The equation for the reaction is:

$$4Fe(s) + 3O_2g \rightarrow 2Fe_2O_3(s)$$

Earlier in this chapter you learned that it is useful to have tabulated standard enthalpies of formation, $\Delta_f H^\ominus$, because they can be used with Hess's law to calculate $\Delta_r H^\ominus$ for many different reactions. Standard free energies of formation, $\Delta_r G^\ominus$, can be used in similar calculations to obtain $\Delta_r G^\ominus$. For the reaction:

$$aA + bB \rightarrow cC + dD$$

$$\Delta_r G^\ominus = c\Delta_f G^\ominus_C + d\Delta_f G^\ominus_D - (a\Delta_f G^\ominus_A + b\Delta_f G^\ominus_B)$$

or:

$$\Delta_r G^\ominus = \sum_i^{\text{products}} \nu_i \Delta_f G^\ominus_i - \sum_j^{\text{reactants}} \nu_j \Delta_f G^\ominus_j$$

The $\Delta_f G^\ominus$ values for some typical substances are found in table 8.6. Worked example 8.13 shows how we can use them to calculate $\Delta_r G^\ominus$ for a reaction.

TABLE 8.6 Standard Gibbs Energies of Formation of Selected Substances at 25 °C

Substance	$\Delta_f G^\ominus$ (kJ mol^{-1})
Ag(s)	0
AgCl(s)	-109.7
Al(s)	0
Al_2O_3(s)	-1576.4
C(s, diamond)	2.9
C(s, graphite)	0
CH_3Cl(g)	-58.6
CH_3OH(l)	-166.2
CH_3COOH(l)	-392.5
CH_4(g)	-50.79
C_2H_2(g)	+209
C_2H_4(g)	+68.12
C_2H_6(g)	-32.9
C_2H_5OH(l)	-174.8
C_8H_{18}(l)	+17.3
CO(g)	-137.3
CO_2(g)	-394.4
$CO(NH_2)_2$(s)	-197.2
Ca(s)	0
$CaCO_3$(s)	-1128.8
$CaCl_2$(s)	-750.2
CaO(s)	-604.2
$Ca(OH)_2$(s)	-896.76
$CaSO_4$(s)	-1320.3
$CaSO_4 \cdot \frac{1}{2}H_2O(s)$	-1435.2
	-1795.7

$CaSO_4 \cdot 2H_2O(s)$	
$Cl_2(g)$	0
Fe(s)	0
$Fe_2O_3(s)$	-741.0
$H_2(g)$	0
$H_2O(g)$	-228.6
$H_2O(l)$	-237.2
HCl(g)	-95.27
$HNO_3(l)$	-79.91
$H_2SO_4(l)$	-689.9
Hg(l)	0
Hg(g)	+31.8
K(s)	0
KCl(s)	-408.3
$K_2SO_4(s)$	-1316.4
$N_2(g)$	0
$NH_3(g)$	-16.7
$NH_4Cl(s)$	-203.9
NO(g)	+86.69
NO2(g)	+51.84
$N_2O(g)$	+103.6
$N_2O_4(g)$	+98.28
Na(s)	0
$Na_2CO_3(s)$	–1048
$NaHCO_3(s)$	–851.9
NaCl(s)	–384.0
NaOH(s)	–382
$Na_2SO_4(s)$	–1266.8
$O_2(g)$	0
PbO(s)	-189.3
S(s, rhombic)	0
$SO_2(g)$	-300.4
$SO_3(g)$	-370.4

WORKED EXAMPLE 8.13

Calculating $\Delta_r G^\ominus$ from $\Delta_f G^\ominus$

Ethanol, C_2H_5OH, is made from grain by fermentation and can be added to petrol to produce a product called gasohol or E10. What is $\Delta_r G^\ominus$ of the combustion of liquid ethanol to give $CO_2(g)$ and $H_2O(g)$?

Analysis We can use the equation:

$$\Delta_r G^\ominus = c\Delta_f G^\ominus_C + d\Delta_f G^\ominus_D - \left(a\Delta_f G^\ominus_A + b\Delta_f G^\ominus_B\right)$$

to calculate the standard Gibbs energy change for the reaction. We will need the standard Gibbs energy changes of formation for each reactant and product. These data can be found in table 8.6 on the next page.

Solution

First, we need the balanced equation for the reaction:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

$$\Delta_r G^\ominus = \left(2\Delta_f G^\ominus_{CO_2(g)} + 3\Delta_f G^\ominus_{H_2O(g)}\right) - \left(\Delta_f G^\ominus_{C_2H_5OH(l)} + 3\Delta_f G^\ominus_{O_2(g)}\right)$$

As with $\Delta_f H^\ominus$, $\Delta_f G^\ominus$ for any element in its standard state is 0. Therefore, using the data from table 8.6:

$$\begin{aligned}
\Delta_r G^\ominus &= [2\times -(394.4)\,\text{kJ mol}^{-1} + 3\times(-228.6)\,\text{kJ mol}^{-1}] \\
&\quad -[1\times(-174.8)\,\text{kJ mol}^{-1} + 3\times 0\,\text{kJ mol}^{-1}] \\
&= (-1474.6\,\text{kJ mol}^{-1}) - (-174.8\,\text{kJ mol}^{-1}) \\
&= -1299.8\,\text{kJ mol}^{-1}
\end{aligned}$$

The standard Gibbs energy change for the reaction is -1299.8 kJ mol^{-1}.

Is our answer reasonable?

There's no quick way to estimate the answer, although we could calculate $\Delta_r G^\ominus$ from $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ following the method used in worked example 8.12 for a thorough check. We know that ethanol is quite flammable under standard conditions, so we expect this combustion reaction to proceed spontaneously. The large negative standard Gibbs energy change makes sense.

PRACTICE EXERCISE 8.15

Calculate $\Delta_r G^\ominus$ for the following reactions using the data in table 8.6.

(a) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

(b) $Ca(OH_2)(s) + 2HCl(g) \rightarrow CaCl_2(s) + 2H_2O(g)$

Gibbs energy and work

One of the chief uses of spontaneous chemical reactions is the production of useful work. For example, fuels are burned in petrol and diesel engines to power cars and heavy machinery, and chemical reactions in batteries power everything from mobile phones to laptop computers.

When chemical reactions occur, however, their energy is not always harnessed to do work. For instance, if petrol is burned in an open dish, the energy evolved is lost entirely as heat and no useful work is accomplished. Engineers, therefore, seek ways to capture as much energy as possible in the form of work. One of their primary goals is to maximise the efficiency with which chemical energy is converted to work and to minimise the amount of energy transferred unproductively to the surroundings as heat.

The maximum conversion of chemical energy to work occurs if a reaction is carried out under conditions that are said to be thermodynamically reversible. A process is defined as thermodynamically reversible if its driving force is opposed by another force that is just slightly weaker, so that the slightest increase in the opposing force will cause the direction of the change to be reversed. An example of a nearly reversible process is illustrated in figure 8.24, where we have a compressed gas in a cylinder pushing against a piston that is held in place by liquid water above it. If a water molecule evaporates, the external pressure drops slightly and the gas can expand just a bit. Gradually, as one water molecule after another evaporates, the gas inside the cylinder slowly expands. At any time, however, the process can be reversed by the condensation of a water molecule.

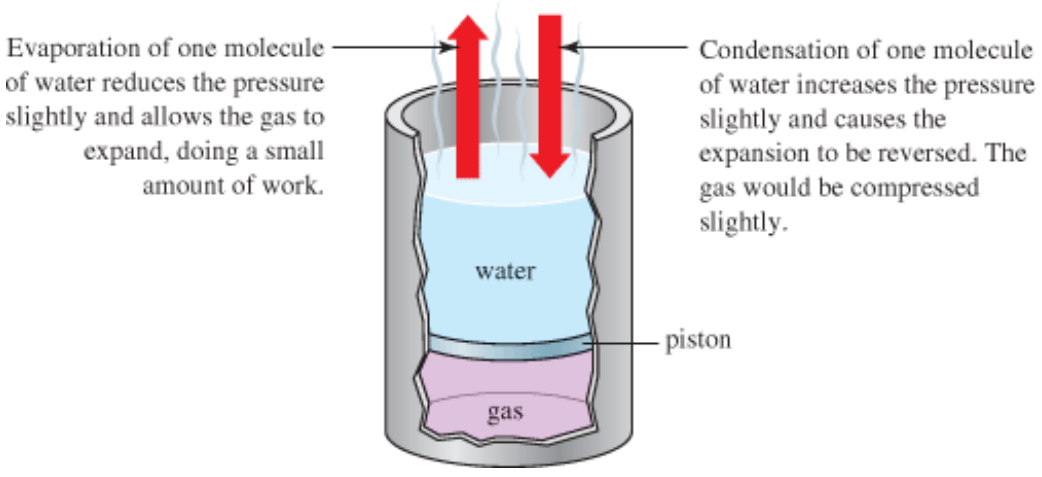


FIGURE 8.24 A reversible expansion of a gas. As water molecules evaporate one at a time, the external pressure gradually decreases and the gas slowly expands. The process would be reversed if a molecule of water were to condense into the liquid. The ability of the expansion to be reversed by the slightest increase in the opposing pressure is what makes this a reversible process.

As we will see in chapter 9, thermodynamic reversibility implies that the system is very close to equilibrium (a state in which there is no driving force for chemical or physical change) at every stage of a process. While we sometimes say that a reaction such as dissociation of a weak acid in water (chapter 11) is ‘reversible’, simply because it runs in both the forward and reverse directions, we cannot say the reaction is *thermodynamically reversible* unless the concentrations are only infinitesimally different from their equilibrium values as the reaction occurs.

Although we could obtain the maximum work by carrying out a change reversibly, a thermodynamically reversible process requires so many steps that it proceeds at an extremely slow speed. If the work cannot be done at a reasonable rate, it is of little value to us. Our goal, then, is to approach thermodynamic reversibility for maximum efficiency, but to carry out the change at a pace that will deliver work at acceptable rates.

The relationship of useful work to thermodynamic reversibility was illustrated earlier (section 8.3, p. 299) in our discussion of the discharge of a car battery. Recall that, when the battery is short-circuited with a heavy spanner, no work is done and all the energy appears as heat. In this case, there is nothing opposing the discharge, and it occurs in the most thermodynamically irreversible manner possible. However, when the current is passed through a small electric motor, the motor itself offers resistance to the passage of the electricity and the discharge takes place slowly. In this instance, the discharge occurs in a more nearly thermodynamically reversible manner because of the opposition provided by the motor, and a relatively large amount of the available energy appears in the form of work accomplished by the motor.

The preceding discussion leads naturally to the question, 'Is there a limit to the amount of the available energy in a reaction that can be harnessed as useful (i.e. non-*pV*) work?' The answer to this question is yes. The limit is the Gibbs energy for the reaction.

The maximum amount of energy produced by a reaction that can be *theoretically* harnessed as non-*pV* work is equal to $\Delta_r G$. This is the energy that need not be lost to the surroundings as heat and is, therefore, available to be used for work. Thus, by determining the value of $\Delta_r G$, we can find out whether a given reaction will be an effective source of useful energy. Also, by comparing the actual amount of non-*pV* work derived from a given system with the $\Delta_r G$ values for the reactions involved, we can measure the efficiency of the system.

WORKED EXAMPLE 8.14

Calculating Maximum non-*pV* work

Calculate the maximum non-*pV* work available from the oxidation of 1 mole of octane, $C_8H_{18}(l)$, by oxygen to give $CO_2(g)$ and $H_2O(l)$ at 25 °C and 10^5 Pa.

Analysis

The maximum non-*pV* work is equal to $\Delta_r G$ for the reaction. Standard thermodynamic conditions are specified, so we need to calculate $\Delta_r G^\ominus$.

Solution

First we need a balanced equation for the reaction. For the combustion of 1 mole of C_8H_{18} we have:

$$C_8H_{18}(l) + 12\tfrac{1}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(1)$$

$$\Delta_r G^\ominus = (8\,\Delta_f G^\ominus_{CO_2(g)} + 9\,\Delta_f G^\ominus_{H_2O(l)}) - (\Delta_f G^\ominus_{C_8H_{18}(l)} + 12\tfrac{1}{2}\,\Delta_f G^\ominus_{O_2(g)})$$

Referring to table 8.6:

$$\begin{aligned}\Delta_r G^{\ominus} &= 8 \times (-394.4\ \text{kJ mol}^{-1}) + 9 \times (-237.2\ \text{kJ mol}^{-1}) \\ &\quad -[1 \times (+17.3\ \text{kJ mol}^{-1}) + 12\tfrac{1}{2} \times 0\ \text{kJmol}^{-1}] \\ &= (-5290\ \text{kJ mol}^{-1}) - (+17.3\ \text{kJ mol}^{-1}) \\ &= -5307\ \text{kJ mol}^{-1}\end{aligned}$$

Thus, at 25 °C and 10^5 Pa, we can expect no more than 5307 kJ of non-pV work from the oxidation of 1 mole of C_8H_{18}.

Is our answer reasonable?

Be sure to check the algebraic signs of each of the terms in the calculation. This is a combustion reaction, so we would expect it to be spontaneous and hence have a negative $\Delta_r G$ value, which it does.

PRACTICE EXERCISE 8.16

Calculate the maximum non-pV work that could be obtained at 25 °C and 10^5 Pa from the oxidation of 1.00 mole of aluminium by $O_2(g)$ to give $Al_2O_3(s)$. (Aluminium was one of the components of the booster rocket that was used to launch the world's first successful scramjet flight in Australia.)

Gibbs energy and equilibrium

We have seen that, when the value of ΔG for a given change is negative, the change occurs spontaneously. We have also seen that a change is nonspontaneous when ΔG is positive. However, when ΔG is neither positive nor negative, the change is neither spontaneous nor nonspontaneous — the system is in a state of equilibrium. This occurs when ΔG is equal to 0. When a system is in a state of dynamic equilibrium at constant temperature and pressure:

$$G_{\text{products}} = G_{\text{reactants}} \text{ and } \Delta G = 0$$

Let's again consider the freezing of water at $p = 1.013 \times 10^5$ Pa:

$$H_2O(l) \rightleftharpoons H_2O(s)$$

Below 0 °C, ΔG for this change is negative and freezing is spontaneous. On the other hand, above 0 °C we find that ΔG is positive and freezing is nonspontaneous. When the temperature is exactly 0 °C, $\Delta G = 0$ and an ice–water mixture exists in a condition of equilibrium. As long as heat is not added or removed from the system, neither overall freezing nor melting is spontaneous and the ice and liquid water can exist together indefinitely. In this state of dynamic equilibrium, the rate at which liquid water freezes to give ice is exactly equal to the rate at which ice melts to give liquid water.

We have identified ΔG as a quantity that specifies the amount of non-pV work available from a system. Since $\Delta G = 0$ at equilibrium, the amount of non-pV work available is 0 also. Therefore, when a system is at equilibrium, no non-pV work can be extracted from it. As an example, we will consider again the common lead storage battery that we use to start a car.

When a battery is fully charged, there are virtually no products of the discharge reaction present. The chemical reactants, however, are present in large amounts. Therefore, the total Gibbs energy of the reactants far exceeds the total Gibbs energy of products and, since:

$$\Delta_r G = G_{\text{products}} + G_{\text{reactants}}$$

the $\Delta_r G$ of the system has a large negative value. This means that a lot of energy is available to do non-pV work. As the battery discharges, the reactants are converted to products and G_{products} gets larger while $G_{\text{reactants}}$ gets smaller; so $\Delta_r G$ becomes less negative, and less energy is available to do non-pV work. Finally, the battery reaches equilibrium. The total free energies of the reactants and the products have become equal, so:

$$G_{\text{products}} - G_{\text{reactants}} = 0 \text{ and } \Delta_r G = 0$$

No further non-pV work can be extracted and we say the battery is flat.

When we have equilibrium in any system, we know that $\Delta G = 0$. For a phase change such as $H_2O(1) \rightarrow H_2O(s)$, equilibrium can be established only at one particular temperature at atmospheric pressure. In this instance, that temperature is 0 °C. Above 0 °C, only liquid water can exist, and below 0 °C all the liquid will freeze to give ice. This yields an interesting relationship between ΔH and ΔS that applies not only to phase changes but also to chemical reactions. Since $\Delta G = 0$:

$$\Delta G = 0 = \Delta H - T\Delta S$$

Therefore:

$$\Delta H = T\Delta S$$

and

$$\Delta S = \frac{\Delta H}{T}$$

Thus, if we know ΔH for a chemical reaction or phase change and the temperature at which equilibrium is established, we can calculate ΔS. We can also rearrange the above equation to give:

$$T = \frac{\Delta H}{\Delta S}$$

Thus, if we know ΔH and ΔS, we can calculate the temperature at which equilibrium will be established.

WORKED EXAMPLE 8.15

Calculating the Equilibrium Temperature for a Phase Change

For the phase change $Br_2(l) \rightarrow Br_2(g)$, $\Delta H^{\ominus} = +30.9$ kJ mol^{-1} and $\Delta S^{\ominus} = 93.2$ J mol^{-1} K^{-1} at 25 °C. Assuming that ΔH and ΔS are temperature independent, calculate the approximate temperature at which $Br_2(l)$ will be in equilibrium with $Br_2(g)$ at 10^5 Pa (i.e. the normal boiling point of liquid Br_2).

Analysis

The temperature at which equilibrium exists is given by:

$$T = \frac{\Delta H}{\Delta S}$$

We are working under standard conditions (10^5 Pa), so we can use $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ in this equation. That is:

$$T = \frac{\Delta H^\ominus}{\Delta S^\ominus}$$

Solution

Substituting the data given in the problem:

$$\begin{aligned} T &= \frac{30.9 \times 10^3 \text{ J mol}^{-1}}{93.2 \text{ J mol}^{-1} \text{ K}^{-1}} \\ &= 332 \text{ K} \\ &= (332 - 273)^\circ\text{C} = 59 \,^\circ\text{C} \end{aligned}$$

Notice that we must express $\Delta H^\ominus$ in J mol^{-1}, not kJ mol^{-1}, so the units cancel correctly. It is also interesting that the boiling point we calculate is quite close to the measured normal boiling point of 58.8 °C.

Is our answer reasonable?

$\Delta H^\ominus$ equals 30 900 and $\Delta S^\ominus$ equals approximately 100, which means the temperature should be about 310 K. Our value, 332 K, is not far from that, so the answer is reasonable.

PRACTICE EXERCISE 8.17

The enthalpy of vaporisation of mercury is 60.7 kJ mol^{-1}. For Hg(l), $S^\ominus_{298\text{ K}} = 76.1$ J mol^{-1} K^{-1}; for Hg(g), $S^\ominus_{298\text{ K}} = 175$ J mol^{-1} K^{-1}.

Estimate the normal boiling point of liquid mercury.

We can also use the equation $T = \frac{\Delta H}{\Delta S}$ to determine the temperature at which a nonspontaneous reaction first becomes spontaneous. To illustrate this, consider the decomposition of calcium carbonate at 25 °C, which occurs according to the equation:

$$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

Using the $\Delta_f H^\ominus$ and $S^\ominus$ data in tables 8.2 and 8.5, or the $\Delta_f G^\ominus$ data in table 8.6, we can calculate that $\Delta G^\ominus$ = 130 kJ mol^{-1} for this reaction at 25 °C. Therefore, the reaction is nonspontaneous at this temperature. However, we showed on p. 327 that the spontaneity of reactions with positive ΔH and ΔS values depends on the temperature, and that such reactions are generally spontaneous at high temperature. We can substitute the values of $\Delta_r H^\ominus = +178$ kJ mol^{-1} and $\Delta S^\ominus = 160.7$ J mol^{-1} K^{-1} for this reaction into the equation:

$$\begin{aligned} T &= \frac{\Delta_r H^\ominus}{\Delta_r S^\ominus} \\ &= \frac{178 \times 10^3 \text{ J mol}^{-1}}{160.7 \text{ J mol}^{-1} \text{ K}^{-1}} \\ &= 1.11 \times 10^3 \text{ K} \end{aligned}$$

This shows that the system will be in equilibrium at 1110 K under standard conditions (assuming that $\Delta_r H^\ominus$

and $\Delta_r S^{\ominus}$ are independent of temperature) and will be spontaneous at any temperature greater than this. We summarise this in figure 8.25.

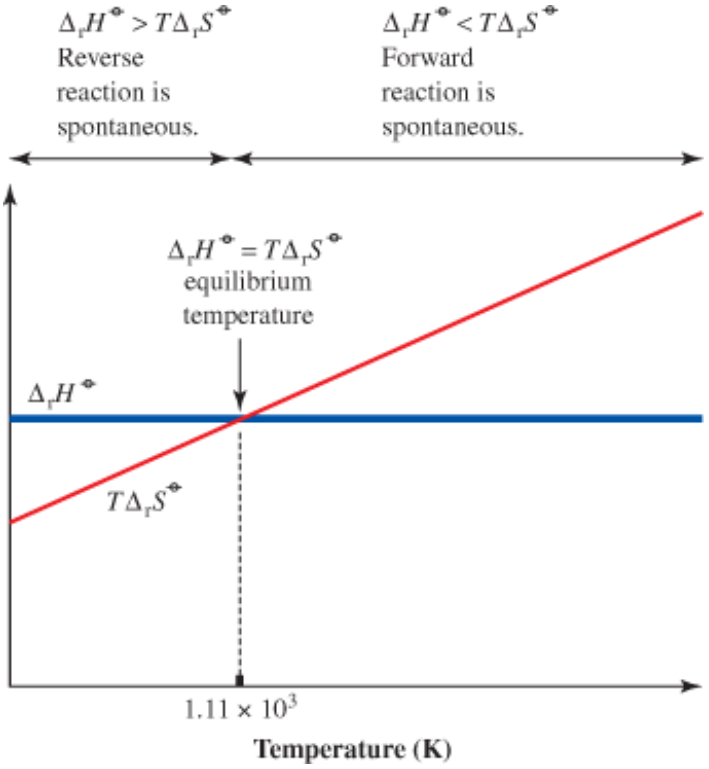


FIGURE 8.25 Diagram showing the relative values of $\Delta_r H^{\ominus}$ and $T\Delta_r S^{\ominus}$ for the decomposition of calcium carbonate. At low temperatures, $\Delta_r H^{\ominus}$ (blue line) is greater than $T\Delta_r S^{\ominus}$ (red line). This means that $\Delta_r G^{\ominus}$ will be positive under these conditions and the reaction will be nonspontaneous. As the temperature increases, the value of $T\Delta_r S^{\ominus}$ increases and eventually, at $T = 1.11 \times 10^3$ K, $\Delta_r H^{\ominus} = T\Delta_r S^{\ominus}$ and the system is at equilibrium. At any temperature greater than 1.11×10^3 K, $\Delta_r H^{\ominus}$ is less than $T\Delta_r S^{\ominus}$. Under these conditions, $\Delta_r G^{\ominus}$ will be negative and the decomposition reaction will be spontaneous.

In this chapter, we have shown that ΔG can be used as the criterion for spontaneity of a chemical reaction or phase change. Furthermore, we have shown that the sign of ΔG depends on the signs of both ΔH and ΔS and that, when $\Delta G = 0$, there is no driving force for chemical or physical change and the system is at equilibrium. We will investigate chemical equilibrium in more detail in the next chapter, and we will see how the value of $\Delta_r G$ measured under standard conditions, $\Delta G^{\ominus}$, is related to the extent of reaction.

Chemistry Research

The Thermodynamics of Crystallisation — the Role in Biology

Professor Kathryn McGrath, Victoria University of Wellington

We often take for granted many things that the biological world sets up and makes avail-able to us: the ability to stand upright; the ability to chew our food; the fact that eggs and seafood come in the tidy package of a shell and that butterflies have intricately and beautifully coloured wings.

Organisms build bones, teeth, shells and other such structures by initiating and controlling the crystallisation of inorganic materials, such as calcium carbonate and silica. This process is known

as biomineralisation. These organisms use specific molecules, such as proteins and carbohydrates to manipulate the crystallisation environment, enabling precise control over the formation of biominerals; these molecules also become an integral component of the final materials.

At the foundation of crystallisation is thermodynamics, which allows us to understand both the initial formation of the seed crystal and its subsequent growth into the final material. A seed crystal will form only if the reaction conditions are energetically favourable: that is, if the Gibbs energy of nucleation is negative. As with all chemical processes, a negative Gibbs energy means that the crystallisation process will be spontaneous. If ΔG is positive, the material will remain in solution and no seed crystal will form.

Once the seed crystal has formed, thermodynamics makes it possible to precisely control the synthesis of the material. For example, let's look at electron micrographs of two very different crystals of calcium carbonate.

Both electron micrographs represent the thermodynamic product of the crystallisation process between calcium ions and carbonate ions. The crystal shown in figure 8.26 was grown in a laboratory with no subsequent intervention. The crystals shown in figure 8.27 were grown by a sea urchin that manipulated the crystallisation thermodynamics at every stage (see figure 8.27). The precisely patterned material (see figure 8.28) made by the sea urchin is several times stronger than the material made in the laboratory. It is also much more resistant to fracture.

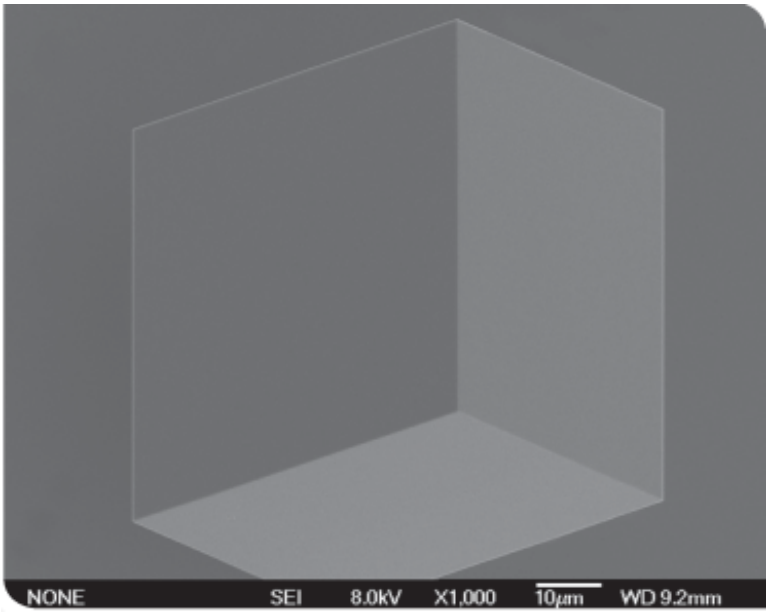


FIGURE 8.26 Electron micrograph image of calcium carbonate grown in a crystallisation dish in a laboratory.

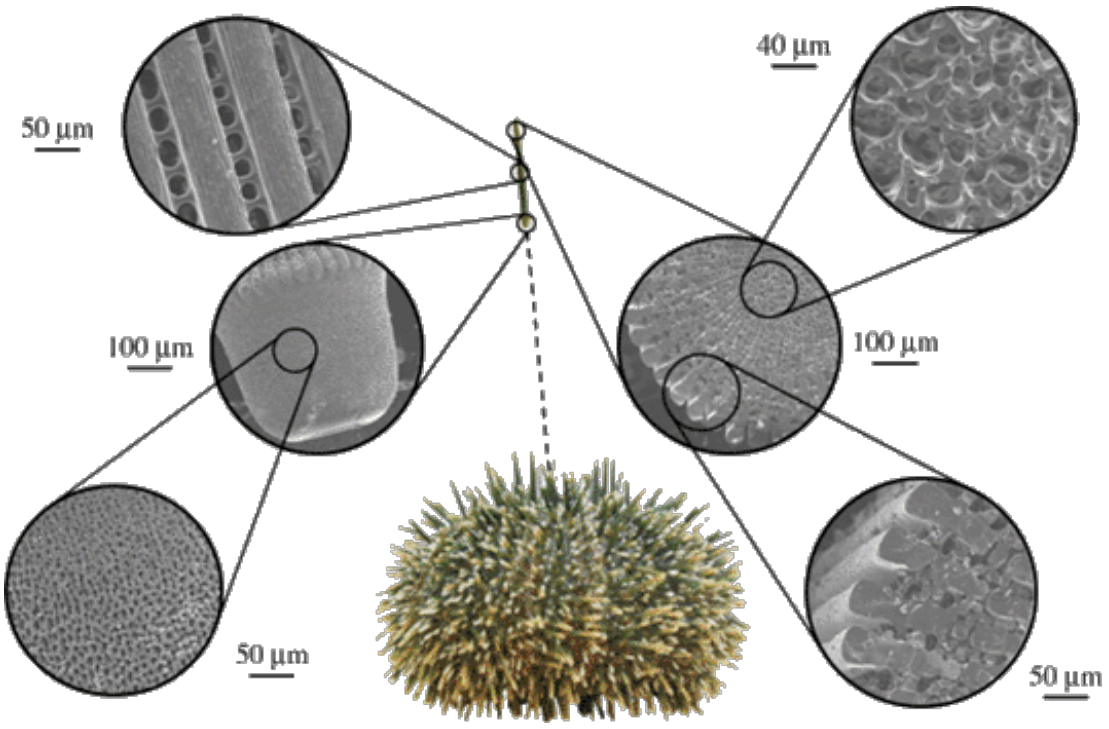


FIGURE 8.27 Electron micrographs at various resolutions of different parts of a sea urchin spine, which is composed of calcium carbonate.

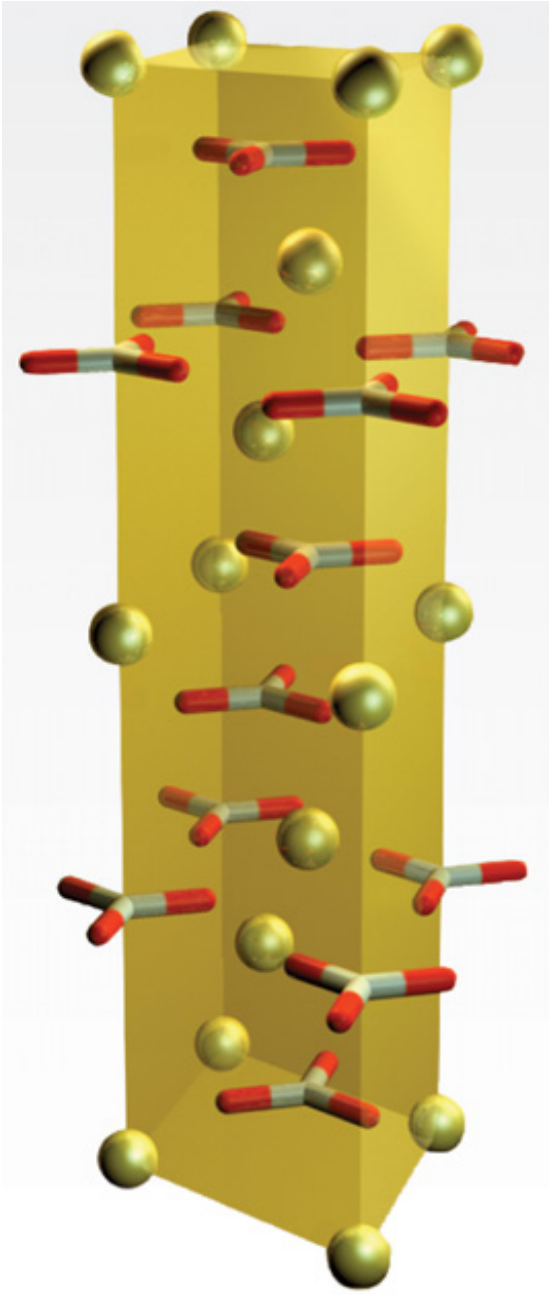


FIGURE 8.28 Crystal structure of calcite, i.e. the form of calcium carbonate grown both in the laboratory and by sea urchins. The spheres represent calcium ions while the red-tipped triangular species represent carbonate ions (the red ends are oxygen atoms and the grey central parts are carbon atoms).

Victoria University of Wellington is studying biomineralisation in the sea urchin *Evechinus chloroticus* to develop a better understanding of the factors that allow an organism to control the thermodynamics of crystallisation. To understand this control, we need to know what is controlling the sign of ΔG. Underlying the Gibbs energy of the crystallisation process are the enthalpy of crystallisation, H, and the entropy of crystallisation, S. For formation of calcium carbonate, $CaCO_3(s)$, ΔS is negative as it changes from a solution state to a solid state. This means that an increase in temperature will result in the formation of fewer crystals and eventual cessation of crystallisation, since the influence of the entropy on the total Gibbs energy is via the term $-T\Delta S$.

Thus, for crystallisation to occur, the enthalpy of crystallisation must be negative. Energy is released as the constituent molecules or ions come together to form the crystal (i.e. the process is exothermic). Hence, manipulation of the growing crystal occurs through the organism's ability to locally manipulate both ΔS and ΔH, which it does with the help of kinetics (see chapter 15).

So what's the point of all this?

Growing hard spines that resist frac-turing is, of course, very important from the sea urchin's perspective, but the study of biomin eralisation isn't just about trying to understand how a sea urchin grows its skeleton, or that $\Delta G = \Delta H - T\Delta S$! It is much more about what we can do once we understand the different control factors that the organism uses. Imagine being able to trigger the body to grow a new tooth when it loses one — no more mushy food in our older years. Or being able to make optical filters (photonic crystals) that can be triggered to change the exact wavelengths being filtered. Or generating a material that has all the incredible chemical features of a high-temperature semiconductor, but that is strong, lightweight, mouldable and durable because of its specifically designed three-dimensional structure, rather than being the dense, brittle material we currently have to work with. Finely tuned manipulation of crystallisation — crystal engineering or crystal tectonics, as it is known — that can make materials with specific chemical and physical characteristics lies open and achievable, but first you have to understand thermodynamics!

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SUMMARY

Introduction to Chemical Thermodynamics

A spontaneous change occurs without outside assistance, whereas a nonspontaneous change requires continuous help and can occur only if it is accompanied by, and linked to, some other spontaneous event.

The science of chemical thermodynamics allows us to predict both the direction and extent of spontaneous chemical and physical change under particular conditions.

Thermodynamic Definitions

We call the object we are interested in the ‘system’, which is enclosed by a ‘boundary’. Everything else in the ‘universe’ is the system's ‘surroundings’.

Chemical thermodynamics uses the SI unit of energy, work and heat, the joule (J) or the kilojoule (kJ). Many thermodynamic equations require the temperature to be expressed in kelvin.

Gibbs energy, G, is defined by the equation $G = H - TS$, where H is the enthalpy of the system, S is the entropy of the system and T is the thermodynamic temperature. We use ΔG to symbolise the change in Gibbs energy that occurs when a chemical system changes from one state to another due to a reaction or physical change at constant temperature and pressure. The value of ΔG allows us to determine whether a particular chemical reaction or physical change is spontaneous and how far it will proceed towards completion.

The First Law of Thermodynamics

The internal energy of a system, U, is the sum of its molecular kinetic and potential energies. It is an extensive property, and the change in internal energy, ΔU, for a chemical process is given by the equation:

$$\Delta_r U = U_{\text{products}} - U_{\text{reactants}}$$

The value of the state function, internal energy, depends only on the current condition or state of the system. Temperature is an intensive property that determines the direction of spontaneous heat flow. Heat, q, is a transfer of energy from an object at a high temperature to one at a lower temperature and can be determined by measuring temperature changes, ΔT, using the equation:

$$q = C \Delta T$$

where C is the heat capacity of the system: that is, the heat needed to change the temperature of the system by 1 kelvin. The specific heat (c) of a pure substance is defined as:

$$c = \frac{C}{m}$$

Heat capacity is specific heat multiplied by mass. Heat capacity calculated on a per mole basis is called molar heat capacity. When the mass and specific heat of an object are known, heat can be calculated using the equation:

$$q = cm \Delta T$$

Heats of reaction are measured at constant volume or at constant pressure. When a gas evolves and pushes against the atmosphere or causes a piston to move in a cylinder, pressure–volume work is being done. When the volume change, ΔV, occurs at constant opposing pressure, p, the associated pressure–volume work is given by $w = -p\Delta V$. The energy expended in doing this pressure–volume work causes heats of reaction measured at constant volume, q_v, to differ numerically from heats measured at constant pressure, q_p.

The first law of thermodynamics states that:

$$\Delta U = q + w$$

The algebraic signs for q and w are negative when the system gives heat to or does work on the surroundings. The signs are positive when the system absorbs heat or receives work energy done to it. When a system has rigid walls, no pressure–volume work can be done to or by the atmosphere so $\Delta U = q_v$. Values of q_v are deter-mined using a bomb calorimeter.

Enthalpy

When a system is under constant pressure (e.g. open to the atmosphere), pressure–volume work is possible and a new thermodynamic property called enthalpy, H, can be defined:

$$H = U + pV$$

Like U, absolute values of H cannot be easily measured or calculated, but a difference in enthalpy between reactants and products can be determined. The heat of reaction is now called the enthalpy change, ΔH. Under constant pressure:

$$\Delta H = \Delta U + p\,\Delta V = q_p$$

While ΔH is a state function, its value differs from that of ΔU by the work involved in interacting with the atmosphere when the change occurs at constant atmospheric pressure. In general, the difference between ΔU and ΔH is quite small.

Exothermic reactions have negative values of $\Delta_r H$; endothermic changes have positive values. A balanced chemical equation that includes both the enthalpy change and the physical states of the substances is called a thermochemical equation. These can be added, reversed (reversing also the sign of the enthalpy change) or multiplied by a constant multiplier (doing the same to the enthalpy change). If substances are cancelled or added, they must be in identical physical states.

Thermochemical equations can be added because enthalpy is a state function. Values of $\Delta_r H^\ominus$ can be determined by the manipulation of any combination of thermochemical equations that add up to the final net equation.

Standard conditions refer to 10^5 Pa and an enthalpy change measured under these conditions at the specified temperature T is called the standard enthalpy of reaction, $\Delta_r H^\ominus$. The value of $\Delta_r H^\ominus$ is a function of the amounts of substances involved in the reaction. If the amount of reactants is doubled, the standard enthalpy of the reaction doubles. There is no standard temperature, but thermodynamic data are often tabulated at 25 °C.

The enthalpy change for the formation of 1 mole of a substance under standard conditions from its elements in their standard states is called the standard enthalpy of formation, $\Delta_f H^\ominus$, and it is generally given in units of kilojoules per mole (kJ mol^{-1}). Hess's law of heat summation is possible because enthalpy is a state function. The value of $\Delta_r H^\ominus$ for a reaction can be calculated as the sum of the $\Delta_f H^\ominus$ values of the products minus the sum of the $\Delta_f H^\ominus$ values of the reactants, each multiplied by the corresponding stoichiometric coefficient in the equation.

The enthalpy change for the complete combustion of 1 mole of a pure substance under standard conditions is called the standard enthalpy of combustion, $\Delta_c H^\ominus$.

The bond enthalpy is the enthalpy change on breaking 1 mole of a particular chemical bond to give electrically neutral fragments. The sum of all the bond enthalpies in a molecule is the atomisation

enthalpy, $\Delta_{at}H$, and, on a mole basis, it corresponds to the energy needed to break 1 mole of molecules into individual atoms.

Entropy

Spontaneity is associated with statistical probability; spontaneous processes tend to proceed from lower probability to higher probability states. The thermodynamic quantity associated with the probability of a state is entropy, *S*. Entropy is a measure of the number of energetically equivalent ways a state can be realised.

The Second Law of Thermodynamics

The second law of thermodynamics states that the entropy of the universe increases whenever a spontaneous change occurs.

In general, gases have much higher entropies than liquids, which have somewhat higher entropies than solids. Entropy increases with volume for a gas and with the temperature. During a chemical reaction, the entropy tends to increase if the number of molecules increases on going from reactants to products.

The Third Law of Thermodynamics

The third law of thermodynamics states that the entropy of a pure crystalline substance is equal to 0 at absolute zero (0 K). Because we know where the zero point is on the entropy scale, it is possible to measure absolute entropies. Standard entropies, $S^{\ominus}$, are calculated at 10^5 Pa (table 8.5) and can be used to calculate $\Delta S^{\ominus}$ for chemical reactions.

Gibbs Energy and Reaction Spontaneity

Gibbs energy is defined as $G = H - TS$. A chemical or physical change at constant temperature and pressure is spontaneous only if the Gibbs energy of the system decreases (ΔG is negative). When ΔH and ΔS have the same algebraic sign, the temperature becomes the critical factor in determining spontaneity.

When ΔG is measured at 10^5 Pa, it is the standard Gibbs energy change, $\Delta G^{\ominus}$. As with enthalpy changes, the standard Gibbs energies of formation, $\Delta_f G^{\ominus}$, (table 8.6) can be used to obtain $\Delta_r G^{\ominus}$ for chemical reactions by a Hess's law type of calculation.

For any system, the value of ΔG is equal to the maximum amount of energy that can be obtained in the form of useful *non-pV* work. This maximum work can be obtained only if the change takes place reversibly. All real changes are irreversible and we always obtain less work than is theoretically available; the rest is lost as heat.

When a system reaches equilibrium, $\Delta G = 0$ and no useful work can be obtained from it. At any particular pressure, an equilibrium between two phases of a substance (e.g. liquid–solid or solid–vapour) can occur at only one temperature. The entropy change can be calculated as $\Delta S = \frac{\Delta H}{T}$. The temperature at which the equilibrium occurs can be calculated from $T = \frac{\Delta H}{\Delta S}$.

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KEY CONCEPTS AND EQUATIONS

Heat capacity and specific heat *(section 8.3)*

The equation:

$$q = C\,\Delta T$$

(q = heat, C = heat capacity, ΔT = temperature change) can be used to calculate the heat of a reaction. Specific heat (c) is defined as:

$$c = C / m$$

Thermochemical equations *(section 8.4)*

We can use thermochemical equations for one set of reactions to write a thermochemical equation for some net reaction.

Hess's law *(section 8.4)*

Hess's law states that the overall enthalpy change for a reaction is the same regardless of how it is carried out. This enables us to use standard enthalpies of formation to calculate the enthalpy of a reaction.

$\Delta_f H^\ominus$ and $S^\ominus$ *(sections 8.4, 8.7)*

Standard enthalpies of formation and standard entropies can be used to calculate, respectively, $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ for a reaction.

ΔG as a predictor of spontaneity *(section 8.8)*

If $\Delta_r G$ for a reaction is negative, the reaction is spontaneous under the defined conditions.

Calculating $\Delta G^\ominus$ from $\Delta H^\ominus$ and $\Delta S^\ominus$ *(section 8.8)*

$\Delta G^\ominus$ values can be calculated from values of $\Delta H^\ominus$, $\Delta S^\ominus$ and T through the equation:

$$\Delta G^\ominus = \Delta H^\ominus - T\,\Delta S^\ominus$$

Using $\Delta_f G^\ominus$ values *(section 8.8)*

Standard Gibbs energy of formation values can be used to calculate $\Delta_r G^\ominus$ for a reaction.

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REVIEW QUESTIONS

Introduction to chemical thermodynamics

8.1 What is the origin of the name ‘thermodynamics’?

Thermodynamic definitions

8.2 What is the name of the thermal property that can have values with each of the following units?

(a) $J\ g^{-1}\ K^{-1}$

(b) $J\ mol^{-1}\ K^{-1}$

(c) $J\ K^{-1}$

8.3 What is the difference between an isolated system and a closed system?

8.4 What is a state function? Give two examples.

The first law of thermodynamics

8.5 Which kind of substance needs more energy to undergo an increase of 5 °C, something with a high or a low specific heat? Explain.

8.6 How do heat capacity and specific heat differ?

8.7 Which kind of substance experiences the larger increase in temperature when it absorbs 100 J, something with a high or a low specific heat?

8.8 If the specific heat values in table 8.1 were in units of $kJ\ kg^{-1}\ K^{-1}$, would the values be numerically different? Explain.

8.9 If an amount of heat, q, is applied to an object, and its temperature changes by ΔT, how much heat must be applied to change the temperature by $10\Delta T$?

8.10 What two pieces of information are necessary to determine the heat capacity of an object? What additional piece of information is necessary to determine its specific heat?

8.11 Suppose object A has twice the specific heat and twice the mass of object B. If the same amount of heat is applied to both objects, how will the temperature change of A be related to the temperature change in B?

8.12 Write the equation that states the first law of thermodynamics. What does this statement mean in terms of energy exchanges between a system and its surroundings?

8.13 If a system containing gases expands and pushes back a piston against a constant opposing pressure, what equation describes the work done on the system?

8.14 What kinds of energy contribute to the internal energy of a system?

8.15 How is a change in the internal energy defined in terms of the initial and final internal energies?

8.16 State the first law of thermodynamics in words. What equation defines the change in the internal energy in terms of heat and work? Define the meaning of the symbols, including the significance of their algebraic signs.

8.17 Which quantities in the statement of the first law of thermodynamics are state functions and which are not?

8.18 What are the units of $p\Delta V$ if pressure is expressed in pascals and volume is expressed in cubic metres?

8.19 How are $\Delta_r U$ and $\Delta_r H$ related to each other?

8.20 When are $\Delta_r U$ and $\Delta_r H$ numerically equal to each other?

8.21 If a system does 45 J of work and receives 28 J of heat, what is the value of ΔU for this change?

8.22 If a system absorbs 48 J of heat and does 22 J of work, what is the value of ΔU for this change?

Enthalpy

8.23 How is enthalpy defined?

8.24 What equation defines ΔH in general terms? How is this expressed when the system involves a chemical reaction? In general, why are chemists and biologists more interested in values of ΔH than ΔU?

8.25 What is the sign of ΔH for an exothermic change?

8.26 What distinguishes a thermochemical equation from an ordinary chemical equation?

8.27 In a thermochemical equation, what do the coefficients represent in terms of the amounts of the reactants and products?

8.28 Why are fractional coefficients permitted in a balanced thermochemical equation? If a thermochemical equation has a coefficient of $\frac{1}{2}$ for a formula, what does it signify?

8.29 What fundamental fact about ΔH makes Hess's law possible?

8.30 What two conditions must be met by a thermochemical equation so that its standard enthalpy change can be given the symbol $\Delta_f H^\ominus$?

8.31 What is Hess's law expressed in terms of standard enthalpies of formation?

8.32 Write Hess's law in terms of standard enthalpies of combustion.

Entropy

8.33 What is entropy?

8.34 Will the entropy change for each of the following be positive or negative?

(a) Moisture condenses on the outside of a cold glass.

(b) Raindrops form in a cloud.

(c) Air is pumped into a tyre.

(d) Frost forms on the windscreen of your car.

(e) Sugar dissolves in coffee.

8.35 On the basis of our definition of entropy, suggest why entropy is a state function.

8.36 How can you estimate the probability of a state of the system?

The second law of thermodynamics

8.37 State the second law of thermodynamics.

8.38 In animated cartoons, visual effects are often created (for amusement) that show events that ordinarily don't occur in real life because they are accompanied by huge entropy decreases. Can you think of an example of this? Explain why there is an entropy decrease in your example.

8.39 How can a process have a negative entropy change for the system and still be spontaneous?

The third law of thermodynamics

8.40 What is the third law of thermodynamics?

8.41 Would you expect the entropy of an alloy (a solution of two metals) to be 0 at 0 K? Explain your answer.

8.42 Why does entropy increase with increasing temperature?

8.43 Does $S = 0$ at 0 K for glass? Explain.

Gibbs energy and reaction spontaneity

8.44 What is a spontaneous change?

8.45 List five changes that you have encountered recently that occurred spontaneously. List five changes that are nonspontaneous that you have caused to occur.

8.46 How do the probabilities of the initial and final states in a process affect the spontaneity of the process?

8.47 An instant cold pack purchased in a pharmacy contains a packet of solid ammonium nitrate, NH_4NO_3, surrounded by a pouch of water. When the packet of NH_4NO_3 is broken, the solid dissolves in water and the mixture cools because the solution process for NH_4NO_3 in water is endothermic. Explain, in terms of what happens to the molecules and ions, why this mixing occurs spontaneously.

8.48 What is the equation expressing the change in the Gibbs energy for a reaction occurring at constant temperature and pressure?

8.49 For each of the following conditions, state in terms of the algebraic signs of ΔH and ΔS the circumstances under which a change will be spontaneous.

(a) at all temperatures

(b) at low temperatures but not at high temperatures

(c) at high temperatures but not at low temperatures

8.50 Under what circumstances will a change be nonspontaneous regardless of the temperature?

8.51 Is it possible to run a combustion reaction in reverse, so that fuel and oxygen are produced from carbon dioxide and water?

8.52 How is Gibbs energy related to useful work?

8.53 What is a thermodynamically reversible process? How is the amount of work obtained from a change related to thermodynamic reversibility?

8.54 How is the rate at which energy is withdrawn from a system related to the amount of that energy that can appear as useful work?

8.55 Why are real, observable changes not considered to be thermodynamically reversible processes?

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REVIEW PROBLEMS

8.56 A certain system absorbs 300 J of heat and has 700 J of work done on it. What is the value of ΔU for the change? Is the overall change exothermic or endothermic?

8.57 The value of ΔU for a certain change is -1455 J. During the change, the system absorbs 812 J of heat. Did the system do work, or was work done on the system? How much work, expressed in joules, was involved?

8.58 How much heat must be removed from 175 g of water to lower its temperature from 25.0 °C to 15.0 °C?

8.59 How much heat is needed to bring 1.0 kg of water from 25 °C to 99 °C (comparable to making four cups of coffee)?

8.60 How much heat is needed to increase the temperature of 15.0 g of Fe from 20.0 °C to 40.0 °C?

8.61 If 250 J is added to 30.0 g of copper, initially at 22 °C, what is its final temperature?

8.62 A 5.00 g mass of a metal was heated to 100 °C and then plunged into 100 g of water at 24.0 °C. The temperature of the resulting mixture was 28.0 °C.

(a) How much heat did the water absorb?

(b) How much heat did the metal lose?

(c) What is the heat capacity of the metal sample?

(d) What is the specific heat of the metal?

8.63 A sample of copper was heated to 120 °C and then plunged into 200 g of water at 25.00 °C. The final temperature of the mixture was 26.50 °C.

(a) How much heat was absorbed by the water?

(b) How much heat was lost by the copper sample?

(c) What was the mass of the copper sample?

8.64 Calculate the molar heat capacity of iron. (The specific heat of iron is 0.4498 J g^{-1} K^{-1}.)

8.65 A vat of 4.54 kg of water underwent a decrease in temperature from 60.25 °C to 58.65 °C. How much energy left the water? (For this range of temperatures, use the value of 4.18 J g^{-1} K^{-1} for the specific heat of water.)

8.66 A container filled with 2.46 kg of water underwent a temperature change from 25.24 °C to 27.31 °C. How much heat did the water absorb?

8.67 Nitric acid, HNO_3, reacts with potassium hydroxide, KOH, as follows:

$$HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$$

A student poured 55.0 mL of 1.3 M HNO_3 into a coffee cup calorimeter, noted that the temperature was 23.5 °C and added 55.0 mL of 1.3 M KOH, also at 23.5 °C. The mixture was stirred quickly with a thermometer, and its temperature rose to 31.8 °C. Calculate the enthalpy of reaction. Assume that the specific heats of all solutions are 4.18 J g^{-1} K^{-1} and that all densities are 1.00 g mL^{-1}. Calculate the enthalpy of reaction per mole of acid.

8.68 A dilute solution of hydrochloric acid with a mass of 610.29 g and containing 0.331 83 mol of HCl was exactly neutralised in a calorimeter by the sodium hydroxide in 615.31 g of a comparably dilute solution. The temperature increased from 16.784 °C to 20.610 °C. The specific heat of the HCl solution was 4.031 J g^{-1} K^{-1} and that of the NaOH solution was 4.046 J g^{-1} K^{-1}. The heat capacity of the calorimeter was 77.99 J K^{-1}. Use this information to calculate the enthalpy change for the following reaction:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

What is the enthalpy of neutralisation per mole of HCl? Assume that the original solutions made independent contributions to the total heat capacity of the system following their mixing.

8.69 A 0.100 mol sample of propane, a gas used for cooking in many rural areas, was placed in a constant pressure with excess oxygen and ignited. The reaction was:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

The initial temperature of the calorimeter was 25.000 °C and its total heat capacity was 97.1 kJ K^{-1}. The reaction raised the temperature of the calorimeter to 27.282 °C.

(a) How much heat was liberated in this reaction?

(b) What is the enthalpy of reaction of propane with oxygen?

8.70 Toluene, C_7H_8, is used in the manufacture of explosives such as TNT (trinitrotoluene). A 1.500 g sample of liquid toluene was placed in a bomb calorimeter along with excess oxygen. When the combustion of the toluene was initiated, the temperature of the calorimeter rose from 25.000 °C to 26.413 °C. The products of the combustion were $CO_2(g)$ and $H_2O(l)$, and the heat capacity of the calorimeter was 45.06 kJ K^{-1}. The reaction was:

$CO_2(g)$ and $H_2O(l)$, and the heat capacity of the calorimeter was 45.06 kJ K^{-1}. The reaction was:

$$C_7H_8(l) + 9O_2(g) \rightarrow 7CO_2(g) + 4H_2O(l)$$

(a) How much heat was liberated by the reaction?

(b) How much heat would be liberated under similar conditions if 1.00 mol of toluene was burned?

8.71 One thermochemical equation for the reaction of carbon monoxide with oxygen is:

$$3CO(g) + \frac{3}{2}O_2(g) \rightarrow 3CO_2(g) \quad \Delta_r H^{\ominus} = -849\,kJ\,mol^{-1}$$

(a) Write the thermochemical equation for the reaction using 2 mol of CO.

(b) (b) What is $\Delta_r H^{\ominus}$ for the formation of 1 mol of CO_2 by this reaction?

8.72 Ammonia reacts with oxygen as follows:

$$4NH_3(g) + 7O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(g) \quad \Delta_r H^{\ominus} = -1132\,kJ\,mol^{-1}$$

(a) Calculate the enthalpy change for the combustion of 1 mol of NH_3.

(b) Write the thermochemical equation for the reaction in which 1 mol of H_2O is formed.

8.73 Aluminium and iron(III) oxide, Fe_2O_3, react to form aluminium oxide, Al_2O_3, and iron. For each mole of aluminium used, 426.9 kJ of energy is released under standard conditions. Write the thermochemical equation that shows the consumption of 4 mol of Al. (All of the substances are solids.)

8.74 Liquid benzene, C_6H_6, burns in oxygen to give carbon dioxide gas and liquid water (when all products are returned to 25 °C and 10^5 Pa). The combustion of 1.00 mol of benzene liberates 3271 kJ. Write the thermochemical equation for the combustion of 3.00 mol of liquid benzene.

8.75 Magnesium burns in air to produce a bright light and is often used in fireworks displays. The combustion of magnesium follows the thermochemical equation:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s) \quad \Delta_r H^{\ominus} = -1203\,kJ\,mol^{-1}$$

How much heat is liberated by the combustion of 6.54 g of magnesium?

8.76 Methanol is the fuel in 'canned heat' containers that are used to heat foods at cocktail parties. The combustion of methanol follows the thermochemical equation:

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l) \quad \Delta_r H^{\ominus} = -1199\,kJ\,mol^{-1}$$

What is the enthalpy change for the combustion of 46.0 g of methanol?

8.77 Show how the equations:

$$N_2O_4(g) \rightarrow 2NO_2(g) \quad \Delta_r H^{\ominus} = +57.93\,kJ\,mol^{-1}$$

$$2NO_2(g) + O_2(g) \rightarrow 2NO_2(g) \quad \Delta_r H^{\ominus} = -113.14\,kJ\,mol^{-1}$$

can be manipulated to give $\Delta_r H^{\ominus}$ for the following reaction:

$$2NO(g) + O_2(g) \rightarrow N_2O_4(g)$$

8.78 We can generate hydrogen chloride by heating a mixture of sulfuric acid and potassium chloride according to the equation:

$$2KCl(s) + H_2SO_4(l) \rightarrow 2HCl(g) + K_2SO_4(s)$$

Calculate $\Delta_r H^{\ominus}$ for this reaction from the following thermochemical equations:

$$HCl(g) + KOH(s) \rightarrow KCl(s) + H_2O(l) \quad \Delta_r H^{\ominus} = -203.6\,kJ\,mol^{-1}$$

$$H_2SO_4(1) + 2KOH(s) \rightarrow K_2SO_4(s) + 2H_2O(l) \quad \Delta_r H^{\ominus} = -342.4\,kJ\,mol^{-1}$$

8.79 Calculate $\Delta_r H^{\ominus}$ for the following reaction, the preparation of nitrous acid, HNO_2, which is unstable:

$$HCl(g) + NaNO_2(s) \rightarrow HNO_2(1) + NaCl(s)$$

Use the following thermochemical equations:

$$2NaCl(s) + H_2O(1) \rightarrow 2HCl(g) + Na_2O(s) \quad \Delta_r H^{\ominus} = +507.31\,kJ\,mol^{-1}$$

$$NO(g) + NO_2(g) + Na_2O(s) \rightarrow 2NaNO_2(s) \quad \Delta_r H^\ominus = -427.14\,kJ\,mol^{-1}$$

$$NO(g) + NO_2(g) \rightarrow N_2O_{(g)} + O_2(g) \quad \Delta_r H^\ominus = -42.68\,kJ\,mol^{-1}$$

$$2HNO_2(l) \rightarrow N_2O(g) + O_2(g) + H_2O(l) \quad \Delta_r H^\ominus = +34.35\,kJ\,mol^{-1}$$

8.80 Barium oxide reacts with sulfuric acid as follows:

$$BaO(s) + H_2SO_4(l) \rightarrow BaSO_4(s) + H_2O(l)$$

Calculate $\Delta_r H^\ominus$ for this reaction. The following thermochemical equations can be used:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l) \quad \Delta_r H^\ominus = -78.2\,kJ\,mol^{-1}$$

$$BaO(s) + SO_3(g) \rightarrow BaSO_4(s) \quad \Delta_r H^\ominus = -213\,kJ\,mol^{-1}$$

8.81 Copper metal can be obtained by heating copper oxide, CuO, in the presence of carbon monoxide, CO, according to the following reaction:

$$CuO(s) + CO(g) \rightarrow Cu(s) + CO_2(g)$$

Calculate $\Delta_r H^\ominus$ using the following thermochemical equations:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \quad \Delta_r H^\ominus = -566.1\,kJ\,mol^{-1}$$

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s) \quad \Delta_r H^\ominus = -310.5\,kJ\,mol^{-1}$$

8.82 Calcium hydroxide reacts with hydrochloric acid according to the following equation:

$$Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$$

Calculate $\Delta_r H^\ominus$ in kilojoules for this reaction, using the following equations as needed:

$$CaO(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) \quad \Delta_r H^\ominus = -186\,kJ\,mol^{-1}$$

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s) \quad \Delta_r H^\ominus = -65.1\,kJ\,mol^{-1}$$

$$Ca(OH)_2(s) \rightarrow Ca(OH)_2(aq) \quad \Delta_r H^\ominus = -12.6\,kJ\,mol^{-1}$$

8.83 Given the following thermochemical equations:

$$CaO(s) + Cl_2(g) \rightarrow Ca(OCl)Cl(s) \quad \Delta_r H^\ominus = -110.9\,kJ\,mol^{-1}$$

$$H_2O(l) + Ca(OCl)Cl(s) + 2NaBr(s) \rightarrow 2NaCl(s) + Ca(OH)_2(s) + Br_2(l) \quad \Delta_r H^\ominus = -60.2\,kJ\,mol^{-1}$$

$$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(l) \quad \Delta_r H^\ominus = +65.1\,kJ\,mol^{-1}$$

calculate the value of $\Delta_r H^\ominus$ for the reaction:

$$\frac{1}{2}Cl_2(g) + NaBr(s) \rightarrow NaCl(s) + \frac{1}{2}Br_2(l)$$

8.84 Given the following thermochemical equations:

$$2Cu(s) + S(s) \rightarrow Cu_2S(s) \quad \Delta_r H^\ominus = -79.5\,kJ\,mol^{-1}$$

$$S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta_r H^\ominus = -297\,kJ\,mol^{-1}$$

$$Cu_2S(s) + 2O_2(g) \rightarrow 2CuO(s) + SO_2(g) \quad \Delta_r H^\ominus = -527.5\,kJ\,mol^{-1}$$

calculate the standard enthalpy of formation of CuO(s).

8.85 Given the following thermochemical equations:

$$4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g) \quad \Delta_r H^\ominus = -1132\,kJ\,mol^{-1}$$

$$6NO_2(g) + 8NH_3(g) \rightarrow 7N_2(g) + 12H_2O(g) \quad \Delta_r H^\ominus = -2740\,kJ\,mol^{-1}$$

calculate the value of $\Delta_r H^\ominus$ for the reaction:

$$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$$

8.86 Given the following thermochemical equations:

8.86 Given the following thermochemical equations:

$$3Mg(s) + 2NH_3(g) \rightarrow Mg_3N_2(s) + 3H_2(g) \quad \Delta_r H^\ominus = -371 kJ\,mol^{-1}$$
$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g) \quad \Delta_r H^\ominus = -46 kJ\,mol^{-1}$$

calculate $\Delta_r H^\ominus$ for the reaction:

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

8.87 Use the following thermochemical equations to calculate the standard enthalpy of formation of $Mg(NO_3)_2(s)$.

$$8Mg(s) + Mg(NO_3)_2(s) \rightarrow Mg_3N_2(s) + 6MgO(s) \quad \Delta_r H^\ominus = -3884\ kJ\,mol^{-1}$$
$$Mg_3N_2(s) \rightarrow 3Mg(s) + N_2(g) \quad \Delta_r H^\ominus = +463\ kJ\,mol^{-1}$$
$$2MgO(s) \rightarrow 2Mg(s) + O_2(g) \quad \Delta_r H^\ominus = +1203\ kJ\,mol^{-1}$$

8.88 Given the following thermochemical equations:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta_r H^\ominus = -571.5\ kJ\,mol^{-1}$$
$$N_2O_5(g) + H_2O(l) \rightarrow 2HNO_3(l) \quad \Delta_r H^\ominus = -76.6\ kJ\,mol^{-1}$$
$$\frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) + \frac{1}{2}H_2(g) \rightarrow HNO_3(l) \quad \Delta_r H^\ominus = -174\ kJ\,mol^{-1}$$

calculate $\Delta_r H^\ominus$ for the reaction:

$$2N_2(g) + 5O_2(g) \rightarrow 2N_2O_5(g)$$

8.89 Which of the following equations has a value of $\Delta_r H^\ominus$ that would properly be labelled as $\Delta_f H^\ominus$?

(a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(b) $Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s)$

(c) $2Cu(s) + O_2(g) \rightarrow 2CuO(s)$

(d) $2Fe(s) + O_2(g) \rightarrow 2FeO(s)$

(e) $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$

(f) $N_2(g) + \frac{5}{2}O_2(g) \rightarrow N_2O_5(g)$

8.90 Write the thermochemical equations, including values of $\Delta_f H^\ominus$ (from table 8.2), for the formation of each of the following compounds from their elements, with all substances in their standard states.

(a) $CH_3COOH(l)$, acetic acid

(b) $NaHCO_3(s)$, sodium bicarbonate

(c) $CaSO_4 \cdot 2H_2O(s)$, gypsum

(d) $CO(NH_2)_2(s)$, urea

(e) $CaSO_4 \cdot \frac{1}{2}H_2O(s)$, plaster of Paris

(f) $CH_3OH(l)$, methanol

8.91 Using the data in table 8.2, calculate $\Delta_r H^\ominus$ in kilojoules for each of the following reactions.

(a) $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

(b) $HCl(g) + NaOH(s) \rightarrow NaCl(s) + H_2O(l)$

(c) $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

(d) $2NH_3(g) + CO_2(g) \rightarrow CO(NH_2)_2(s) + H_2O(l)$

8.92 Write the thermochemical equations that would be associated with the standard enthalpy of formation of each of the following compounds.

(a) $HCl(g)$

(b) $NH_4Cl(s)$

(c) $CH_3COOH(l)$

(d) $Na_2CO_3(s)$

8.93 Sucrose, $C_{12}H_{22}O_{11}$, has a $\Delta_c H^\ominus$ value of -5.65 × 10^3 kJ mol^{-1}. The sole products of the combustion of sucrose are $CO_2(g)$ and $H_2O(l)$. Write the thermochemical equation for the combustion of 1 mol of sucrose and calculate the value of $\Delta_f H^\ominus$ for this compound.

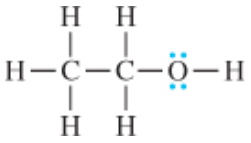
8.94 The thermochemical equation for the combustion of ethyne (acetylene) gas, $C_2H_2(g)$, is:

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l) \quad \Delta_r H^\ominus = -2599.3 \text{kJ mol}^{-1}$$

Using the data in table 8.2, determine the value of $\Delta_f H^\ominus$ for ethyne (acetylene) gas.

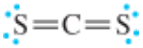
8.95 Use the data in table 8.4 to calculate the approximate atomisation enthalpy of NH_3.

8.96 The standard enthalpy of formation of ethanol vapour, $C_2H_5OH(g)$, is –235.3 kJ mol^{-1}. Use the data in table 8.3 and the average bond enthalpies for C—C, C—H and O — H bonds to estimate the C—O bond enthalpy in this molecule. The structure of the molecule is:



8.97 The standard enthalpy of formation of ethene, $C_2H_4(g)$, is +52.284 kJ mol^{-1}. Calculate the C═C bond enthalpy in this molecule.

8.98 Carbon disulfide, CS_2, has the Lewis structure:



For $CS_2(g)$, $\Delta_f H^\ominus = +115.3$ kJ mol^{-1}. Use the data in table 8.3 to calculate the average C═S bond enthalpy in this molecule.

8.99 Gaseous hydrogen sulfide, $H_2S(g)$, has $\Delta_f H^\ominus = -20.15$ KJ mol^{1}. Use the data in table 8.3 to calculate the average S —H bond enthalpy in this molecule.

8.100 For $SF_6(g)$, $\Delta_f H^\ominus = -1209$ kJ mol^{-1}. Use the data in table 8.3 to calculate the average S—F bond enthalpy in this molecule.

8.101 Use the results of question 8.100 and the data in table 8.2 to calculate the standard enthalpy of formation of $SF_4(g)$. The measured value of $\Delta_f H^\ominus$ for $SF_4(g)$ is –718.4 kJ mol^{-1}. What is the percentage difference between your calculated value of $\Delta_f H^\ominus$ and the experimentally determined value?

8.102 Use the data in tables 8.3 and 8.4 to estimate the standard enthalpy of formation of ethyne (acetylene), H—C≡C—H, in the gaseous state.

8.103 Calculate the approximate enthalpy of formation of CCl_4 vapour at 25 °C and 10^5 Pa.

8.104 Which substance should have the more exothermic enthalpy of formation, CF_4 or CCl_4?

8.105 Would you expect the value of $\Delta_f H^\ominus$ for benzene, C_6H_6, calculated from tabulated bond enthalpies, to be very close to the experimentally measured value of $\Delta_r H^\ominus$? Justify your answer.

8.106 Use the data from table 8.2 to calculate $\Delta_r H^\ominus$ for each of the following reactions.

(a) $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$

(b) $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$

(c) $3CaO(s) + 2Fe(s) \rightarrow 3Ca(s) + Fe_2O_3(s)$

(d) $Ca(OH)_2(s) \rightarrow CaO(s) + H\,O(l)$

(e) $2NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + 2HCl(g)$

(f) $2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$

(g) $C_2H_2(g) + 5N_2O(g) \rightarrow 2CO_2(g) + H_2O(s)\ 5N_2(g)$

(h) $Fe_2O_3(s) \rightarrow 2Al(s) \rightarrow Al_2O_3(s) + Fe(s)$

(i) $NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$

(j) $Ag(s) + KCl(s) \rightarrow AgCl(s) + (K(s)$

8.107 Predict the algebraic sign of the entropy change for each of the following reactions.

(a) $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$

(b) $SO_2(g) + CaO(s) \rightarrow CaSO_3(s)$

(c) $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$

(d) $Ni(s) + 2HCl(aq) \rightarrow H_2(g) + NiCl_2(aq)$

(e) $I_2(s) \rightarrow I_2(g)$

(f) $Br_2(g) + 3Cl_2(g) \rightarrow 2BrCl_3(g)$

(g) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

(h) $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$

8.108 Calculate $\Delta_r S^\ominus$ for each of the following reactions from the data in table 8.5.

(a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(b) $CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$

(c) $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$

(d) $Ca(OH)_2(s) + H_2SO_4(l) \rightarrow CaSO_4(s) + 2H_2O(l)$

(e) $S(s) + 2N_2O(g) \rightarrow SO_2(g) + 2N_2(g)$

(f) $Ag(s) + \frac{1}{2}Cl_2(g) \rightarrow AgCl(s)$

(g) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$

(h) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(1)$

(i) $CaCO_3(s) + H_2SO_4(l) \rightarrow CaSO_4(s) + H_2O(g) + CO_2(g)$

(j) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

8.109 Calculate $\Delta_f S^\ominus$ for each of the following compounds.

(a) $C_2H_4(g)$

(b) $N_2O(g)$

(c) $NaCl(s)$

(d) $CH_3COOH(l)$

(e) $CaSO_4 \cdot 2H_2O(s)$

(f) $Al_2O_3(s)$

(g) $CaCO_3(s)$

(h) $N_2O_4(g)$

(i) $CaSO_4 \cdot \frac{1}{2}H_2O(s)$

(j) $NH_4Cl(s)$

8.110 Nitrogen dioxide, NO_2, an air pollutant, dissolves in rainwater to form a dilute solution of nitric acid. The equation for the reaction is:

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$$

Calculate $\Delta_r S^\ominus$ for this reaction.

8.111 Good wine will turn to vinegar if it is left exposed to air because the alcohol is oxidised to acetic acid. The equation for the reaction is:

$$C_2H_5OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(l)$$

Calculate $\Delta_r S^{\ominus}$ for this reaction.

8.112 Aluminium oxidises rather easily but forms a thin, protective coating of Al_2O_3 that prevents further oxidation of the aluminium beneath. Use the data for $\Delta_f H^{\ominus}$ (table 8.2) and $S^{\ominus}$ to calculate $\Delta_f G^{\ominus}$ for $Al_2O_3(s)$.

8.113 Calculate $\Delta_r G^{\ominus}$ for each of the following reactions, using the data in table 8.6.

(a) $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

(b) $2NH_4Cl(s) + CaO(s) \rightarrow CaCl_2(s) + H_2O(l) + 2NH_3(g)$

(c) $CaSO_4(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2SO_2(l)$

(d) $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(l)$

(e) $Ca(s) + 2H_2SO_4(l) \rightarrow CaSO_4(s) + SO_2(g) + 2H_2O(l)$

(f) $2HCl(g) + CaO(s) \rightarrow CaCl_2 + H_2O(g)$

(g) $H_2SO_4(l) + 2NaCl(s) \rightarrow 2HCl(g) + Na_2SO_4(s)$

(h) $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(l) + NO(g)$

(i) $2AgCl(s) + Ca(s) \rightarrow CaCl_2(s) + 2Ag(s)$

(j) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

8.114 Plaster of Paris, $CaSO_4 \cdot \frac{1}{2}H_2O(s)$, reacts with liquid water to form gypsum, $CaSO_4 \cdot 2H_2O(s)$. Write a chemical equation for the reaction and calculate $\Delta_r G^{\ominus}$, using the data in table 8.6.

8.115 Given the following information:

$$4NO(g) \rightarrow 2N_2O(g) + O_2(g) \quad \Delta_r G^{\ominus} = -139.56\ \text{kJ mol}^{-1}$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \quad \Delta_r G^{\ominus} = -69.70\ \text{kJ mol}^{-1}$$

Calculate $\Delta_r G^{\ominus}$ for this reaction.

$$2N_2O(g) + 3O_2(g) \rightarrow 4NO_2(g)$$

8.116 Given these reactions and their $\Delta_r G^{\ominus}$ values:

$$COCl_2(g) + 4NH_3(g) \rightarrow CO(NH_2)_2(s) + 2NH_4Cl(s) \quad \Delta_r G^{\ominus} = -332.0\ \text{kJ mol}^{-1}$$

$$COCl_2(g) + H_2O(l) \rightarrow CO_2(g) + 2HCl(g) \quad \Delta_r G^{\ominus} = -141.8\ \text{kJ mol}^{-1}$$

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) \quad \Delta_r G^{\ominus} = -91.96\ \text{kJ mol}^{-1}$$

calculate the value of $\Delta_r G^{\ominus}$ for the reaction:

$$CO(NH_2)_2(s) + H_2O(s) \rightarrow CO_2(g) + 2NH_3(g)$$

8.117 Gasohol or E10 is a mixture of petrol and ethanol, C_2H_5OH. Calculate the maximum work that could be obtained at 25 °C and 10^5 Pa by burning 1 mol of C_2H_5OH:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

8.118 What is the maximum amount of useful work that could theoretically be obtained at 25 °C and 10^5 Pa from the combustion of 48.0 g of natural gas, $CH_4(g)$, to give $CO_2(g)$ and $H_2O(g)$?

8.119 Chloroform, $CHCl_3$, was formerly used as an anaesthetic and is now believed to be a carcinogen (cancer-causing agent). It has an enthalpy of vaporisation ($\Delta_{vap} H$) of 31.4 kJ mol^{-1}. The change, $CHCl_3(l) \rightarrow CHCl_3(g)$, has $\Delta S^{\ominus} = 94.2$ J mol^{-1} K^{-1}. At what temperature do we expect $CHCl_3$ to boil (i.e. at what temperature will liquid and vapour be in equilibrium at 10^5 Pa)?

8.120 Isooctane, an important constituent of petrol, has a boiling point of 99.3 °C and an enthalpy of vaporisation of 37.7 kJ mol^{-1}. What is ΔS for the vaporisation of 1 mol of isooctane?

8.121 Acetone, $(CH_3)_2CO$, has a boiling point of 56.2 °C. The change $(CH_3)_2CO(l) \rightarrow (CH_3)_2CO(g)$ has $\Delta H^{\ominus} = 31.9$ kJ

mol^{-1}. What is $\Delta S^{\ominus}$ for this change?

8.122 Determine whether the following reaction will be spontaneous. Do we expect appreciable amounts of products to form?

$$C_2H_4(g) + 2HNO_3(l) \rightarrow CH_3COOH(l) + H_2O(l) + NO(g) + NO_2(g)$$

8.123 Which of the following unbalanced equations represent a reaction that would be expected to be spontaneous at 25 °C and 10^5 Pa?

(a) $PbO(s) + NH_3(g) \rightarrow Pb(s) + N_2(g) + H_2O(g)$

(b) $NaOH(s) + HCl(g) \rightarrow NaCl(s) + H_2O(l)$

(c) $Al_2O_3(s) + Fe(s) \rightarrow Fe_2O(s) + Al(s)$

(d) $2CH_4(g) \rightarrow C_2H_6(g) + H_2(g)$

8.124 Calculate the value of $\Delta_r G^{\ominus}_{373\ k}$ for the following reactions, using data in tables 8.2 and 8.5. Assume that $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ are independent of temperature.

(a) $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

(b) $5SO_3(g) + 2NH_3(g) \rightarrow 2NO(g) + 5SO_2(g) + 3H_2O(g)$

8.125 How much work is accomplished by the following chemical reaction if it occurs inside a bomb calorimeter?

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$$

How much work is done if the reaction is carried out at 10^5 Pa, with all reactants and products at 25 °C? (For $C_4H_{10}(g)$, $\Delta_f H^{\ominus} = -126$ kJ mol^{-1}.)

8.126 A cylinder fitted with a piston contains 5.00 L of a gas at a pressure of 4×10^5 Pa. The entire apparatus is maintained at a constant temperature of 25 °C. The piston is released and the gas expands until the pressure inside the cylinder equals the atmospheric pressure outside, which is 10^5 Pa. Assume ideal gas behaviour and calculate the amount of work done by the gas as it expands at constant temperature.

8.127 The experiment described in question 8.126 is repeated, but this time a weight, which exerts a pressure of 2×10^5 Pa, is placed on the piston. When the gas expands, its pressure drops to this 2×10^5 Pa pressure. Then the weight is removed and the gas is allowed to expand again to a final pressure of 10^5 Pa. Throughout both expansions, the temperature of the apparatus was held at a constant 25 °C. Calculate the amount of work done by the gas in each step. How does the combined total amount of work in this two-step expansion compare with the amount of work done by the gas in the one-step expansion described in question 8.96?

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ADDITIONAL EXERCISES

8.128 A body of water with a mass of 750 g changed in temperature from 25.50 °C to 19.50 °C.

(a) What would have to be done to cause such a change?

(b) How much energy is involved in this change?

8.129 A bar of hot iron with a mass of 1.000 kg and a temperature of 100.00 °C was plunged into an insulated vat of water. The mass of the water was 2.000 kg, and its initial temperature was 25.00 °C. What was the temperature of the resulting system when it stabilised?

8.130 Sulfur trioxide reacts with water to produce sulfuric acid according to the following equation:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$$

Calculate $\Delta_r H^{\ominus}$ for the reaction.

8.131 Iron metal can be obtained from iron ore, which we can assume for this question to be Fe_2O_3, by its reaction with hot carbon:

$$2Fe_2O_3(s) + 3C(s) \rightarrow 4Fe(s) + 3CO_2(g)$$

What is $\Delta_r H^{\ominus}$ for this reaction? Is the reaction exothermic or endothermic?

8.132 In the recovery of iron from iron ore, the reduction of the ore is actually accomplished by reactions involving carbon monoxide. Use the following thermochemical equations:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \quad \Delta_r H^{\ominus} = -28\ \text{kJ mol}^{-1}$$
$$3Fe_2O_3(s) + CO(g) \rightarrow 2Fe_3O_4(s) + CO_2(g) \quad \Delta_r H^{\ominus} = -59\ \text{kJ mol}^{-1}$$
$$Fe_3O_4(s) + CO(g) \rightarrow 3FeO(s) + CO_2(g) \quad \Delta_r H^{\ominus} = +38\ \text{kJ mol}^{-1}$$

to calculate $\Delta_r H^{\ominus}$ for the reaction:

$$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$$

8.133 Use the results of question 8.132 and the data in table 8.2 to calculate the value of $\Delta_f H^{\ominus}$ for FeO.

8.134 Phosphorus burns in air to give tetraphosphorus decaoxide:

$$4P(s) + 5O_2(g) \longrightarrow P_4O_{10}(s) \quad \Delta_r H^{\ominus} = -3062\ \text{kJ mol}^{-1}$$

The product combines with water to give phosphoric acid, H_3PO_4:

$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(l) \quad \Delta_r H^{\ominus} = -257.2\ \text{kJ mol}^{-1}$$

Using these equations (and any others in the chapter, as needed), write the thermochemical equation for the formation of 1 mol of $H_3PO_4(l)$ from the elements, and calculate $\Delta_f H^{\ominus}$.

8.135 The amino acid glycine, H_2NCH_2COOH, is one of the compounds used by the body to make proteins. The equation for its combustion is:

$$4H_2NCH_2COOH(s) + 9O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l) + 2N_2(g)$$

For each mole of glycine that burns, 973.49 kJ of heat is liberated. Use this information plus values of $\Delta_f H^{\ominus}$ for the products of combustion to calculate $\Delta_f H^{\ominus}$ for glycine.

8.136 Calculate $\Delta_r H^{\ominus}$ for the reaction:

$$2Ag(s) + Zn(NO_3)_2(aq) \rightarrow Zn(s) + 2AgNO_3(aq)$$

using the following thermochemical equations:

$$Cu(NO_3)_2(aq) + Zn(s) \rightarrow Zn(NO_3)_2(aq) + Cu(s) \quad \Delta_r H^{\ominus} = -258\text{kJ mol}^{-1}$$
$$2AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s) \quad \Delta_r H^{\ominus} = -106\text{kJ mol}^{-1}$$

8.137 Calculate $\Delta_r H^{\ominus}$ for the following reaction:

$$LiOH(aq) + HCl(aq) \rightarrow LiCl(aq) + H_2O(l)$$

Use the following thermochemical equations as needed:

$$Li(s) + \frac{1}{2}O_2(g) + \frac{1}{2}H_2(g) \rightarrow LiOH(s) \quad \Delta_r H^{\ominus} = -487.0\ \text{kJ mol}^{-1}$$

$$2Li(s) + Cl_2(g) \rightarrow 2LiCl(s) \quad \Delta_r H^{\ominus} = -815.0\ kJ\ mol^{-1}$$
$$LiOH(s) \rightarrow LiOH(aq) \quad \Delta_r H^{\ominus} = -19.2\ kJ\ mol^{-1}$$
$$HCl(g) \rightarrow HCl(aq) \quad \Delta_r H^{\ominus} = -77.0\ kJ\ mol^{-1}$$
$$LiCl(g) \rightarrow LiCl(aq) \quad \Delta_r H^{\ominus} = -36.0 kJ\ mol_{-1}$$

Also, use any other equations, as needed, along with thermodynamic data found either in this chapter or in appendix A.

8.138 The value of $\Delta_f H^{\ominus}$ for HBr(g) was first evaluated using the following standard enthalpy values obtained experimentally:

$$Cl_2(g) + 2KBr(aq) \rightarrow Br_2(aq) + 2KCl(aq) \quad \Delta_r H^{\ominus} = -96.2\ kJ\ mol^{-1}$$
$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \quad \Delta_r H^{\ominus} = -184\ kJ\ mol^{-1}$$
$$HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l) \quad \Delta_r H^{\ominus} = -57.3\ kJ\ mol^{-1}$$
$$HBr(aq) + KOH(aq) \rightarrow KBr(aq) + H_2O(l) \quad \Delta_r H^{\ominus} = -57.3\ kJ\ mol^{-1}$$
$$HCl(g) \rightarrow HCl(aq) \quad \Delta_r H^{\ominus} = -77.0\ kJ\ mol^{-1}$$
$$Br_2(g) \rightarrow Br_2(aq) \quad \Delta_r H^{\ominus} = -4.2\ kJ\ mol^{-1}$$
$$HBr(g) \rightarrow HBr(aq) \quad \Delta_r H^{\ominus} = -79.9\ kJ\ mol^{-1}$$

Use this information to calculate the value of $\Delta_f H^{\ominus}$ for HBr(g).

8.139 The reaction for the metabolism of sucrose, $C_{12}H_{22}O_{11}$, in the body is the same as for its combustion in oxygen to yield CO_2(g) and H_2O(l). The standard enthalpy of formation of sucrose is -2230 kJ mol^{-1}. Use data in table 8.2 to calculate the amount of energy released by metabolising 28.4 g of sucrose.

8.140 Consider the following thermochemical equations:

$$CH_3OH(l) + O_2(g) \longrightarrow HCOOH(l) + H_2O(l) \quad \Delta_r H^{\ominus} = -411\ kJ\ mol^{-1} \quad (8.1)$$

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l) \quad \Delta_r H^{\ominus} = -128\ kJ\ mol^{-1} \quad (8.2)$$

$$HCO\ OH(l) \longrightarrow CO(g) + H_2O(l) \quad \Delta_r H^{\ominus} = -33\ kJ\ mol^{-1} \quad (8.3)$$

Suppose equation 1 is reversed and divided by 2, equations 2 and 3 are multiplied by $\frac{1}{2}$, and then the three adjusted equations are added. What is the net reaction, and what is the value of $\Delta_r H^{\ominus}$ for the net reaction?

8.141 Given the following thermochemical equations:

$$Cu(s) + \tfrac{1}{2}O_2(g) \rightarrow CuO(s) \quad \Delta_r H^{\ominus} = -155\ kJ\ mol^{-1}$$
$$Cu(s) + S(s) \rightarrow CuS(s) \quad \Delta_r H^{\ominus} = -53.1\ kJ\ mol^{-1}$$
$$S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta_r H^{\ominus} = -297\ kJ\ mol^{-1}$$
$$4CuS(s) + 2CuO(s) \rightarrow 3Cu_2S(s) + SO_2(g) \quad \Delta_r H^{\ominus} = -13.1\ kJ\ mol^{-1}$$

calculate $\Delta_r H^{\ominus}$ for the reaction:

$$CuS(s) + Cu(s) \rightarrow Cu_2S(s)$$

8.142 What is the algebraic sign of $\Delta_r S$ for each of the following changes?

(a) $2Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s)$

(b) $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

(c) $NH(g) \rightarrow NH_3(aq)$

(d) naphthalene(g) → naphthalene(s)

(e) A gas being cooled from 40 °C to 25 °C

(f) A gas being compressed at constant temperature from 4.0 L to 2.0 L

8.143 The reaction Cl_2 (g) + Br(g) → 2BrCl(g) has a very small value for $\Delta_r S^{\ominus}$ (+ 11.6 JK^{-1}). Why?

8.144 For a phase change at a given pressure, why is there only one temperature at which there can be an equilibrium between the

phases?

8.145 The enthalpy of combustion, $\Delta_c H^\ominus$, of oxalic acid, $H_2C_2O_4(s)$, is -246.05 kJ mol^{-1}. Consider the following data:

Substance	$\Delta_f H^\ominus$ (kJ mol^{-1})	$S^\ominus$ (J mol^{-1} K^{-1})
C(s)	0	5.69
$CO_2(g)$	-393.5	213.6
$H_2(g)$	0	130.6
$H_2O(l)$	-285.9	69.96
$O_2(g)$	0	205.0
$H_2C_2O_4(s)$	?	120.1

(a) Write the balanced thermochemical equation that describes the combustion of 1 mol of oxalic acid.

(b) Write the balanced thermochemical equation that describes the formation of 1 mol of oxalic acid.

(c) Use the information in the table and your equations in and(b) to calculate $\Delta_f H^\ominus$ for oxalic acid.

(d) Calculate $\Delta_f S^\ominus$ for oxalic acid and $\Delta_r S^\ominus$ for the combustion of 1 mol of oxalic acid.

(e) (e) Calculate $\Delta_f G^\ominus$ for oxalic acid and $\Delta_r G^\ominus$ for the combustion of 1 mol of oxalic acid.

8.146 Many biochemical reactions have positive values for $\Delta_r G^\ominus$ and so should not be expected to be spontaneous. They occur, however, because they are chemically coupled with other reactions that have negative values of $\Delta_r G^\ominus$. An example is the set of reactions that begins the sequence of reactions involved in the metabolism of glucose, a sugar. Given these reactions and their corresponding $\Delta_r G^\ominus$ values:

$$\text{glucose} + \text{phosphate} \rightarrow \text{glucose-6-phosphate} + H_2O \quad \Delta_r G^\ominus = +13.13\,\text{kJ mol}^{-1}$$

$$\text{ATP} + H_2O \rightarrow \text{ADP} + \text{Phds} \quad \Delta_r G^\ominus = -32.22\,\text{kJ mol}^{-1}$$

calculate $\Delta_r G^\ominus$ for the coupled reaction:

$$\text{glucose} + \text{ATP} \rightarrow \text{glucose} - 6 - \text{phosphate} + \text{ADP}$$

8.147 Cars, trucks and other machines that use petrol or diesel engines for power have cooling systems. In terms of thermodynamics, what makes these cooling systems necessary?

8.148 Ethanol, C_2H_5OH, has been suggested as an alternative to petrol as a fuel. In worked example 8.13, we calculated $\Delta_r G^\ominus$ for combustion of 1 mol of C_2H_5OH; in worked example 8.14, we calculated $\Delta_r G^\ominus$ for combustion of 1 mol of octane. We will assume that petrol has the same properties as octane (one of its constituents). The density of C_2H_5OH is 0.7893 g mL^{-1}; the density of octane, C_8H_{18}, is 0.7025 g mL^{-1}. Calculate the maximum work that could be obtained by burning 1 L each of C_2H_5OH and C_8H_{18}. On a volume basis, which is a better fuel? Explain your answer.

8.149 Use the data in table 8.3 to calculate the bond enthalpy in the nitrogen molecule and in the oxygen molecule.

8.150 The enthalpy of vaporisation of carbon tetrachloride, CCl_4, is29.9 kJ mol^{-1}. Using this information and data in tables 8.3 and 8.4, estimate the standard enthalpy of formation of liquid CCl_4.

8.151 Ammonium nitrate, NH_4NO_3, is a white, crystalline substance manufactured on an enormous scale, for use as a fertiliser, from the reaction of anhydrous ammonia with concentrated nitric acid. However, ammonium nitrate must be handled with care as it is potentially explosive.

(a) The standard enthalpy of formation ($\Delta_f H^\ominus$) of $NH_4NO_3(s)$ is –365.56 kJ mol^{-1}. Write the balanced chemical equation to which this value refers. Specify the standard state for each species in this reaction.

(b) Write the balanced chemical equation for the formation of $NH_4NO_3(s)$ from $NH_3(g)$ and $HNO_3(l)$. Calculate $\Delta_r H^\ominus$ for this reaction.

(c) When gently heated, $NH_4NO_3(s)$ can decompose according to the following equation:

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_4O(g)$$

Calculate $\Delta_r H^\ominus$ for this reaction.

(d) When vigorously heated, NH_4NO_3 can decompose explosively according to the following equation:

(d) When vigorously heated, NH_4NO_3 can decompose explosively according to the following equation:

$$NH_4NO_3(s) \rightarrow N_2(g) + 2H_2O(g) + \frac{1}{2}O_2(g)$$

Calculate the enthalpy change if 1.000 kg of NH_4NO_3 decomposes completely according to this equation under standard conditions.

(e) If the energy released from the reaction in (d) was used to heat 100 kg of water, initially at 25.0 °C, what would be the final temperature of the water?

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KEY TERMS

atomisation enthalpy ($\Delta_{at}H$)
bomb calorimeter
bond enthalpy
boundary
calorimeter
chemical thermodynamics
combustion reaction
endothermic
enthalpy (H)
entropy (S)
exothermic
extensive property
first law of thermodynamics
Gibbs energy (*G*)
heat (q)
heat capacity (C)
heat of reaction at constant pressure (qp)
heat of reaction at constant volume (qv)
Hess's law
intensive property
internal energy (U)
joule (J)
kilojoule (kJ)
molar heat capacity
second law of thermodynamics
specific heat (c)
specific heat capacity (c)
spontaneous
standard enthalpy of combustion $\Delta_c H^\ominus$
standard enthalpy of formation $\left(\Delta_f H^\ominus\right)$
standard enthalpy of reaction $\left(\Delta_r H^\ominus\right)$
standard entropy $\left(S^\ominus\right)$
standard entropy of formation $\Delta_f S^\ominus$. Values of $\Delta_r S^\ominus$
standard entropy of reaction $\left(\Delta_r S^\ominus\right)$
standard Gibbs energy change $\left(\Delta G^\ominus\right)$
standard states
state function
surroundings
system
thermochemical equation
thermodynamic temperature
third law of thermodynamics
universe
work (w)

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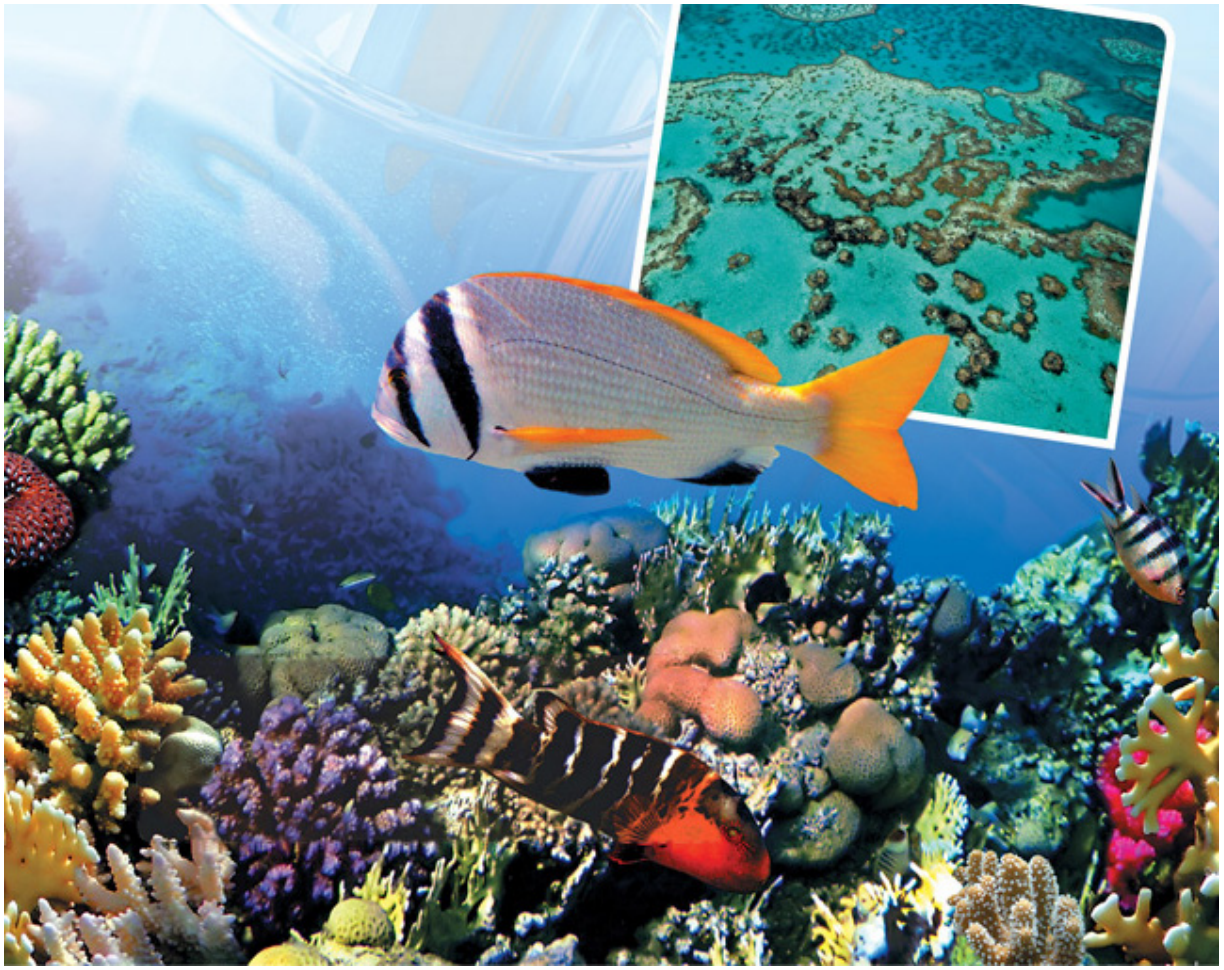
CHAPTER

9 Chemical Equilibria

The Earth's oceans are extremely complex chemical systems, comprising vast quantities of dissolved inorganic salts, dissolved organic matter and dissolved gases. Of the gases, carbon dioxide is very important because it provides a source of carbonate ions for the growth of coral, the exoskeleton of which is composed of calcium carbonate. The rate at which coral reefs grow therefore depends critically on the amount of dissolved carbon dioxide in the ocean, and any process which alters this amount will affect coral reefs.

We know that carbon dioxide levels in the Earth's atmosphere are currently increasing and the pH of the Earth's oceans is decreasing. It is also becoming increasingly apparent that the Earth's average temperature is rising. All of these factors can influence the chemical equilibrium between solid and dissolved calcium carbonate in the oceans, thereby potentially putting coral reefs, such as the Great Barrier Reef, at risk.





This chapter will introduce the concept of chemical equilibrium, the factors that can affect the behaviour of chemical systems at equilibrium and how a system in which equilibrium has been perturbed must respond to re-establish equilibrium. An understanding of chemical equilibrium is necessary in all forms of chemistry, and we will study important applications of chemical equilibrium in detail in chapters 10, 11 and 12.

KEY TOPICS

9.1 Chemical equilibrium
9.2 The equilibrium constant, *K*, and the reaction quotient, *Q*
9.3 Equilibrium and Gibbs energy
9.4 How systems at equilibrium respond to change
9.5 Equilibrium calculations

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9.1 Chemical Equilibrium

In chapters 8, we learned how to use the value of ΔG to predict whether a particular chemical reaction or physical change would be spontaneous under the specified conditions. We also briefly introduced the concept of equilibrium and showed that a system is at equilibrium when $\Delta G = 0$; under these conditions, no non- pV work can be extracted from the system, and there is no driving force for chemical or physical change. In this chapter, we will develop the idea of equilibrium further; most importantly, we will show that equilibria in chemical reactions can be quantified using the equilibrium constant, K, and that this is related to the thermodynamic functions we encountered in chapter 8.

It is important to realise that a negative value of ΔG for a particular chemical reaction under specific conditions tells us only that spontaneous chemical change will occur in the forward direction — it does *not* necessarily mean that *complete* conversion of reactants to products will occur. In fact, many chemical reactions proceed only part way to completion and give a mixture of reactants and products. We will illustrate this using the Haber–Bosch process, the catalysed formation of gaseous ammonia, NH_3, from the reaction of nitrogen gas, N_2, and hydrogen gas, H_2:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The stoichiometric coefficients tell us that:

- $N_2(g)$ always reacts with $H_2(g)$ in a 1 : 3 mole ratio.
- The amount of $NH_3(g)$ formed in this reaction is twice the amount of $N_2(g)$ and two-thirds the amount of $H_2(g)$ that has reacted.

We cannot, however, conclude from the balanced chemical equation that mixing 1 mole of $N_2(g)$ with 3 moles of $H_2(g)$ will produce 2 moles of $NH_3(g)$. If we mixed 1 mole of N_2 with 3 moles of H_2 at elevated temperature and pressure over a catalyst (the uncatalysed reaction is very slow) and monitored the composition of the reaction mixture over time, we would indeed see the concentration of $NH_3(g)$ increase and the concentrations of $N_2(g)$ and $H_2(g)$ decrease; eventually, however, the concentrations of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ would stop changing, and we would end up not with pure $NH_3(g)$ but with a mixture of reactants and products. We say that the reaction mixture has come to **chemical equilibrium** and we distinguish this by using a double-headed arrow $\rightleftharpoons$ (called an equilibrium arrow):

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The equilibrium arrow highlights a very important point — a chemical reaction can proceed in both the forward and reverse directions at the same time. At equilibrium, N_2 and H_2 are still reacting to give NH_3, and NH_3 is also reacting to give N_2 and H_2, but *the rates of the forward and reverse reactions are equal*. This means that the concentrations of the reactants and products in the reaction mixture remain constant and there is *no net change in the overall composition of the reaction mixture*. Since both the forward and reverse reactions are still occurring, we say that the system is in a state of **dynamic equilibrium**.

In a chemical equilibrium, the terms ‘reactants’ and ‘products’ do not have the usual significance because the reaction is proceeding in both directions simultaneously. Instead, we use ‘reactants’ and ‘products’ simply to identify the substances on the left- and right-hand sides, respectively, of the equation for the equilibrium.

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9.2 The Equilibrium Constant, *K*, and the Reaction Quotient, *Q*

A classic experiment that demonstrates many important concepts of equilibrium is the decomposition of $N_2O_4(g)$ (dinitrogen tetroxide) to give $NO_2(g)$ (nitrogen dioxide) (figure 9.1):



FIGURE 9.1 Equilibrium mixtures of $N_2O_4(g)$ and $NO_2(g)$ at different temperatures. In ice (right-hand side), colourless N_2O_4 predominates and the mixture is pale. At high temperature (left-hand side), dark brown NO_2 predominates. At room temperature (middle), there is a mixture of the gases, with N_2O_4 in the larger amount.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

This reaction is easily monitored by observing the colour of the reaction mixture. Pure $N_2O_4(g)$ is colourless, while pure $NO_2(g)$ is brown; as N_2O_4 decomposes, the mixture becomes more and more brown. Figure 9.2 shows how the concentrations of the two gases change over time as pure $N_2O_4(g)$ is converted to an equilibrium mixture of $N_2O_4(g)$ and $NO_2(g)$.

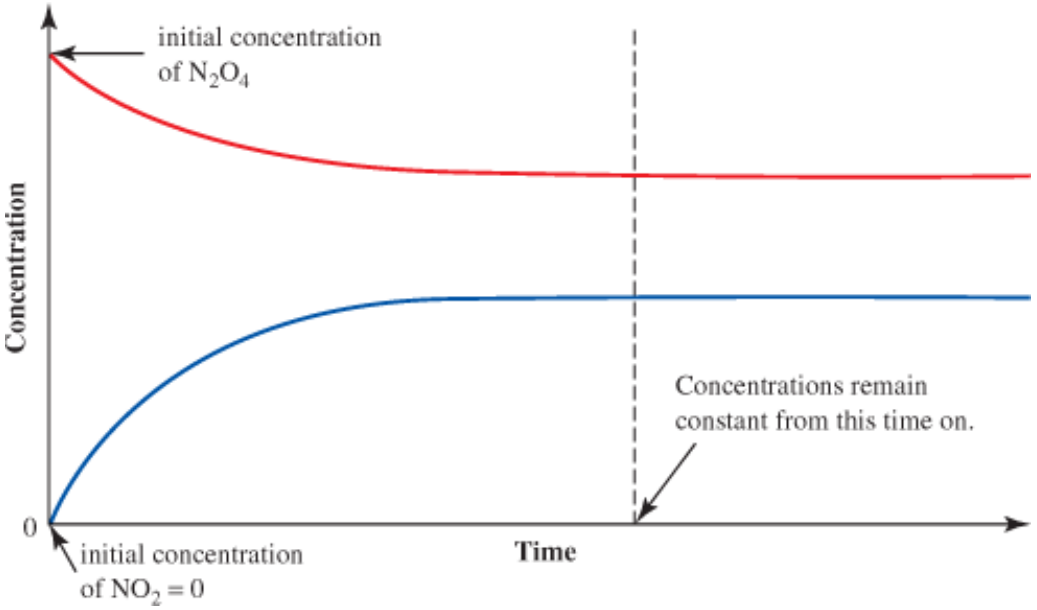


FIGURE 9.2 The approach to equilibrium. In the decomposition of $N_2O_4(g)$ into $NO_2(g)$, $N_2O_4(g)$ $N_2O_4 \rightleftharpoons$ $2NO_2(g)$, the concentrations of N_2O_4 and NO_2 change relatively quickly at first. As time passes, the

concentrations change more and more slowly. When equilibrium is reached, the concentrations of N_2O_4 and NO_2 no longer change with time; they remain constant. Note that the concentration change of NO_2 over the course of the reaction is twice the concentration change of N_2O_4.

Suppose we set up the two experiments shown in figure 9.3 at constant temperature. In the first 1-litre flask, we put 0.0350 mol N_2O_4. Since no NO_2 is present, some N_2O_4 must decompose for the mixture to reach equilibrium, so the reaction will proceed in the forward direction (i.e. from left to right). When equilibrium is reached, we find the concentration of N_2O_4 has dropped to 0.0292 mol L^{-1} and the concentration of NO_2 has become 0.0116 mol L^{-1}.

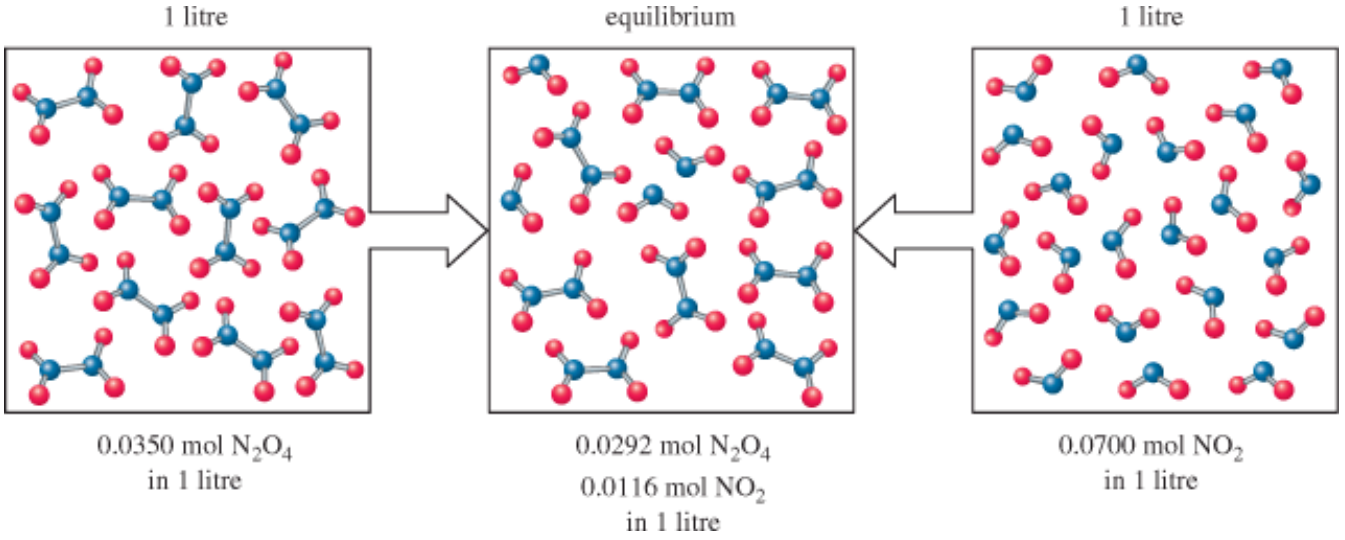


FIGURE 9.3 Reaction reversibility for the equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The same equilibrium composition is reached from either the forward or reverse direction, provided the *overall* system composition is the same. Because pure NO_2 is brown and pure N_2O_4 is colourless, the amber colour of the equilibrium mixture indicates that both species are present at equilibrium.

In the second 1-litre flask we put 0.0700 mol of NO_2 (*precisely* the amount of NO_2 that would form if 0.0350 mol of N_2O_4 — the amount placed in the first flask — decomposed completely). In this second flask, there is no N_2O_4 present initially, so NO_2 molecules must combine, following the reverse reaction (right to left) shown above, to give N_2O_4. When we measure the concentrations at equilibrium in the second flask, we find, once again, 0.0292 mol L^{-1} of N_2O_4 and 0.0116 mol L^{-1} of NO_2. (In practice, these experiments are difficult, if not impossible, to carry out, because $N_2O_4(g)$ and $NO_2(g)$ are always in equilibrium, so they cannot be obtained absolutely pure.)

We see here that the same equilibrium composition is reached, whether we begin with pure NO_2 or pure N_2O_4, as long as the *total* amount of N and O to be divided between these two substances is the same. Similar observations apply to other chemical systems as well, which leads to the following generalisation: For a given *overall* system composition at constant temperature, we always reach the same equilibrium concentrations whether equilibrium is approached from the forward or reverse direction.

For any reaction involving only gases or species in solution (generally aqueous) in which *a* moles of substance *A* react with *b* moles of substance *B* to give *c* moles of substance *C*and *d* moles of substance *D*:

$$aA + bB \rightleftharpoons cC + dD$$

the following holds when equilibrium is established:

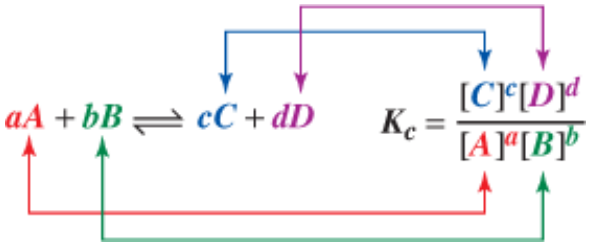
$$K_c = \frac{\left(\frac{[C]_e}{c^\ominus}\right)^c \left(\frac{[D]_e}{c^\ominus}\right)^d}{\left(\frac{[A]_e}{c^\ominus}\right)^a \left(\frac{[B]_e}{c^\ominus}\right)^b}$$

K_c is called the **equilibrium constant** (or, occasionally, the concentration-based equilibrium constant) and the above expression is called the **equilibrium constant expression**. The square brackets refer to concentrations in mol L^{-1}, and $c^\ominus$, the standard concentration, equals 1 mol L^{-1}.

Because each concentration term is divided by 1 mol L^{-1}, each term in parentheses is dimension-less, and this means that K_c has no units. Although the expression on p. 347 looks rather daunting, you will be pleased to know that, in practice, it is usually simplified. Because they are numerically equal to 1, the $c^\ominus$ terms are often omitted; however, it is still understood that each term is dimensionless. The subscript 'e' is also generally omitted, as it is implicit that the concentrations used in an equilibrium constant expression must be equilibrium concentrations. Having made these simplifications, we obtain the more common version of the equilibrium constant expression:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Note that we will use this form throughout the book, and all equilibrium constants will be dimensionless. This expression is derived from the balanced chemical equation as follows:



Notice that the products (the species to the right of the equilibrium arrow) always appear on the top line of the expression (the numerator), and the reactants always appear on the bottom (the denominator). Each reactant and product is raised to the power of the appropriate stoichiometric coefficient (*a*, *b*, *c* or *d*) from the balanced chemical equation (i.e. the coefficients become the exponents). Note that we are not restricted to reactions involving two products and two reactants; we simply include all gaseous or aqueous reactants and products in the equilibrium constant expression. For example, the equilibrium constant expression for the reaction in the experiment on pp. 346–7:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

is:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

The value of K_c for a particular reaction depends on the temperature, so it is important that the temperature is always specified when K_c is reported. Tabulated values of K_c generally refer to 25.0 °C and concentrations in mol L^{-1}.

Table 9.1 gives the results of four further experiments using differing initial concentrations of $N_2O_4(g)$ and $NO_2(g)$. The final column shows that the value of K_c is constant (within experimental error). We can, therefore, say that the equilibrium constant for this reaction:

TABLE 9.1 Equilibrium mixture compositions for various initial concentrations of $NO_2(g)$ and $N_2O_4(g)$

Initial concentration	Equilibrium concentration

$[N_2O_4]$ (mol L^{-1})	$[NO_2]$ (mol L^{-1})	$[N_2O_4]$(mol L^{-1})	$[NO_2]$ (mol L^{-1})	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$
0.0450	0	0.0384	0.013 3	$\frac{(0.0133)^2}{0.0384} = 4.61 \times 10^{-3}$
0.0150	0	0.0114	0.007 24	$\frac{(0.00724)^2}{0.0114} = 4.60 \times 10^{-3}$
0	0.0600	0.0247	0.010 7	$\frac{(0.0107)^2}{0.0247} = 4.64 \times 10^{3}$
0	0.0500	0.0202	0.009 64	$\frac{(0.00964)^2}{0.0202} = 4.60 \times 10^{-3}$

The values of K_c are equal within experimental error.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

is:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 4.61 \times 10^{-3} \text{ at } 25.0°C$$

Similarly, if we were to study the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

at different initial concentrations of $H_2(g)$, $I_2(g)$ and HI(g) at 400 °C, we would find that, when the system came to equilibrium:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 49.5 \text{ at } 400°C$$

We can apply the equilibrium constant expression to any system at equilibrium. We can also write an expression for systems that are not at equilibrium. We call this the **reaction quotient *(Q)***. For:

$$aA + bB \rightleftharpoons cC + dD$$

we can write the **reaction quotient expression**:

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Note that the expression takes a similar form to that for K_c, and we have made the same simplifications for Q_c as we did for K_c. Q_c and K_c differ in that:

- K_c involves equilibrium concentrations and so refers to a system *at equilibrium*
- Q_c refers to systems that are not necessarily at equilibrium.

K_c can have only one positive value at a particular temperature, while Q_c can have any positive value.

It is important to realise that *all chemical systems will eventually come to equilibrium*. When equilibrium is established, $Q_c = K_c$. In systems where $Q_c \neq K_c$, a comparison of their values can tell us how a system must change to establish equilibrium, as shown in figure 9.4.

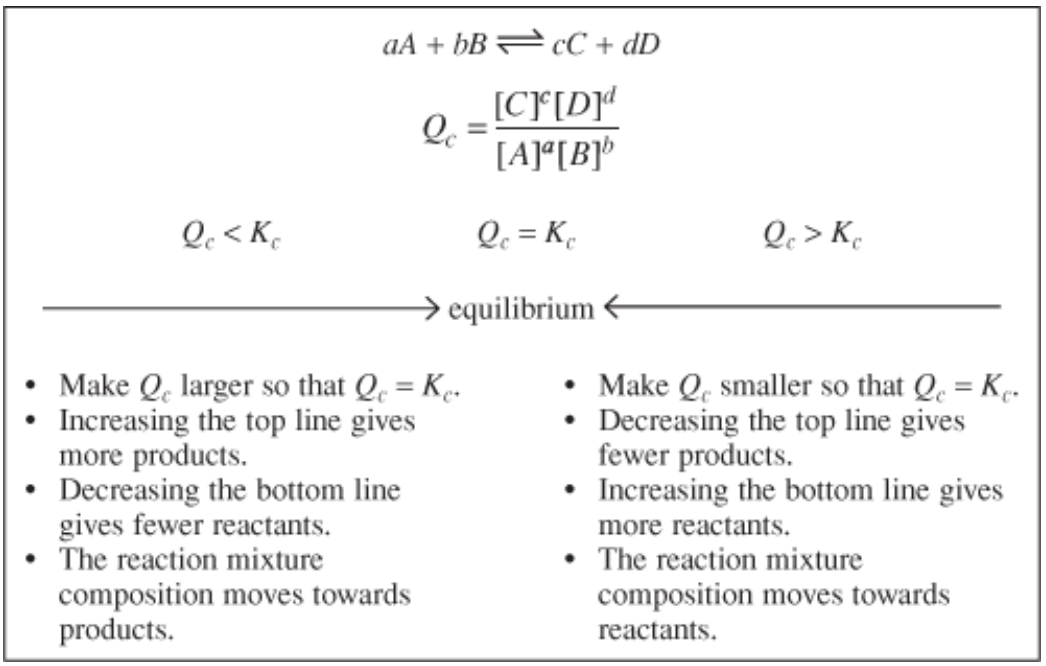


FIGURE 9.4 How a system must change to establish equilibrium.

If $Q_c > K_c$, the system reacts to use up products and generate more reactants, thereby decreasing Q_c to the point where it equals K_c; that is, the system is at equilibrium. If $Q_c < K_c$, the opposite occurs; the system reacts to use up reactants and form more products, thereby increasing Q_c to the point where it equals K_c, again meaning the system is at equilibrium. We will discuss this in more detail in section 9.4

The subscript '*c*' in both Q_c and K_c refers to the fact that we are expressing the composition of the reaction mixtures in terms of concentration. For equilibria involving gases, we can also express the composition of the equilibrium mixture in terms of partial pressure (p. 226), rather than concentration. When we do this, the equilibrium constant expression takes the form:

$$K_p = \frac{\left(\frac{p_C}{p^\ominus}\right)^c \left(\frac{p_C}{p^\ominus}\right)^d}{\left(\frac{p_A}{p^\ominus}\right)^a \left(\frac{p_B}{p^\ominus}\right)^b}$$

where p_A, p_B, p_C and p_D are the equilibrium partial pressures of *A*, *B*, *C* and *D*, respectively, and $p^\ominus$ is the standard pressure. Because $p^\ominus = 1 \times 10^5$ Pa, we cannot make the simplification that we made earlier for K_c as, in this case, the $p^\ominus$ terms affect the actual value of K_p. Therefore, expressions for K_p must be written in full, including the $p^\ominus$ terms when pressures are measured in Pa. Like K_c, K_p has no units.

WORKED EXAMPLE 9.1

Writing Expressions for K_c

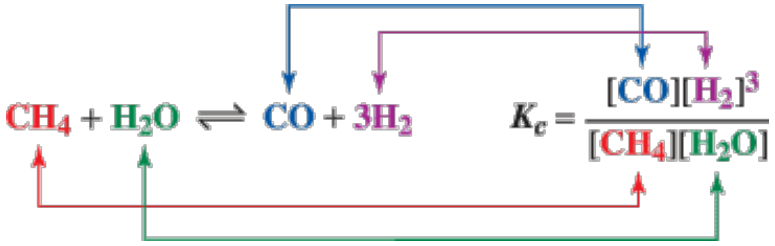
Interest is growing in the potential use of hydrogen as an alternative fuel to replace fossil fuels. Currently, much of the hydrogen produced in the world is derived from methane, CH_4, in natural gas using the forward reaction of the equilibrium:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Write the expression for K_c for this reaction.

Analysis

To write the equilibrium constant expression, we place the concentrations of the products in the numerator and the concentrations of the reactants in the denominator, each raised to the value of the appropriate stoichiometric coefficient. As stated earlier, it is usual to ignore the $c^{\ominus}$ terms as these do not affect the value of K_c.



Solution

The equilibrium constant expression is:

$$K_c = \frac{[CO]\,[H_2]^3}{[CH_4]\,[H_2O]}$$

Is our answer reasonable?

Check to see that products are on the top line and that reactants are on the bottom. Also check the superscripts and be sure that they are the same as those in the balanced chemical equation. Notice that we omit the exponent when it is equal to 1.

PRACTICE EXERCISE 9.1

Write the equilibrium constant expression K_c for each of the following reactions.

(a) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$

(b) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$

WORKED EXAMPLE 9.2

Writing Expressions for K_p

Most of the world's supply of methanol, CH_3OH, is produced by the following reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Write the expression for K_p for this equilibrium.

Analysis

For K_p, we use partial pressures in the equilibrium constant expression. We put the equilibrium partial pressures of the products in the numerator and the equilibrium partial pressures of the reactants in the denominator. The coefficients in the equation become exponents of the pressures. Because we are working in SI units, in which $p^\ominus = 1 \times 10^5$ Pa, we must explicitly divide each term by $p^\ominus$ to calculate K_p.

Solution

The expression for K_p for this reaction is:

$$K_p = \frac{\left(\frac{p_{CH_3OH}}{p^\ominus}\right)}{\left(\frac{p_{CO}}{p^\ominus}\right)\left(\frac{p_{H_2}}{p^\ominus}\right)^2}$$

Is our answer reasonable?

Check to make sure you have written the expression in terms of products over reactants, and not the other way around. Check each superscript against the coefficients in the balanced chemical equation.

PRACTICE EXERCISE 9.2

Using partial pressures, write the equilibrium constant expression for the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The Relationship Between K_p and K_c

Recall from chapter 6 that pressure (p) may be related to concentration (c) through the ideal gas equation:

$$pV = nRT$$

where V is volume (in m^3), n is amount, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is temperature (in K) and the pressure is in Pa.

We can rearrange this equation to give:

$$p = \frac{n}{V}RT = cRT$$

where c is in mol m^{-3}. To obtain concentrations in the more usual units of mol L^{-1}, we must modify this expression to give:

$$p = 1000\, cRT$$

(The factor of 1000 arises from the fact that 1 m^3 = 1000 L.) We can use this equation to obtain the relationship between K_p and K_c for a particular reaction. Knowing that p = 1000 cRT, K_p can be changed to K_c by replacing each partial pressure term in the expression for K_p with the product 1000 cRT. Similarly, because $c = \frac{p}{1000\,RT}$, K_c can be changed to K_p by substituting $\frac{p}{1000\,RT}$ for each concentration term. This sounds like a lot of work, and it is. Fortunately, there is a general equation derived from these relationships that we can use to make these conversions simpler:

$$K_p = K_c\left(\frac{1000\,RT}{p^{\ominus}}\right)^{\Delta n_g}$$

Note that, as $p^{\ominus} = 1 \times 10^5$, this can also be written as:

$$K_p = K_c\left(\frac{RT}{100}\right)^{\Delta n_g}$$

In this equation, the value of Δn_g is equal to the change in the *amount of gas* in going from the reactants to the products:

$$\Delta n_g = (\text{amount of } \textit{gaseous} \text{ products}) - (\text{amount of } \textit{gaseous} \text{ reactants})$$

We use the coefficients of the balanced equation for the reaction to calculate the numerical value of Δn_g. For example, in the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

there are 2 moles of gaseous products and 4 moles of gaseous reactants. Therefore, for this reaction, Δn_g = 2 - 4 = –2.

For some reactions, the value of Δn_g is equal to 0. An example is the decomposition of HI:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Notice that there are 2 moles of gas on each side of the equation. This means that $\Delta n_g = 0$. Because $\frac{1000\,RT}{p^{\ominus}}$ raised to the power of 0 is equal to 1, $K_p = K_c$. This will be the case for all reactions in which $\Delta n_g = 0$.

WORKED EXAMPLE 9.3

Converting From K_c to K_p

At 500 °C, the reaction between N_2 and H_2 to form ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

has $K_c = 6.0 \times 10^{-2}$. What is the numerical value of K_p for this reaction?

Analysis

The equation that we wish to use is:

$$K_p = K_c\left(\frac{1000\,RT}{p^{\ominus}}\right)^{\Delta n_g}$$

In the discussion on the previous page, we saw that $\Delta n_g = -2$ for this reaction. We use this equation with temperature, T, in kelvin and $R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$.

Solution

Begin by listing the data:

$$K_c = 6.0 \times 10^{-2} \quad T = (500 + 273)\text{K} = 773\ \text{K} \quad R = 8.314\ \text{J mol}^{-1}\text{K}^{-1} \quad \Delta n_{g=-2}$$

Substituting these into the equation for K_p gives:

$$\begin{aligned} K_p &= 6.0 \times 10^{-2}\left(\frac{1000(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(773\ \text{k})}{1 \times 10^5\ \text{Pa}}\right)^{-2} \\ &= 1.5 \times 10^{-5} \end{aligned}$$

In this case, K_p has a numerical value quite different from that of K_c.

Is our answer reasonable?

You should note (and, indeed, prove for yourself) that under all reasonable conditions of temperature (above 12 K) the term:

$$\left(\frac{1000\,RT}{p^{\ominus}}\right)^{\Delta n_g}$$

will be less than 1 when Δn_g is negative. Therefore the product:

$$K_c\left(\frac{1000\,RT}{p^{\ominus}}\right)^{\Delta n_g}$$

will *always* give an answer that is less than K_c. Therefore, in situations where Δn_g is negative, we would always expect the value of K_p to be less than that of K_c. Our answer is in agreement with this.

PRACTICE EXERCISE 9.3

Nitrous oxide, N_2O, is a gas used as an anaesthetic; it is sometimes called 'laughing gas'. This compound has a strong tendency to decompose into nitrogen and oxygen according to the equation:

$$2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$$

but the reaction is so slow that the gas appears to be stable at room temperature (25 °C). The decomposition reaction has $K_c = 7.3 \times 10^{34}$ at 25 °C. What is the value of K_p for this reaction at 25 °C?

CONVERTING From K_p to K_c

At 25 °C, K_p for the reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

has a value of 0.114. Calculate the value of K_c for this reaction.

Analysis

The equation we need is:

$$K_P = K_c\left(\frac{1000\,RT}{p^{\ominus}}\right)^{\Delta n_g}$$

and $\Delta n_g = 2 - 1 = +1$.

Solution

Tabulating the data, we have:

$$K_p = 0.114 \quad \Delta n_g = +1 \quad T = 298\,\text{k} \quad R = 8.314\,\text{J mol}^{-1}\text{K}^{-1}$$

Solving the equation for K_c gives:

$$K_c = \frac{K_p}{\left(\frac{1000\,RT}{p^{\ominus}}\right)^{\Delta n_g}}$$

Substituting values into this equation yields:

$$K_c = \frac{0.114}{\left(\frac{1000(8.314\,\text{J mol}^{-1}\,\text{K}^{-1}) \times (298\ \text{K})}{1 \times 10^5\,\text{Pa}}\right)^1}$$

$$= 4.60 \times 10^{-3}$$

As in worked example 9.3, there is a significant difference between the values of K_p and K_c.

Is our answer reasonable?

In this case, you can show that, provided the temperature is above 12 K, the term:

$$\left(\frac{1000\,RT}{p^{\ominus}}\right)^{\Delta n_g}$$

will be greater than 1 when Δn_g is positive. Therefore the product:

$$K_c\left(\frac{1000\,RT}{p^{\ominus}}\right)^{\Delta n_g}$$

will *always* give an answer that is greater than K_c. Therefore, in situations where Δn_g is positive, we would always expect the value of K_p to be greater than that of K_c. Providing we

have made no arithmetical errors, our answer is likely to be correct.

PRACTICE EXERCISE 9.4

Methanol, CH_3OH, is a promising fuel that can be synthesised from carbon monoxide and hydrogen according to the equation:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

$K_p = 3.8 \times 10^{-2}$ for this reaction at 200 °C. Do you expect K_p to be larger or smaller than K_c? Calculate the value of K_c at this temperature.

The exact thermodynamic treatment of equilibrium uses **activities**, rather than concentrations, in the equilibrium expression. Activities are dimensionless quantities that take account of the fact that neither gases in gas mixtures nor species in solution behave ideally; atoms, molecules and ions in the gas or solution phase tend to interact with each other, with the magnitude of the interaction increasing as the concentration increases. Activities can, therefore, be thought of as 'effective' concentrations and, as they are dimensionless, this leads to equilibrium constants having no units. Providing that we work at low gas pressures or with dilute solutions, activities approximate concentrations to an acceptable degree. Equilibrium constants obtained using activities, rather than pressures or concentrations, are often called **thermodynamic equilibrium constants**.

Manipulating Equilibrium Constant Expressions

Sometimes it is useful to be able to combine chemical equilibria to obtain the equation for some other reaction of interest. In doing this, we perform various operations such as reversing an equation, multiplying the coefficients by some factor and adding the equations to give the desired equation. In our discussion of thermochemistry, you learned how such manipulations affect Δ *H*values. Some different rules apply to equilibrium constant expressions.

Changing the Direction of an Equilibrium

When the direction of an equation is reversed, the new equilibrium constant is the reciprocal of the original. As an example, when we reverse the equilibrium:

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 \quad K_c = \frac{[PCl_5]}{[PCl_3]\,[Cl_2]}$$

we obtain:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \quad K_c' = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

The equilibrium constant expression for the second reaction is the reciprocal of that for the first, so $K_c' = \frac{1}{K_c}$.

Multiplying the Coefficients by a Factor

When the coefficients in an equation are multiplied by a factor, the equilibrium constant is raised to a power equal to that factor. For example, if we multiply the coefficients of the equation:

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 \quad K_c = \frac{[PCl_5]}{[PCl_3]\,[Cl_2]}$$

by 2, this gives:

$$2PCl_3 + 2Cl_2 \rightleftharpoons 2PCl_5 \quad K_c'' = \frac{[PCl_5]^2}{[PCl_3]^2[Cl_2]^2}$$

Comparing equilibrium constant expressions, we see that $K_c'' = K_c^2$.

Adding Chemical Equilibria

When chemical equilibria are added, their equilibrium constants are multiplied. For example, suppose we add the following two equations:

$$2N_2 + O_2 \rightleftharpoons \cancel{2N_2O} \quad K_{c1} = \frac{[N_2O]^2}{[N_2]^2[O_2]}$$

$$\cancel{2N_2O} + 3O_2 \rightleftharpoons 4NO_2 \quad K_{c2} = \frac{[NO_2]^4}{[N_2O]^2[O_2]^3}$$

$$2N_2 + 4O_2 \rightleftharpoons 4NO_2 \quad K_{c3} = \frac{[NO_2]^4}{[N_2]^2[O_2]^4}$$

We have numbered the equilibrium constants just to distinguish between them. If we multiply the equilibrium constant expression for K_{c1} by that for K_{c2}, we obtain the equilibrium constant expression for K_{c3}:

$$\frac{\cancel{[N_2O]^2}}{[N_2]^2[O_2]} \times \frac{[NO_2]^4}{\cancel{[N_2O]^2}\,[O_2]^3} = \frac{[NO_2]^4}{[N_2]^2[O_2]^4}$$

Therefore, $K_{c3} = K_{c1} \times K_{c2}$.

PRACTICE EXERCISE 9.5

At 25 °C, $K_c = 7.0 \times 10^{25}$ for the reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What is the value of K_c for the reaction

$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)\ ?$$

PRACTICE EXERCISE 9.6

At 25 °C, the equilibrium constants for the following reactions are as shown.

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \quad K_c = 3.3 \times 10^{91}$$

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \quad K_c = 9.1 \times 10^{80}$$

Use these data to calculate K_c for the reaction:

$$H_2O(g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g)$$

The Magnitude of the Equilibrium Constant

Because the concentrations of the products are always on the top line of the equilibrium constant expression K_c, the value of the equilibrium constant gives us a measure of how far the reaction has proceeded towards completion when equilibrium is reached. For example, the reaction:

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

has $K_c = 9.1 \times 10^{80}$ at 25 °C. This means that when there is an equilibrium between these gases:

$$K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]} = 9.1 \times 10^{80} = \frac{9.1 \times 10^{80}}{1}$$

By writing K_c as a fraction, $\frac{9.1 \times 10^{80}}{1}$, we see that the top line (numerator) of the equilibrium constant expression is enormous compared with the bottom line (denominator), which means that the concentration of H_2O has to be enormous compared with the concentrations of H_2 and O_2. At equilibrium, therefore, most of the hydrogen and oxygen atoms in the system are found in H_2O and very few are present in H_2 and O_2. The enormous value of K_c tells us that the reaction between H_2 and O_2 goes essentially to completion and that the products are strongly favoured at equilibrium.

The reaction between N_2 and O_2 to give NO:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

has a very small equilibrium constant: $K_c = 4.8 \times 10^{-31}$ at 25 °C. The equilibrium constant expression for this reaction is:

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 4.8 \times 10^{-31}$$

Since $10^{-31} = \frac{1}{10^{31}}$, we can write this as:

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 4.8 \times \frac{1}{10^{31}} = \frac{4.8}{10^{31}}$$

Here the bottom line is huge compared with the top line, so the concentrations of N_2 and O_2 must be very much larger than the concentration of NO at equilibrium. This means that, in a mixture of N_2 and O_2 at this temperature, the amount of NO that is formed is negligible. The reaction hardly proceeds at all towards completion before equilibrium is reached, so the reactants are favoured at equilibrium.

The relationship between the equilibrium constant and the position of equilibrium is summarised in figure 9.5. Consider the reaction:

$$\text{reactant} \rightleftharpoons \text{product}$$

When K_c is very large ($K_c >> 1$), there is a large amount of product and very little reactant in the reaction mixture at equilibrium, so we say *the position of equilibrium lies to the right.* When $K_c \approx 1$, similar

amounts of reactant and product are present at equilibrium. When $K_c << 1$, the reaction mixture contains a large amount of reactant at equilibrium and very little product, so we say *the position of equilibrium lies to the left.*

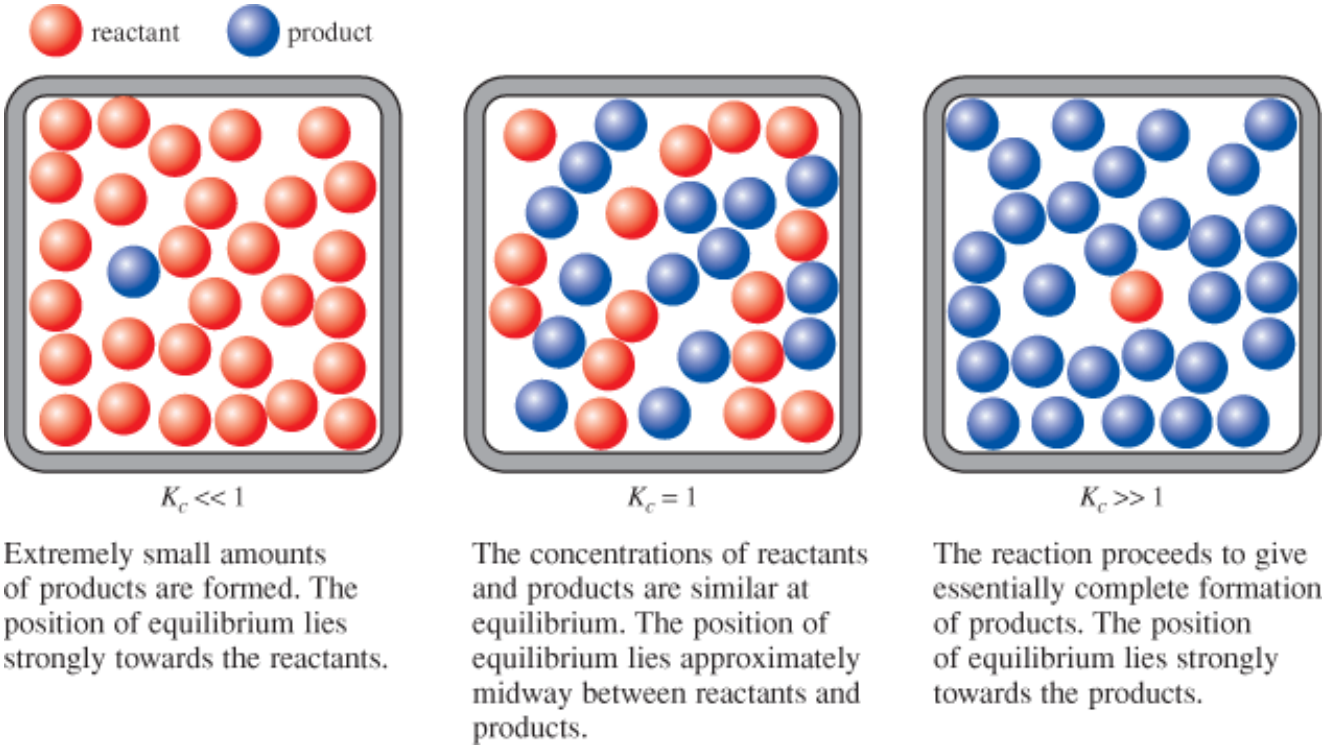


FIGURE 9.5 The magnitude of K_c and the position of equilibrium.

One of the ways that we can use equilibrium constants is to compare the extents to which two or more reactions proceed to completion. Take care in making such comparisons, however, because, unless the K values are greatly different, the comparison is valid *only if both reactions have the same number of reactant and product molecules appearing in their balanced chemical equations*. Note also that the magnitude of the equilibrium constant tells us nothing about how rapidly a system reaches equilibrium. For example, we saw on p. 354 that K_c for the formation of water from H_2 and O_2 is enormous, yet a mixture of H_2 and O_2 is stable almost indefinitely at room temperature. However, once initiated by a spark, the reaction proceeds rapidly to completion with explosive force.

PRACTICE EXERCISE 9.7

Which of the following reactions tends to proceed furthest towards completion?

(a) $CH_4(g) + H_2O(g) \rightleftharpoons CH_3OH(g) + H_2(g) \qquad K_c = 2.8 \times 10^{-21}$

(b) $2NO(g) \rightleftharpoons N_2(g) + O_2(g) \qquad K_c = 2.1 \times 10^{30}$

(c) $2BrCl \rightleftharpoons Br_2 + Cl_2$ (in CCl_4 solution) $\qquad K_c = 0.145$

Equilibrium Constant Expressions for Heterogeneous Systems

In a **homogeneous reaction** — or a **homogeneous equilibrium** — all of the reactants and products are in the same phase. Equilibria among gases are homogeneous because all gases mix freely with each other, so

a single phase exists. There are also many equilibria in which reactants and products are dissolved in the same liquid phase.

When more than one phase exists in a reaction mixture, we call it a **heterogeneous reaction**. A common example is the combustion of wood, in which a solid fuel reacts with gaseous oxygen. Another is the thermal decomposition of sodium bicarbonate (baking soda), which occurs when the compound is sprinkled on a fire:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

Safety-minded cooks keep a box of baking soda nearby because this reaction makes it an excellent fire extinguisher for burning fats or oil. The fire is smothered by the products of the reaction.

Heterogeneous reactions reach equilibrium just as homogeneous reactions do. If $NaHCO_3$ is placed in a sealed container so that no CO_2 or H_2O can escape, the gases and solids come to a **heterogeneous equilibrium**.

$$2NaHCO_3(s) \rightleftharpoons NaCO_3(s) + H_2O(g) + CO_2(g)$$

When we write the equilibrium constant expression for this, and in fact any heterogeneous equilibrium, *we do not include concentrations of pure solids or pure liquids*. Therefore, the equilibrium constant expression becomes:

$$K_c = [H_2O(g)]\,[CO_2(g)]$$

If we consider the reverse reaction:

$$Na_2CO_3(s) + H_2O(g) + CO_2(g) \rightleftharpoons 2NaHCO_3(s)$$

the equilibrium constant expression is:

$$K_c = \frac{1}{[H_2O(g)]\,[CO_2(g)]}$$

The reason we do not include pure solids and pure liquids is that the concentration of a pure liquid or solid is unchangeable at a given temperature. *For any pure liquid or solid at constant temperature, the ratio of amount of substance to volume of substance is constant.* For example, at 25.0 °C and 1.013×10^5 Pa, 1 mole of $NaHCO_3$ will occupy a volume of 38.9 mL and 2 moles of $NaHCO_3$ will occupy twice this volume, 77.8 mL, but the *ratio* of the amount to volume (i.e. the molar concentration) remains the same (figure 9.6).



1 mol $NaHCO_3(s)$

38.9 mL

$$\text{concentration} = \frac{1 \text{ mol } NaHCO_3}{0.0389 \text{ L}} = 25.7 \text{ mol L}^{-1}$$



2 mol $NaHCO_3(s)$

77.8 mL

$$\text{concentration} = \frac{2 \text{ mol } NaHCO_3}{0.0778 \text{ L}} = 25.7 \text{ mol L}^{-1}$$

FIGURE 9.6 The concentration of a substance in the solid state is constant. Doubling the amount also doubles the volume, but the ratio of amount to volume remains the same.

For $NaHCO_3$, the concentration of the solid is:

$$\frac{1 \text{ mol}}{0.0389 \text{ L}} = \frac{2 \text{ mol}}{0.0778 \text{ L}} = 25.7 \text{ mol L}^{-1}$$

This is the concentration of $NaHCO_3$ in the solid, regardless of the size of the solid sample. In other words, the concentration of $NaHCO_3(s)$ is constant, provided there is some of it present in the reaction mixture. Even though neither $NaHCO_3(s)$ nor $Na_2CO_3(s)$ appears in the equilibrium constant expression for the reaction:

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

it is important to realise that some $NaHCO_3(s)$ and $Na_2CO_3(s)$ *must* be present in the reaction mixture in order for equilibrium to be established. In any equilibrium, the presence of *all* reactants and products in the balanced chemical equation is necessary at all times after the reaction is initiated in order for the system to reach equilibrium.

WORKED EXAMPLE 9.5

Writing the Equilibrium Constant Expression for a Heterogeneous Reaction

The air pollutant sulfur dioxide can be removed from a gas mixture by passing it over calcium oxide. The equation for this reaction is:

$$CaO(s) + SO_2(g) \rightleftharpoons CaSO_3(s)$$

Write the equilibrium constant expression for K_c for this reaction.

Analysis

The concentrations of the two solids, CaO and $CaSO_3$, are incorporated into the equilibrium constant, K_c, for the reaction. The only concentration that should appear in the equilibrium constant expression is that of $SO_2(g)$.

Solution

The equilibrium constant expression is simply:

$$K_c = \frac{1}{[SO_2]}$$

Is our answer reasonable?

There is no easy way to check this result without testing it experimentally, but this equilibrium constant expression is typical for reactions that involve solids or liquids. Pure liquids, pure solids and the solvents in dilute solutions are built into the equilibrium constant and do not appear in the equilibrium constant expression.

PRACTICE EXERCISE 9.8

Write the equilibrium constant expression for each of the following heterogeneous reactions.

(a) $2Hg(l) + Cl_2(g) \rightleftharpoons Hg_2Cl_2(s)$

(b) $NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$

(c) $Na(s) + H_2O(l) \rightleftharpoons NaOH(aq) + H_2(g)$

(d) $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$

(e) $CaCO_3(s) + H_2O(l) + CO_2(aq) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$

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9.3 Equilibrium and Gibbs Energy

In chapter 8 we introduced the concept of Gibbs energy. In this section, we will detail the relationship between Gibbs energy and chemical equilibrium.

Gibbs Energy Diagrams

We have seen in chapter 8 that the sign of ΔG tells us the direction of spontaneous change in a chemical or physical system, and in this chapter we have seen that the equilibrium constant, K, gives us a measure of how far a spontaneous process will proceed towards completion. What then is the relationship between Gibbs energy and K? To answer this question, we will first consider phase changes and then look at chemical reactions.

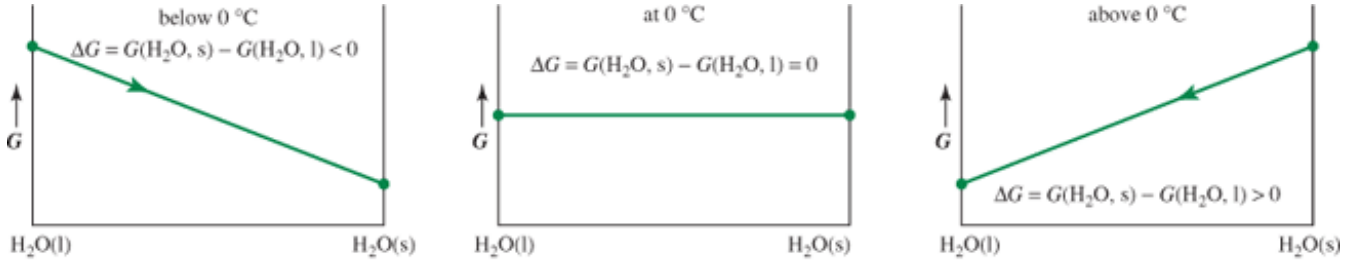
Phase Changes

In a phase change such as $H_2O(l) \rightarrow H_2O(s)$, equilibrium can exist for a given pressure only at one particular temperature; for water at a pressure of 1.013×10^5 Pa (atmospheric pressure), this temperature is 0 °C, the normal freezing point. At other temperatures, the phase change proceeds to completion in one direction or the other. One way to gain a better understanding of this is by studying **Gibbs energy diagrams**, which depict how the Gibbs energy changes as we proceed from the 'reactants' to the 'products'.

Let us consider the phase c hange:

$$H_2O(1) \rightarrow H_2O(s)$$

at three different temperatures: below 0 °C, at 0 °C and above 0 °C. We know, from experience that below 0 °C this process will occur spontaneously, while above 0 °C this process will not occur — in fact, the reverse process will be spontaneous. At 0 °C, we will obtain an equilibrium mixture of ice and water. Why is this? Inspection of the three Gibbs energy diagrams in figure 9.7, which correspond to these three situations, provides an answer. Each diagram shows how the Gibbs energy, G, of the system varies with the composition of the system, from pure liquid water on the left of each diagram to pure solid water (ice) on the right. In each case, $\Delta G$for the phase change $H_2O(l) \rightarrow H_2O(s)$ is equal to $G(H_2O, s) - G(H_2O, l)$.



Gibbs energy decreases in the direction $H_2O(l) \longrightarrow \mathbf{H_2O(s)}$ so the mixture freezes spontaneously to give complete formation of $H_2O(s)$.

Ice–liquid equilibrium can exist for any ratio of solid to liquid. The Gibbs energy is constant across the entire range of compositions of the system.

Gibbs energy decreases in the direction $H_2O(s) \longrightarrow \mathbf{H_2O(1)}$ so the mixture melts spontaneously to give complete formation of $H_2O(1)$.

FIGURE 9.7 Gibbs energy diagrams (not to scale) for the phase change $H_2O(l) \rightleftarrows H_2O(s)$ at 1.013×10^5 Pa. The horizontal axis represents the amount of $H_2O(l)$ and $H_2O(s)$ present. At the left of each diagram the system consists entirely of $H_2O(l)$, while at the right of each diagram only $H_2O(s)$ is present. The green line shows the direction of decreasing G, and hence spontaneous change, in each case.

Below 0 °C, we see that the Gibbs energy of the liquid is higher than that of the solid. You have learned that a spontaneous change occurs if the Gibbs energy can decrease. Therefore, the first diagram tells us that the liquid phase, or any mixture of liquid or solid, below 0 °C freezes until only the solid is present. This is

because the Gibbs energy decreases continuously until all the liquid has frozen. At this point, G is minimised. In other words, ΔG for the reaction $H_2O(l) \rightarrow H_2O(s)$ is negative at this temperature.

Above 0 °C, we have the opposite situation. The Gibbs energy of the solid is greater than that of the liquid. It therefore decreases in the direction of $H_2O(s) \rightarrow H_2O(l)$, and it continues to drop until all the solid has melted. This means that ice, or any mixture of ice and liquid water, above 0 °C continues to melt until only the liquid is present. ΔG for the melting of ice at this temperature is therefore negative.

Above or below 0 °C, the system is unable to establish an equilibrium mixture of liquid and solid. Melting or freezing occurs spontaneously until only one phase is present. However, at 0 °C, the Gibbs energies of both $H_2O(l)$ and $H_2O(s)$ are the same. Therefore, there is no change in Gibbs energy if either melting or freezing occurs, so there is no driving force for either change. Therefore, as long as a system of ice and liquid water is insulated from warmer or colder surroundings, any particular mixture of the two phases is stable and a state of equilibrium exists. Remember that this is a dynamic equilibrium; the ice melts and the water freezes, but both processes occur at the same rate, so no overall change is observed.

Chemical Reactions

The Gibbs energy changes that occur in most chemical reactions are more complex than those in phase changes. As an example, let's study a reaction you've seen before — the decomposition of N_2O_4 into NO_2:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

In our previous discussion of chemical equilibrium, we noted that equilibrium in this system can be approached from *either* direction, with the same equilibrium concentrations being achieved provided we begin with the same overall system composition.

Figure 9.8 shows the Gibbs energy diagram for the reaction. Notice that, in going from reactant to product, the Gibbs energy has a minimum, in contrast to the diagrams in figure 9.7; it drops below that of both pure N_2O_4 and pure NO_2.

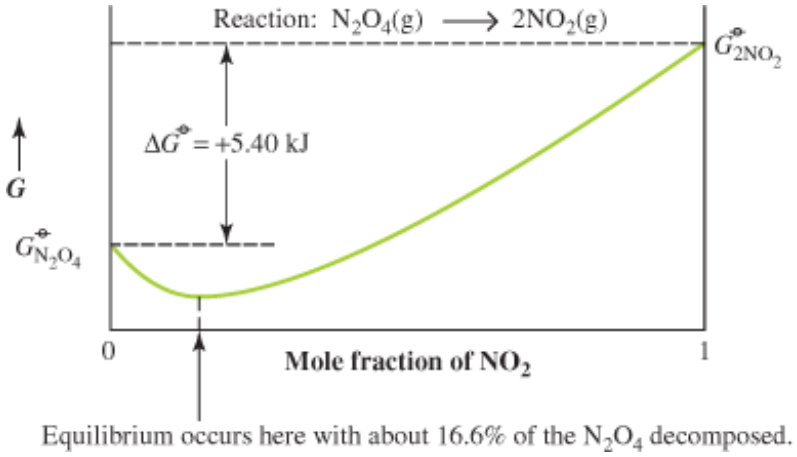


FIGURE 9.8 Gibbs energy diagram for the decomposition of $N_2O_4(g)$. The minimum on the curve indicates the composition of the reaction mixture at equilibrium. Because $\Delta_r G^\ominus$ is positive, the position of equilibrium lies close to the reactants. Not much product forms by the time the system reaches equilibrium.

Why is this? Let's suppose we start with pure $N_2O_4(g)$ and allow the reaction to come to equilibrium. As the reaction proceeds, $NO_2(g)$ molecules start to form, and they mix spontaneously with the remaining $N_2O_4(g)$ molecules so that the reaction mixture is homogeneous at all times. This spontaneous mixing has an associated Gibbs energy change, $\Delta_{mix} G$, that is *negative* at all possible reaction mixture compositions — this simply means that, no matter what the proportions of NO_2 and N_2O_4 are in the reaction mixture, the two

gases *always* mix spontaneously as this leads to an increase in entropy of the system relative to the unmixed gases. Hence, the total Gibbs energy change for the system becomes the Gibbs energy change for the chemical reaction *plus* the Gibbs energy change of mixing. Surprisingly, it is the contribution from $\Delta_{mix} G$ that leads to the minimum in the Gibbs energy diagram (figure 9.9).

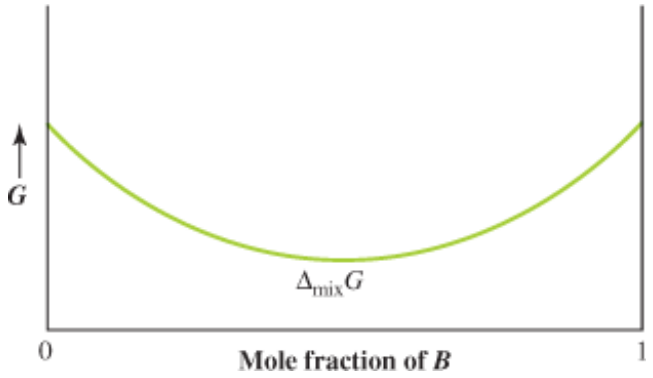


FIGURE 9.9 Gibbs energy diagram for mixing *A*(g) and *B*(g) in the hypothetical reaction *A*(g) → *B*(g). The minimum corresponds to an equimolar mixture of *A*(g) and *B*(g).

If the NO_2(g) molecules formed in the reaction did not mix with the N_2O_4(g) molecules, we would find that the Gibbs energy diagram would simply be a straight line joining $G^{\ominus}_{N_2O_4(g)}$ with $G^{\ominus}_{NO_2(g)}$, similar to that shown on the right of figure 9.7 (H_2O(l) and H_2O(s) are different phases and hence cannot mix). However, when we add the contribution from $\Delta_{mix} G$, we always find that a minimum exists in the Gibbs energy curve, with its position depending primarily on the sign and magnitude of $\Delta_r G^{\ominus}$, the standard Gibbs energy change for the reaction.

We said in the previous chapter that $\Delta G = 0$ at equilibrium. Let's now look at this statement with reference to figure 9.10.

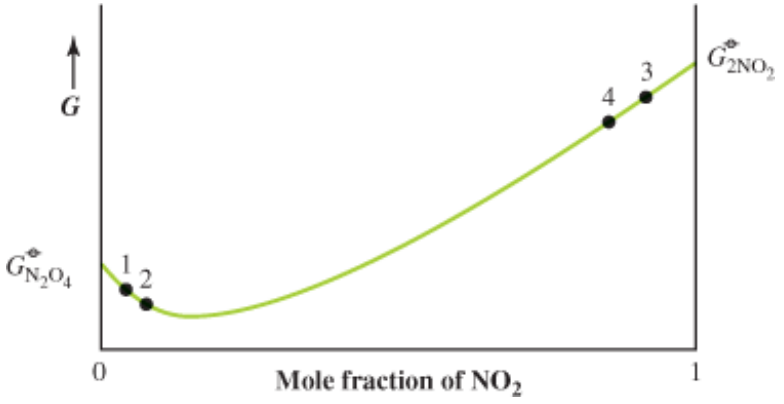


FIGURE 9.10 Gibbs energy diagram for the decomposition of N_2O_4(g). ΔG for any change in composition of the reaction mixture is given by $G_{final} - G_{initial}$.

Again, let us imagine a reaction mixture having the composition indicated by point 1 on the curve and see what happens when the system changes to the composition indicated by point 2. $\Delta_r G$ for this change is $G_2 - G_1$ and is negative — thus, we expect the system at point 1 to undergo a spontaneous reaction to use up N_2O_4(g) and give more NO_2(g). The reverse reaction, where the system at point 2 changes to give the system at point 1 does not occur as $\Delta_r G$ for this change, $G_1 - G_2$, is positive. Similarly, we can see that the system at point 3 changes spontaneously to point 4 as $\Delta_r G$ for this change, $G_4 - G_3$, is negative — in other words, NO_2(g) is consumed and N_2O_4(g) is produced. As we approach the minimum in the curve from either direction, $\Delta_r G$ for any small change in composition of the reaction mixture starts becoming less negative, until, when we reach the minimum, $\Delta_r G$ for any infinitesimally small change in composition of the reaction mixture becomes 0, so the system is at equilibrium. Obviously, when the system has a composition

corresponding to the minimum in the Gibbs energy diagram, $\Delta_r G$ for *any* change in composition is positive, so no change in composition occurs.

It is very important that you appreciate the difference between $\Delta_r G$ and $\Delta_r G^\ominus$ You will notice from figure 9.8 that $\Delta_r G^\ominus$ for the reaction $N_2O_4(g) \rightarrow 2NO_2(g)$ is positive so you might ask why the reaction proceeds in the forward direction at all. To answer this question, we need to remember that $\Delta_r G^\ominus$ is the Gibbs energy change for the conversion of reactants *in their standard state* to products *in their standard state* — in this case, the standard state is the pure gas, each at $p^\ominus$. A sample of $N_2O_4(g)$ at $p^\ominus$ reacts spontaneously to give some $NO_2(g)$; however, the pressure of $NO_2(g)$ at equilibrium is much less than p^ooso $N_2O_4(g)$ predominates in the equilibrium mixture. A more familiar example is the vaporisation of water, for which $\Delta G^\ominus$ is +8.6 kJ mol^{-1} at 25.0 °C. You know from experience that water evaporates spontaneously at 25.0 °C; in this case, the positive value of $\Delta G^\ominus$ simply means that the partial pressure of water never reaches $p^\ominus$ under these conditions when the system is at equilibrium. Similarly, a negative value of $\Delta G^\ominus$ simply means that the products are present in a large amount at equilibrium, but there are also some reactants in the equilibrium mixture. Hence, we can see that the sign of $\Delta_r G^\ominus$ tells us about *the composition of the reaction mixture at equilibrium* $\Delta_r G^\ominus$ should not be used as a criterion of spontaneity *except in the very rare case when the reaction is carried out under standard conditions*. It is the *one of the most important equationssign* of $\Delta_r G$ that tells us whether a particular change in composition of the reaction mixture is spontaneous.

You might also ask why both the forward and reverse reactions occur spontaneously at equilibrium when the fact that $\Delta_r G = 0$ might suggest that no spontaneous reaction should occur. This apparent contradiction is possibly more a matter of semantics than anything else. Although it is customary to talk of the value of $\Delta_r G$ for a particular reaction, it is more correct, and indeed probably more instructive, to talk of $\Delta_r G$ for a particular *change in the composition of the reaction mixture*. When $\Delta_r G$ is negative, it means that the reaction mixture undergoes a spontaneous change such that reactants are used up and more products are formed in order to minimise the Gibbs energy of the system. Likewise, the term ‘spontaneous reaction’ can be confusing — when any system is at dynamic equilibrium, the forward and reverse reactions both occur spontaneously, with their rates being governed by both their respective activation energies and the temperature, as we will see in chapter 15. However, there is no spontaneous change in the *composition of the reaction mixture* at equilibrium, and we are referring to this when we talk about whether a particular ‘reaction’ is spontaneous.

The extent to which a reaction proceeds is very sensitive to the magnitude of $\Delta_r G^\ominus$. If the $\Delta_r G^\ominus$ value for a reaction is reasonably large — about 20 kJ mol^{-1} or more — and positive, almost no observable reaction occurs at room temperature. On the other hand, the reaction eventually goes almost to completion under the same conditions if $\Delta_r G^\ominus$ is both large and negative. From a practical standpoint, then, *the size and sign of* $\Delta_r G^\ominus$ *indicate whether an observable spontaneous reaction occurs.*

WORKED EXAMPLE 9.6

Using $\Delta_r G^\ominus$ as a predictor of the outcome of a reaction

Would we expect to be able to observe formation of products in the following reaction at 25 °C?

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$$

Analysis

We need to determine the magnitude and sign of $\Delta_r G^\circ$ for the reaction. If $\Delta_r G^\circ$ is reasonably large and positive, the reaction won't be observed. If it is reasonably large and negative, we can expect to see the reaction go nearly to completion.

Solution

First, let's calculate $\Delta_r G^\circ$ for the reaction using the data in table 8.6 on p. 329. The procedure is the same as that discussed on pp. 327–8.

$$\begin{aligned}\Delta_r G^\circ &= (\Delta_f G^\circ_{NH_3(g)} + \Delta_f G^\circ_{HCl(g)}) - (\Delta_f G^\circ_{NH_4Cl(s)}) \\ &= [1 \times (-16.7\ \text{KJ mol}^1) + (1 \times (-95.27\ \text{KJ mol}^{-1})] - [1 \times (-203.9\ \text{KJ mol}^{-1})] \\ &= +91.9\ \text{KJ mol}^{-1}\end{aligned}$$

Because $\Delta_r G^\circ$ is large and positive, we expect to observe the spontaneous formation of only extremely small amounts of products at this temperature.

Is our answer reasonable?

Be sure to check the algebraic signs of each term in the calculation.

PRACTICE EXERCISE 9.9

Use the data in table 8.6 to determine whether the reaction:

$$SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$$

should produce measurable amounts of $SO_3(g)$ at 25 °C.

PRACTICE EXERCISE 9.10

Use the data in table 8.6 to determine whether we should expect to see the formation of $CaCO_3(s)$ in the following reaction at 25 °C:

$$CaCl_2(s) + H_2O(g) + CO_2(g) \rightarrow CaCO_3(s) + 2HCl(g)$$

The Relationship Between $\Delta_r G^\circ$ and *K*

In the preceding discussion, we learned in a qualitative way that the position of equilibrium in a reaction is determined by the sign and magnitude of $\Delta_r G^\circ$. We also learned that the direction in which a reaction

proceeds depends on where the system composition stands relative to the minimum on the Gibbs energy curve. Thus, the reaction proceeds spontaneously in the forward direction only if it lowers the Gibbs energy (i.e. if $\Delta_r G$ is negative).

Quantitatively, the relationship between $\Delta_r G$ and $\Delta_r G^\ominus$ is expressed by the following equation, which is derived from the ideal gas equation (chapter 6, p. 216):

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature in kelvin and ln Q is the natural logarithm of the reaction quotient. For gaseous reactions, Q_p is calculated using partial pressures expressed in Pa, while, for reactions in solution, Q_c is calculated from molar concentrations. This equation allows us to predict the direction of the spontaneous change in a reaction mixture if we know $\Delta_r G^\ominus$ and the composition of the mixture, as illustrated in worked example 9.7.

WORKED EXAMPLE 9.7

Determining the Direction of a Spontaneous Reaction

The reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ has $\Delta_r G^\ominus = -5.40\ \text{KJ mol}^{-1}$ at 298 K. At the instant of mixing samples of the two gases, the partial pressure of NO_2 is 0.25×10^5 Pa and the partial pressure of N_2O_4 is 0.60×10^5 Pa. How must the composition of the reaction mixture change to reach equilibrium?

Analysis

Since we know that reactions proceed spontaneously *towards equilibrium*, we are really being asked to determine whether the reaction proceeds spontaneously in the forward or reverse direction. We can calculate $\Delta_r G$ for the forward reaction. If $\Delta_r G$ is negative, the forward reaction is spontaneous. However, if the calculated $\Delta_r G$ is positive, the reverse reaction is spontaneous.

Solution

First, we need the correct form for the reaction quotient expression. Expressed in terms of partial pressures in Pa, this is:

$$Q_p = \frac{\frac{p_{N_2O_4}}{p^\ominus}}{\left(\frac{p_{NO_2}}{p^\ominus}\right)^2}$$

Therefore, the equation we use is:

$$\Delta_r G = \Delta_r G^\ominus + RT \ln \left(\frac{\frac{p_{N_2O_4}}{p^\ominus}}{\left(\frac{p_{NO_2}}{p^\ominus}\right)^2} \right)$$

Next, let's assemble the data:

$$\Delta_r G^\ominus = -5.40\ \text{kJ mol}^{-1} = -5.40 \times 10^3\ \text{J mol}^{-1} \qquad R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$$

$$T = 298\ \text{K} \qquad p_{N_2O_4} = 0.60 \times 10^5 \text{Pa} \qquad p_{NO_2} = 0.25 \times 10^5 \text{Pa} \qquad p^\ominus = 1 \times 10^5\ \text{Pa}$$

Notice that we must change the units of $\Delta_r G^\ominus$ to J mol^{-1} so they are compatible with those of R. Substituting quantities gives:

$$\begin{aligned}
\Delta_r G &= -5.40 \times 10^3\ \text{J mol}^{-1} + \left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\right)(298\ \text{K})\ \ln\left(\frac{\frac{0.60 \times 10^5}{1 \times 10^5}}{\left(\frac{0.25 \times 10^5}{1 \times 10^5}\right)^2}\right) \\
&= -5.40 \times 10^3\ \text{J mol}^{-1} + \left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\right)(298\ \text{K})(2.26) \\
&= -5.40 \times 10^3\ \text{J mol}^{-1} + 5.60 \times 10^3\ \text{J mol}^{-1} \\
&= +20 \times 10^2\ \text{J mol}^{-1}
\end{aligned}$$

Since $\Delta_r G$ is positive, the forward reaction is nonspontaneous so the reverse reaction occurs; to reach equilibrium, the composition of the reaction mixture changes to increase the amount of NO_2 and decrease the amount of N_2O_4.

Is our answer reasonable?

There is no simple check. However, we can check that the energy units in both terms on the right are the same. Notice that here we have changed the units for $\Delta_r G^\ominus$ to J mol^{-1}, to match those of R. Also notice that the temperature is expressed in kelvin, to match the temperature units in R.

PRACTICE EXERCISE 9.11

In which direction will the reaction described in worked example 9.7 proceed to reach equilibrium if the partial pressure of NO_2 is 0.60×10^5 Pa and the partial pressure of N_2O_4 is 0.25×10^5 Pa?

At this point, we have two seemingly separate criteria for determining whether or not a system is at equilibrium. We know that, when $\Delta_r G = 0$ for an infinitesimal change in composition of a reaction mixture, or when $Q = K$ for a particular set of reaction conditions, the system is at equilibrium. We will now substitute these conditions into the equation:

$$\Delta_r G = \Delta_r G^\ominus + RT\ \ln Q$$

If $\Delta_r G = 0$, $Q = K$, and thus:

$$0 = \Delta_r G^\ominus + RT\ \ln K$$

and therefore:

$$\Delta_r G^\ominus = -RT\ \ln K$$

This is one of the most important equations in thermodynamics, if not all of chemistry. It allows us to use tabulated values of $\Delta_r G^{\ominus}$ to calculate the equilibrium constant for a particular reaction, and, conversely, we can use measured values of the equilibrium constant to determine $\Delta_r G^{\ominus}$ for a reaction. K in the reaction as written corresponds to K_p for reactions involving gases and K_c for reactions involving species in solution.

From this equation you can see that, if $\Delta_r G^{\ominus}$ for a reaction is large and negative, ln$K$ is large and positive, and hence K is large — the equilibrium position lies towards products. Similarly, if $\Delta_r G^{\ominus}$ is large and positive, ln$K$ is negative, and hence K is small — the equilibrium position lies towards reactants.

WORKED EXAMPLE 9.8

Equilibrium Constants

The brownish haze associated with air pollution is caused by nitrogen dioxide, NO_2, a red-brown gas (figure 9.11). Nitric oxide, NO, is formed in car engines and some of it escapes into the air, where it is oxidised to NO_2 by oxygen:



FIGURE 9.11 The atmospheric pollutant nitrogen dioxide, NO_2, produces a characteristic brown haze.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The value of K_p for this reaction is 1.7×10^{12} at 25 °C. What is $\Delta_r G^{\ominus}$ for the reaction at this temperature?

Analysis

We can calculate $\Delta_r G^{\ominus}$ from the given value of K_p using the following relationship:

$$\Delta_r G^{\ominus} = -RT\ln K_p$$

We'll need the following data:

$$R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \quad T = 298\ \text{K} \quad K_p = 1.7 \times 10^{12}$$

Solution

Substituting these values into the equation, we have:

$$\begin{aligned}\Delta_r G^{\ominus} &= -(8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}) \ln(1.7 \times 10^{12}) \\ &= -(8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K})(28.16) \\ &= -7.0 \times 10^{4}\ \text{J mol}^{-1} \text{(to two significant figures)}\end{aligned}$$

Expressed in kilojoules per mole, $\Delta_r G^{\ominus} = -70 \times 10^{1}\ \text{kJ mol}^{-1}$.

Is our answer reasonable?

The value of K_p tells us that the position of equilibrium lies far to the right, which means $\Delta_r G^{\ominus}$ must be large and negative. Therefore, the answer, -70 kJ mol^{-1}, seems reasonable.

WORKED EXAMPLE 9.9

Equilibrium Constants

Sulfur dioxide, which is sometimes present in polluted air, reacts with oxygen when it passes over the catalyst in a car's catalytic converter, producing the very acidic oxide SO_3.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$\Delta_r G^{\ominus} = -1.40 \times 10^{2}\ \text{kJ mol}^{-1}$ for this reaction at 25 °C. What is the value of K_p at this temperature?

Analysis

As in worked example 9.8, we use the equation:

$$\Delta_r G^{\ominus} = -RT \ln K_p$$

Our data are:

$R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$ $T = 298\ \text{K}$ $\Delta_r G^{\ominus} = -1.40 \times 10^{2}\ \text{KJ mol}^{-1} = -1.40 \times 10^{5}\ \text{J mol}^{-1}$

To calculate K_p, it is easiest to rearrange the equation and solve for ln K_p.

$$\ln K_p = \frac{-\Delta_r G^{\ominus}}{RT}$$

Solution

Substituting values gives:

$$\ln K_p = \frac{-(-1.40 \times 10^5\ \text{J mol}^{-1})}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}$$
$$= +56.5$$

To calculate K_p, we take the antilogarithm:

$$K_p = e^{56.5}$$
$$= 3 \times 10^{24}$$

Notice that we have expressed the answer to only one significant figure. This is because, as we saw in chapter 2, when taking a logarithm, the number of digits written after the decimal place equals the number of significant figures in the number. Conversely, the number of significant figures in the antilogarithm equals the number of digits after the decimal in the logarithm.

Is our answer reasonable?

The value of $\Delta_r G^\ominus$ is large and negative, so the position of equilibrium should favour the products. The large value of K_p is therefore reasonable.

PRACTICE EXERCISE 9.12

The reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ has $K_p = 6.9 \times 10^5$ at 25.0 °C. Calculate $\Delta_r G^\ominus$ for this reaction.

PRACTICE EXERCISE 9.13

The reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ has $\Delta_r G^\ominus = +3.3\ \text{kJ mol}^{-1}$ at 25.0 °C. What is the value of K_p at this temperature?

We can use thermodynamic data collected at 25 °C to calculate good approximations of the values of equilibrium constants at temperatures other than 25 °C. This is because the values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ do not change much with temperature, so we can use these to calculate $\Delta_r G^\ominus$ and, hence, K at the new temperature.

WORKED EXAMPLE 9.10

calculating *K* at Temperatures Other than 25 °C

Nitrous oxide, N_2O, is an anaesthetic known as laughing gas because it sometimes relieves patients of their inhibitions. The decomposition of nitrous oxide has $K_p = 1.8 \times 10^{36}$ at 25 °C. The equation is:

$$2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$$

For this reaction, $\Delta_r H^\ominus = -163\ \text{kJ mol}^{-1}$ and $\Delta_r S^\ominus = +148\ \text{J mol}^{-1}\ \text{K}^{-1}$. What is the approximate value of K_p for this reaction at 40 °C?

Analysis

We need a value of $\Delta_r G^\ominus$ at 40 °C (313 K), which we can represent as $\Delta_r G^\ominus_{313\ \text{K}}$. We can estimate $\Delta_r G^\ominus_{313\ \text{K}}$ using the values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ measured at 25 °C and the equation $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$. Hence:

$$\Delta_r G^\ominus_{313K} \approx \Delta_r H^\ominus_{298K} - (313\ \text{K})\Delta_r S^\ominus_{298\ \text{k}}$$

Solution

Substituting the values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ provided in the question gives:

$$\Delta_r G^\ominus_{313\ \text{k}} \approx -1.63 \times 10^5\ \text{J mol}^{-1} - (313\ \text{K})\left(+148\ \text{J mol}^{-1}\ \text{K}^{-1}\right)$$

Notice that we have converted kJ mol^{-1} to J mol^{-1}. Performing the arithmetic gives:

$$\Delta_r G^\ominus_{313\ \text{k}} \approx -2.09 \times 10^5 \text{J mol}^{-1}$$

The next step is to use this value of $\Delta_r G^\ominus_{313\ \text{k}}$ to calculate K_p. First, let's solve for ln$K\,p$.

$$\ln K_p = \frac{-\Delta_r G^\ominus_{313\ \text{k}}}{RT}$$

Substituting with R = 8.314 J mol^{-1} K^{-1} and T = 313 K gives:

$$\begin{aligned} \ln K_p &= \frac{2.09 \times 10^5\ \text{J mol}^{-1}}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(313\ \text{K})} \\ &= +80.3 \end{aligned}$$

Taking the antilogarithm: $\begin{aligned} K_p &= e^{80.3} \\ &= 7 \times 10^{34} \end{aligned}$

Notice that, at this higher temperature, $N_2O(g)$ is actually slightly more stable with respect to dissociation into its elements than at 25 °C, as reflected in the slightly smaller value for the equilibrium constant for its decomposition.

Is our answer reasonable?

As we will learn in the next section, the equilibrium constant for an exothermic reaction decreases with increasing temperature. Therefore, the answer is reasonable.

PRACTICE EXERCISE 9.14

The reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ has

a standard enthalpy of reaction of -92.4 kJ mol^{-1} and a standard entropy of reaction of -198.3 J mol^{-1} K^{-1}. Estimate the value of K_p for this reaction at 50 °C.

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9.4 How Systems at Equilibrium Respond to Change

We have seen that the composition of a reaction mixture changes in the direction of decreasing Gibbs energy until it reaches equilibrium. What we have not yet discussed is how a system at equilibrium behaves when a change is made that perturbs the system. Such a change might be a change in temperature, volume or pressure of the system, addition or removal of chemical species to or from the system, or addition of a catalyst. Such knowledge is important as it may allow us to optimise reaction conditions to obtain the maximum amount of a desired product.

Le Châtelier'S Principle

One of the first to study in detail the effect of change on a system at equilibrium was the French chemist Henri Le Châtelier (1850–1936) who proposed what came to be known as **Le Châtelier's principle**. This states that, *if an outside influence upsets an equilibrium, the system undergoes a change in a direction that counteracts the disturbing influence and, if possible, returns the system to equilibrium.* This is often interpreted as meaning that, if a chemical species is added to one side of an equilibrium, the equilibrium position will shift to use up the added species. Le Châtelier's principle is useful as a predictive tool in many circumstances. Consider, for example, the equilibrium:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

for which the forward reaction is exothermic under standard conditions. According to Le Châtelier's principle, addition of $NO_2(g)$ to the reaction mixture at equilibrium will result in the production of more $N_2O_4(g)$, as the equilibrium position will move to the right to use up the added $NO_2(g)$. Using similar reasoning, we can see that addition of $N_2O_4(g)$ to the reaction mixture at equilibrium will result in the production of more $NO_2(g)$. If we take the system on the previous page at equilibrium and increase the volume of the container in which the reaction is occurring, this will have the effect of decreasing the pressure in the container. To counteract this disturbing influence, we would predict, from Le Châtelier's principle, that the equilibrium position will move to the left to produce more $NO_2(g)$, as this will minimise the pressure decrease by maximising the amount of gas in the container. Finally, as the forward reaction is exothermic, it gives out heat, which we can therefore consider as being a 'product' of the reaction; in other words, we can write the equation:

$$2NO_2(g) \rightarrow N_2O_4(g) + \text{heat}$$

If we now take the system at equilibrium and increase its temperature, the equilibrium position will shift to the left to use up the added heat, resulting in the production of more $NO_2(g)$.

However, predictions made on the basis of Le Châtelier's principle can be incorrect if it is not applied correctly; in fact, adding a reactant or product to a system at equilibrium does not necessarily result in a shift of the equilibrium position. For example, addition of AgCl(s) to a saturated aqueous solution of AgCl in equilibrium with excess AgCl(s) does not result in an increase in $[Ag^+(aq)]$ and $[Cl^-(aq)]$ in the solution (we will see the reason why on p. 366). Most importantly, Le Châtelier's principle does not explain *why* the equilibrium position does or does not change on perturbation of the equilibrium. Therefore, it is better to consider the perturbation of systems at equilibrium by comparison of the values of the equilibrium constant, K, and the reaction quotient, Q, for a particular chemical process. We start with a system at equilibrium for which $Q = K$. We then perturb the system and consider how this alters the value of Q and how the system must alter to make Q again equal to K. We will consider a number of different scenarios using this method.

Adding or Removing a Product or Reactant

The addition or removal of a product or reactant instantaneously alters the concentration of that species in the reaction mixture, provided that the reactant or product in question is not a pure solid or liquid. When this happens, the value of Q changes so that $Q \neq K$ and the system is no longer at equilibrium. We will illustrate this using the equilibrium:

$$\underset{\text{blue}}{[Cu(H_2O)_4]^{2+}(aq)} + 4Cl^-(aq) \rightarrow \underset{\text{yellow}}{[CuCl_4]^{2-}(aq)} + 4H_2O(l)$$

$[Cu(H_2O)_4]^{2+}$ is blue and $[CuCl_4]^{2-}$ is yellow; mixtures of the two have an intermediate colour and, therefore, appear blue-green, as illustrated in figure 9.12.

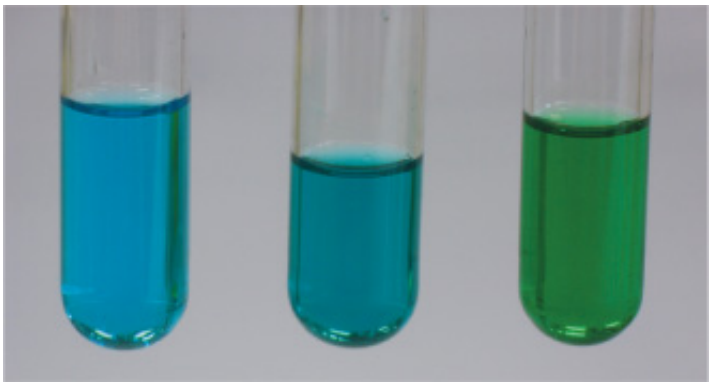


FIGURE 9.12 The effect of concentration changes on the position of equilibrium. The solution in the centre contains a mixture of blue $[Cu(H_2O)_4]^{2+}$ and yellow $[CuCl_4]^{2-}$, so it has a blue-green colour. The tube on the right contains some of the same mixture after the addition of concentrated HCl. It has a more pronounced green colour because the equilibrium is shifted towards $[CuCl_4]^{2-}$. At the left is some of the original mixture after removal of some Cl^- as insoluble AgCl and subsequent filtering. It is blue because the equilibrium has shifted towards $[Cu(H_2O)_4]^{2+}$.

What happens when we increase the chloride ion concentration by adding a small volume of a concentrated aqueous solution of HCl to the solution at equilibrium? To answer this question, we need to write the expression for Q, the reaction quotient. Recalling from the section on heterogeneous systems (p. 356) that H_2O does not appear in the expression for Q because it is a pure liquid, we can write:

$$Q = \frac{[CuCl_4{}^{2-}]}{[Cu(OH_2)_4{}^{2+}][Cl^-]^4}$$

Only reactants and products that appear in the expression for Q can influence the position of the equilibrium. We can see that, immediately after adding the HCl solution, the $[Cl^-]$ of the solution increases. This has the effect of *decreasing* the value of Q, because $[Cl^-]$ appears on the bottom line of the quotient. Thus, we now have the situation where the solution is no longer at equilibrium and $Q < K$. Obviously, to restore equilibrium, we must alter the concentrations of the reactants and products to increase Q so that it again equals K (remember that K is a constant at constant temperature, so we must alter the value of Q). With reference to the expression for Q, there are two ways that we can increase its value; we can make the top line larger, by increasing the amount and, therefore, concentration of $[CuCl_4]^{2-}$, or we can make the bottom line smaller, by decreasing the amounts and, therefore, concentrations of $[Cu(OH_2)_4]^{2+}$ and Cl^-. These, in fact, equate to the same thing — a shift of the equilibrium position towards *products*. The pronounced green colour of the solution at the right of figure 9.12 shows that this is in fact what happens; there is more yellow $[CuCl_4]^{2-}$ and less blue

$[Cu(OH_2)_4]^{2+}$ present in the solution after the system re-establishes equilibrium following addition of concentrated HCl(aq).

We can use the same reasoning to predict the effect of removing a reactant from the system. If we take the system at equilibrium and add a small volume of a concentrated solution of silver perchlorate, $AgClO_4$, the Ag^+ ions react with free Cl^- ions to form insoluble AgCl(s), thus effectively removing Cl^- ions from the mixture. Again, looking at our expression for *Q*, we can see that lowering $[Cl^-]$ makes the bottom line of the quotient smaller, which leads to an instantaneous *increase* in the value of *Q*. The system is no longer at equilibrium, and *Q* is greater than *K*. The concentrations of reactants and products must, therefore, change to *decrease* the value of *Q* so that it again is equal to *K*. This may be achieved by either decreasing the top line of the quotient (lowering the amount and, therefore, concentration of $[CuCl_4]^{2}$–) or increasing the bottom line (increasing the amounts and, therefore, concentrations of $[Cu(OH_2)_4]^{2+}$ and Cl^-). Again, figure 9.12 shows that the colour of the solution becomes more blue following removal of some Cl^- as insoluble AgCl (and subsequent filtering), consistent with the production of more $[Cu(OH_2)_4]^{2+}$.

The treatment on p. 365 is purely qualitative but allows us to predict the manner in which an equilibrium shifts *without having to know the actual values of K and Q*.

An important example already alluded to (p. 365) is that of a sparingly soluble ionic salt in equilibrium with its constituent aqueous ions. Consider, for instance, a saturated aqueous solution of silver chloride, AgCl, in the presence of solid AgCl. The balanced chemical equation for this is:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

and we write the reaction quotient as:

$$Q = [Ag^+][Cl^-]$$

Note that pure solids and pure liquids do not appear in the expressions for either *K* or *Q*. What would be the effect of adding more solid AgCl to the equilibrium mixture? AgCl(s) does not appear in the expression for *Q* so addition of AgCl(s) has *no effect* on the position of equilibrium. Le Châtelier's principle can lead to incorrect predictions in problems of this type (in this case, it would predict an increase in $[Ag^+]$ and $[Cl^-]$), and it is preferable to use the comparison of *Q* and *K* to determine the effect of adding or removing reactants or products.

We will see more of these sorts of problems in chapter 10.

Changing the Pressure in Gaseous Reactions

There are two ways of changing the total pressure in a gaseous reaction mixture at equilibrium:

- changing the volume of the system
- adding an inert gas.

We will look at these in turn.

Changing the Volume of the System

Changing the volume of a gas mixture at equilibrium changes both the concentrations and partial

pressures of the reactant and product gases, thereby altering Q. Increasing the volume will decrease the partial pressures of all gases and therefore decrease the total pressure, whereas decreasing the volume will have the opposite effect. We will consider the effect of increasing the volume of the reaction vessel on the equilibrium position for the formation of ammonia from nitrogen and hydrogen:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

For this reaction, we would normally write Q_p as:

$$Q_p = \frac{\left(\frac{p_{NH_3}}{p^{\ominus}}\right)^2}{\left(\frac{p_{N_2}}{p^{\ominus}}\right)\left(\frac{p_{H_2}}{p^{\ominus}}\right)^3}$$

However, in this case, it is more convenient to use Q_c to determine the effect of changing the volume of the reaction mixture. Hence, we can write:

$$Q_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

Remembering that $c = \frac{n}{V}$, we can rewrite this as:

$$Q_c = \frac{\frac{(n_{NH_3})^2}{V^2}}{\frac{n_{N_2}}{V} \times \frac{(n_{H_2})^3}{V^3}}$$

As $\frac{n}{V}$ is the same as nV^{-1}, we can simplify this expression as follows:

$$\begin{aligned} Q_c &= \frac{\frac{(n_{NH_3})^2}{V^2}}{\frac{n_{N_2}}{V} \times \frac{(n_{H_2})^3}{V^3}} \\ &= \frac{(n_{NH_3})^2 V^{-2}}{(n_{N_2})V^{-1} \times (n_{H_2})^3 V^{-3}} \\ &= \frac{(n_{NH_3})^2}{(n_{N_2})(n_{H_2})^3} \times \frac{V^{-2}}{V^{-4}} = \frac{(n_{NH_3})^2}{n_{H_2}(n_{H_2})^3} \times V^2 \end{aligned}$$

While this may look somewhat daunting, the important point is that we have shown that Q_c *is proportional to* V^2 — in other words, when we increase V, we increase Q. Using the same reasoning as on p. 366, we can say that increasing the volume of the reaction vessel, V, will increase Q, making $Q > K$. The system will then change in a way that makes Q smaller: that is, making the top line of the quotient smaller by reducing n_{NH3} or making the bottom line larger by increasing n_{N2} and n_{H2}. This means that, when the volume of the reaction mixture is increased, the reaction mixture composition shifts towards reactants, resulting in the production of more N_2 and H_2. Increasing the volume of the reaction vessel in gas phase reactions which have a larger number of reactant molecules than product molecules will always result in a shift of the reaction mixture composition towards reactants.

If we consider the equilibrium:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

a similar treatment to that above shows that:

$$\begin{aligned} Q_c &= \frac{\frac{(n_{HI})^2}{V^2}}{\frac{n_{H_2}}{V} \times \frac{n_{I_2}}{V}} \\ &= \frac{(n_{HI})^2 V^{-2}}{n_{H_2} V^{-1} \times n_{I_2} V^{-1}} \\ &= \frac{(n_{HI})^2}{n_{H_2} n_{I_2}} \times \frac{V^{-2}}{V^{-2}} = \frac{(n_{HI})^2}{n_{H_2} n_{I_2}} \end{aligned}$$

In this case, Q_c *does not depend on V*. Thus, increasing or decreasing the volume of this reaction mixture has *no effect* on the position of the equilibrium. This is always the case when there is the same amount of gas on each side of the equation in a gas phase reaction.

The final example uses the familiar equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

To look at the effect of increasing the volume of the system at equilibrium, we use the same treatment as above to give:

$$\begin{aligned} Q_c &= \frac{\frac{(n_{NO_2})^2}{V^2}}{\frac{n_{N_2O_4}}{V}} \\ &= \frac{(n_{NO_2})^2 V^{-2}}{n_{N_2O_4} V^{-1}} \\ &= \frac{(n_{NO_2})^2}{n_{N_2O_4}} \times \frac{V^{-2}}{V^{-1}} = \frac{(n_{NO_2})^2}{n_{N_2O_4}} \times \frac{1}{V} \end{aligned}$$

and we can see that Q_c *is proportional to the inverse of V* — in other words, as the volume increases, Q_c decreases so $Q < K$. To re-establish equilibrium, the system will respond to increase Q: that is, making the top line of the quotient larger by increasing n_{NO_2} or making the bottom line smaller by decreasing $n_{N_2O_4}$. Both scenarios correspond to an equilibrium shift towards products following an increase in volume of the reaction mixture. Increasing the volume of the reaction vessel in gas phase reactions which have a larger number of product molecules than reactant molecules will always result in a shift of the equilibrium towards products.

In summary, we have shown that Q_c is proportional to $V^{-\Delta ng}$, where Δn_g is defined the same way as on p. 351, namely as the number of moles of gaseous products minus the number of moles of gaseous reactants. Knowing this proportionality allows us to determine the effect of changing the volume of the reaction vessel on any system at equilibrium.

Adding an Inert Gas at Constant Volume

Adding an inert gas (which, by definition, is unreactive) to a gaseous reaction mixture at equilibrium increases the total pressure of the system, but *does not alter the position of equilibrium*. To prove this, let's consider adding the inert gas helium to the N_2O_4/NO_2 equilibrium mixture. As helium does not react with either the reactant or product, our expressions for both Q_c and Q_p for this equilibrium remain

unchanged in the presence of helium. Hence, as there is no term for [He] or p_{He} in Q_c or Q_p, respectively, addition of helium *cannot have any effect on the position of equilibrium*as it cannot alter the value of Q. This is true in all cases where the total pressure of the reaction mixture is altered by addition of an inert gas.

Changing the Temperature of a Reaction Mixture

The value of the equilibrium constant, K, for any reaction can be changed only by altering the temperature of the reaction mixture. We can predict the effect of changing the temperature of a reaction mixture at equilibrium from the sign of $\Delta_r H^\ominus$ for the forward reaction. The **van't Hoff equation**. (figures 9.13 and 9.14) states:



FIGURE 9.13 Jacobus Henricus van't Hoff (1852–1911), a Dutch chemist, was the first winner of the Nobel Prize in chemistry in 1901 for his significant contributions to chemical thermodynamics. However, possibly his most remarkable achievement was in organic chemistry, with his realisation that carbon atoms bearing four attached atoms adopt a tetrahedral, rather than a square planar, arrangement. What made this so remarkable was that he published this work at the age of 22 — not much older than most of you reading this.

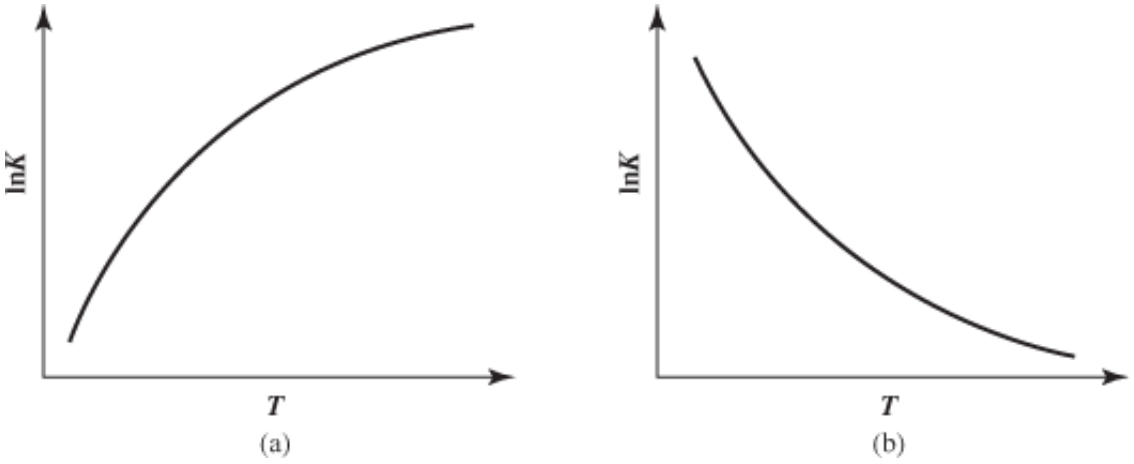


FIGURE 9.14 Plots of ln$K$ versus T for situations where $\Delta_r H^\ominus$ is **(a)** positive and **(b)** negative.

$$\frac{\mathrm{d}\ \ln k}{\mathrm{d}T} = \frac{\Delta_r H^\ominus}{RT^2}$$

and this means that the slope of the plot of ln$K$ versus T has the same sign as that of $\Delta_r H^\ominus$. For example,

the reaction of nitrogen and hydrogen to form ammonia is exothermic:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta_r H^\ominus = -92.38\ \text{kJ mol}^{-1}$$

so the graph of ln*K* versus *T* should have a negative slope. This means that, as we increase the temperature, ln*K*, and hence *K*, should *decrease*. Thus, the production of ammonia becomes less favourable as we increase the temperature of the reaction mixture. We can make the following generalisations about the effect of temperature changes on the position of equilibrium:

- For an *endothermic* reaction ($\Delta_r H$ is positive), increasing the temperature *increases* the equilibrium constant, so products are favoured (figure 9.14a).
- For an *exothermic* reaction ($\Delta_r H$ is negative), increasing the temperature *decreases* the equilibrium constant, so reactants are favoured (figure 9.14b).

Figure 9.15 demonstrates the temperature dependence of the equilibrium involving complexes of Cu^{2+} discussed previously (p. 365), for which the forward reaction is endothermic. Cooling the reaction mixture *decreases* the equilibrium constant, giving a shift towards the re actants; heating the mixture *increases* the equilibrium constant, so more product is formed.



FIGURE 9.15 The effect of temperature on the equilibrium $[Cu(H_2O)_4]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 4H_2O$ The tube in the centre shows an equilibrium mixture of the two complexes. When the solution is cooled in ice (left), the equilibrium shifts towards the blue $[Cu(H_2O)_4]^{2+}$. When heated in boiling water (right), the equilibrium shifts towards the yellow $[CuCl_4]^{2-}$. This behaviour indicates that the reaction is endothermic in the forward direction.

This illustrates the qualitative use of the van't Hoff equation. We can also use it quantitatively; if we know the value of an equilibrium constant, *K*, at a particular temperature, T_1, we can use the following form of the van't Hoff equation to determine the value of the equilibrium constant at another temperature, T_2:

$$\ln K_{T_2} - \ln K_{T_1} = \frac{-\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This assumes that $\Delta_r H^\ominus$ is constant over the temperature range T_1 to T_2.

Addition of a Catalyst

Catalysts are substances that affect the rates of chemical reactions without actually being used up. While addition of a catalyst helps bring a system to chemical equilibrium more rapidly, the pos ition of equilibrium is not affected. This is because catalysts are not included in the overall balanced chemical equation for the reaction, and so do not appear in the expression for the reaction quotient, *Q*.

WORKED EXAMPLE 9.11

Predicting Equilibrium Shifts

The reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is endothermic, with $\Delta_r H^\ominus = +56.9\ \text{kJ mol}^{-1}$. If we start with an equilibrium mixture of $N_2O_4(g)$ and $NO_2(g)$, how is the amount of NO_2 in the mixture affected by (a) adding N_2O_4, (b) lowering the pressure by increasing the volume of the container, (c) raising the temperature and (d) adding a catalyst to the system? Which of these changes alters the value of K_c?

Analysis

We are taking an equilibrium mixture of $N_2O_4(g)$ and $NO_2(g)$ and making various changes to the system. We must determine, via comparison of Q and K, whether these changes alter the equilibrium position and, therefore, how this affects the amount of $NO_2(g)$.

Solution

To answer these questions, first write the expression for Q and then use it to determine the effect of the change made:

$$Q_c = \frac{[NO_2]^2}{[N_2O_4]}$$

(a) Adding $N_2O_4(g)$ instantaneously decreases Q_c so $Q_c < K_c$. To make $Q_c = K_c$, the equilibrium shifts to the right to increase Q_c, resulting in the production of more $NO_2(g)$. The amount of $NO_2(g)$ *increases*.

(b) We have seen on pp. 366–8 that increasing the volume of the container reduces Q_c because Q_c is inversely proportional to V. Hence, to make $Q_c = K_c$, the equilibrium shifts to the right to increase Q_c, resulting in the production of more $NO_2(g)$. The amount of $NO_2(g)$ *increases*.

(c) The forward reaction is endothermic, meaning that $\Delta_r H^\ominus$ is positive; by applying the van't Hoff equation, a plot of ln$K$ c versus T has a positive slope. Thus ln$K$ c, and there-fore K_c, increases with increasing temperature, so $Q_c < K_c$. To make $Q_c = K_c$, Q_c must increase, resulting in the production of more $NO_2(g)$ at equilibrium. The amount of $NO_2(g)$ *increases*.

(d) As stated above, a catalyst can have no effect on the position of equilibrium. The amount of $NO_2(g)$ remains unchanged.

Finally, the only change that alters K_c is a change in temperature.

Is our answer reasonable?

Compare each of our answers with examples given in this section to confirm that they are logically consistent.

PRACTICE EXERCISE 9.15

Consider the equilibrium $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, for which $\Delta_r H^\circ = -88\ \text{kJ mol}^{-1}$. How is the amount of Cl_2 at equilibrium affected by (a) adding PCl_3, (b) adding PCl_5, (c) raising the temperature and (d) decreasing the volume of the container? How (if at all) does each of these changes affect K_p for the reaction?

Chemical Connections

Air Pollution and Equilibrium

Cars are one of the most serious sources of air pollution (figure 9.16). Every moment a car engine runs, potentially harmful compounds such as carbon monoxide, CO, carbon dioxide, CO_2, and a number of nitrogen oxides leave its engine as exhaust gases.



FIGURE 9.16 Air pollution from car exhaust emissions can pose a health hazard. This can be particularly severe in large cities where heavy traffic and atmospheric conditions can combine to produce dangerous levels of smog.

When air is drawn into a car's engine, both N_2 and O_2 are present. During combustion of the petrol or diesel, oxygen reacts with the hydrocarbons in the fuel to produce CO_2 through complete combustion, CO through incomplete combustion, and H_2O. However, N_2 and O_2 can also react to form nitric oxide, NO, at these elevated temperatures, according to the equation:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Although nitric oxide is an important biological molecule (it is involved in signalling in the body), it also reacts rapidly with oxygen in the atmosphere to form the toxic brown gas nitrogen dioxide, NO_2. At room temperature, K_c for the formation of NO from N_2 and O_2 is 4.8×10^{-31}. Its small value tells us that the

equilibrium concentration of NO should be very small. Therefore, we don't find N_2 reacting with O_2 under ambient conditions.

The reaction of N_2 and O_2 to form NO is endothermic. The van't Hoff equation (p. 368) tells us that at high temperatures, such as those found in the cylinders of a petrol or diesel engine during combustion, this equilibrium should be shifted to the right, and some NO does indeed form at high temperatures. Unfortunately, when the exhaust gases leave the engine, they cool so rapidly that the reaction rate becomes too slow for the NO to decompose back to N_2 and O_2. As a result, some NO is present among the exhaust gases. Once in the atmosphere, this NO reacts with oxygen to give NO_2, which is responsible for the brownish haze often associated with severe air pollution.

Various methods have been devised to minimise the amount of nitrogen oxides that enter the atmosphere. For instance, almost all modern cars are equipped with catalytic converters. These devices catalyse the decomposition of nitrogen oxides to N_2 and O_2. Catalytic converters are expensive, however, as the catalysts used in these are based on precious metals such as platinum, palladium and rhodium. Other methods of accomplishing the same goals are being studied.

One way to reduce the amount of NO_2 pollution of the atmosphere is to reduce the amount of NO that is formed in car engines. Since the extent to which the reaction proceeds towards the formation of NO increases as the temperature increases, the amount of NO formed can be reduced simply by running the combustion reaction at a lower temperature. This can be accomplished by lowering the compression ratio of the engine; this is the ratio between the volume of the cylinder when the piston is at the bottom of its stroke and its volume after the piston has compressed the air–fuel mixture. At high compression ratios, the air–fuel mixture is heated to a high temperature before it is ignited. After combustion, the gases are very hot, which favours the production of NO. Lowering the compression ratio lowers the maximum combustion temperature, which decreases the tendency for NO to be formed. Unfortunately, lowering the compression ratio also lowers the efficiency of the engine, which reduces fuel economy.

Another method for controlling NO emissions that has been trialled is to mix water with the air–fuel mixture. Some of the heat from the combustion is absorbed by the water vapour, so the mixture of exhaust gases does not get as hot as it would otherwise. At these lower temperatures, the concentration of NO in the exhaust is greatly reduced.

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9.5 Equilibrium Calculations

You have seen that the magnitude of an equilibrium constant gives us some feel for the composition of a reaction mixture at equilibrium. Sometimes, however, it is necessary to have more than merely a qualitative knowledge of equilibrium concentrations. This requires that we be able to use the equilibrium constant expression for quantitative calculations.

Equilibrium calculations for gaseous reactions can be performed using either K_p or K_c, but for reactions in solution we must use K_c. Whether we deal with concentrations or partial pressures, however, the same basic principles apply.

Overall, we can divide equilibrium calculations into two main categories:

1. calculating equilibrium constants from known equilibrium concentrations or partial pressures
2. calculating one or more equilibrium concentrations or partial pressures using a known value of K_c or K_p, given initial concentrations of reactants and products.

Calculating K_c from Equilibrium Concentrations

One way to determine the value of K_c is to carry out the reaction, measure the concentrations of reactants and products after equilibrium has been reached, and then substitute these equilibrium values into the equilibrium constant expression to calculate K_c. As an example, let's look again at the decomposition of N_2O_4:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

In section 9.2, we saw that, if 0.0350 mol of N_2O_4 is placed into a 1 L flask at 25 °C, the concentrations of N_2O_4 and NO_2 at equilibrium are:

$$[N_2O_4] = 0.0292 \text{ mol L}^{-1}$$
$$[NO_2] = 0.0116 \text{ mol L}^{-1}$$

To calculate K_c for this reaction, we substitute the equilibrium concentrations into the equilibrium constant expression:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0116)^2}{0.0292}$$

Therefore:

$$K_c = 4.61 \times 10^{-3}$$

Although calculating an equilibrium constant in this way is usually straightforward, sometimes we have to do some stoichiometric manipulations, as shown in worked example 9.12. This example introduces the use of a **concentration table**, an extremely useful tool for solving equilibrium problems.

WORKED EXAMPLE 9.12

Calculating K_c from Equilibrium Concentrations

At a certain temperature, a mixture of H_2 and I_2 was prepared by placing 0.200 mol of H_2 and 0.200 mol of I_2 into a 2.00 L flask. After a period of time, the equilibrium:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

was established. The purple colour of the I_2 vapour was used to monitor the reaction, and it was determined that, at equilibrium, the I_2 concentration had dropped to 0.020 mol L^{-1}. What is the value of K_c for this reaction at this temperature?

Analysis

The first step in any equilibrium problem is to write the balanced chemical equation and the equilibrium constant expression. The equation is already given, and its corresponding equilibrium constant expression is:

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

To calculate the value of K_c, we must substitute the *equilibrium concentrations* of H_2, I_2 and HI into the equilibrium constant expression. But what are they? We have been given only one directly, the value of $[I_2]$. To obtain the others, we have to do some stoichiometric calculations.

The system starts with a set of initial concentrations, and a chemical change occurs to reach equilibrium. There is no HI present initially, so the reaction above must proceed to the right, because there has to be some HI present for the system to be at equilibrium. This change increases the HI concentration and decreases the concentrations of H_2 and I_2. If we can determine what the *changes* are, we can calculate the equilibrium concentrations. In fact, the key to solving almost all equilibrium problems is determining how the concentrations change as the system comes to equilibrium.

To help us in our analysis, we will construct a concentration table beneath the chemical equation. We will do this for most of the equilibrium problems we encounter from now on, so let's examine the general form of the table.

In the first row, we write the initial *molar concentrations* of the reactants and products. (Strictly speaking, we should use amounts, rather than concentrations, in these calculations. However, as long as the system remains at constant volume, the calculations will be the same, regardless of whether we use amounts or concentrations.) In the second row, we enter the changes in concentration, using a positive sign if the concentration is increasing and a negative sign if it is decreasing. Finally, adding the changes to the initial concentrations gives the equilibrium concentrations:

$$\begin{pmatrix}\text{equilibrium}\\ \text{concentration}\end{pmatrix} = \begin{pmatrix}\text{initial}\\ \text{concentration}\end{pmatrix} + \begin{pmatrix}\text{change in}\\ \text{concentration}\end{pmatrix}$$

To set up the concentration table, it is essential that you realise that the changes in concentration must be in the same ratio as the coefficients of the balanced equation. This is because the changes are caused by the chemical reaction proceeding in one direction or the other. In this problem, the coefficients of H_2 and I_2 are the same, so, as the reaction proceeds to the right, the concentrations of H_2 and I_2 must decrease by the *same* amount. Similarly, because the coefficient of HI is twice that of H_2 or I_2, the concentration of HI must increase by *twice* as much. Now, let's look at the finished concentration table, how the individual entries are obtained and the solution to the problem.

Solution

To construct the concentration table, we begin by entering the data given in the statement of the problem. These are shown in the row labelled 'Initial concentration'. The other values are then derived as described below. Note that, in all concentration tables, we will highlight the known concentration data.

	$H_2(g)$	+	**$I_2(g)$**	$\rightleftharpoons$	**2HI(g)**
Initial concentration (mol L^{-1})	0.100		0.100		0
Change in concentration (mol L^{-1})	-0.080		-0.080		+2 × (0.080)
Equilibrium concentration (mol L^{-1})	0.020		0.020		0.160

Initial concentration: Notice that we have calculated the ratio of amount to volume for both H_2 and I_2, i.e. 0.200 mol/2.00 L = 0.100 m. Because no HI was placed into the reaction mixture, its initial concentration has been set to exactly 0 at the instant of mixing H_2 and I_2. *Change in concentration:* We have been given both the initial and equilibrium concentrations of I_2, so, by difference, we can calculate the change for I_2 (-0.080 m). The other changes are then calculated from the mole ratios specified in the chemical equation. As noted above, because H_2 and I_2 have the same coefficients (i.e. 1), their changes are equal. The coefficient of HI is 2, so its change must be twice that of I_2. Reactant concentrations decrease, so the change is negative, while product concentrations increase, so the change in HI concentration is positive.

*Equilibrium concentration:*For H_2 and HI, we just add the change to the initial value.

Now we can substitute the equilibrium concentrations into the equilibrium constant expression and calculate K_c.

$$\begin{aligned} K_c &= \frac{[HI]^2}{[H_2]\,[I_2]} \\ &= \frac{(0.160)^2}{(0.020)(0.020)} \\ &= 64 \end{aligned}$$

Is our answer reasonable?

First, carefully examine the equilibrium constant expression. As always, products must be placed in the numerator and reactants in the denominator. Be sure that each exponent corresponds to the correct coefficient in the balanced chemical equation for the reaction.

Now check the concentration table. Notice that the changes for both reactants have the same sign, and this sign is the opposite of that of the product. This relationship between the signs of the changes is always true and can serve as a useful check when you construct a concentration table.

Finally, check that each of the equilibrium concentrations is properly placed in the equilibrium constant expression. The equilibrium constant we obtained is greater than 1. That implies that a significant amount of product should be present at equilibrium, and examination of the concentration table shows that this is so.

The Concentration Table — a Summary

Let us review some key points that apply not only to worked example 9.12 but also to others that deal with equilibrium calculations.

1. The only values that we can substitute into the equilibrium constant expression are equilibrium concentrations — the values that appear in the last row of the table.
2. When we enter initial concentrations into the table, they should be in units of moles per litre (mol L^{-1}). The initial concentrations are those present in the reaction mixture when it is prepared; we imagine that no reaction occurs until everything is mixed.
3. The changes in concentrations *always* occur in the same ratio as the coefficients in the balanced equation. For example, if we are dealing with the equilibrium:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

and we find that the $N_2(g)$ concentration decreases by 0.10 M during the approach to equilibrium, the entries in the 'Change in concentration' row would be as follows:

	$3H_2(g)$	+	$N_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Change in concentration (mol L^{-1})	-3×(0.10) = -0.30		1×(0.10) = -0.10		+2×(0.10) =+0.20

4. In constructing the 'Change in concentration' row, be sure that the reactant concentrations all change in the same direction and that the product concentrations all change in the opposite direction. If the concentrations of the reactants decrease, all the entries for the reactants in the 'Change in concentration' row should have a negative sign and all the entries for the products should be positive.

Keep these points in mind as we construct the concentration tables for other equilibrium problems.

PRACTICE EXERCISE 9.16

The water-gas shift reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

is used in industry to prepare hydrogen. At equilibrium, the following concentrations were found for this reaction at 500 °C: [CO] = 0.180 M, $[H_2O]$ = 0.0411 M, $[CO_2]$ = 0.150 M and $[H_2]$ = 0.200 M. What is the value of K_c for this reaction?

PRACTICE EXERCISE 9.17

In a particular experiment, it was found that, when $O_2(g)$ and CO(g) were mixed, they reacted according to the equation:

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

and the O_2 concentration had decreased by 0.030 mol L^{-1} when the reaction reached equilibrium. How had the concentrations of CO and CO_2 changed?

PRACTICE EXERCISE 9.18

A student placed 0.200 mol of $PCl_3(g)$ and 0.100 mol of $Cl_2(g)$ into a 1.00 L container at 250 °C. After the reaction:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

came to equilibrium, it was found that the container contained 0.120 mol of PCl_3.

(a) What were the initial concentrations of the reactants and product?

(b) By how much had the concentrations changed when the reaction reached equilibrium?

(c) What were the equilibrium concentrations?

(d) What is the value of K_c for this reaction at

this temperature?

Calculating Equilibrium Concentrations from Initial Concentrations

A more complex type of calculation involves the use of initial concentrations and K_c to calculate equilibrium concentrations. Although some of these problems can be so complicated that a calculator is needed to solve them, we can learn the general principles involved by working on simple calculations. Even these, however, require a little applied algebra. This is where the concentration table can be very helpful.

WORKED EXAMPLE 9.13

Using K_c to Calculate Equilibrium Concentrations — 1

The water-gas shift reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

has K_c = 4.06 at 500 °C. If 0.100 mol of CO and 0.100 mol of H_2O(g) are placed in a 1.00 L reaction vessel at this temperature, what are the concentrations of the reactants and products when the system reaches equilibrium?

Analysis

The key to solving this kind of problem is recognising that, at equilibrium:

$$K_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = 4.06$$

We must find values for the concentrations that satisfy this condition.

Because we don't know what these concentrations are, we represent them algebraically as unknowns. This is where the concentration table is very helpful. To build the table, we need quantities to enter into the ‘Initial concentration’, ‘Change in concentration’ and ‘Equilibrium concentration’ rows.

Initial concentration: The initial concentrations of CO and H_2O are both 0.100 mol L^{-1} = 0.100 m. Since no CO_2 or H_2 is initially placed into the reaction vessel, their initial concentrations are both exactly 0 at the instant of mixing CO and H_2O.

Change in concentration: Some CO_2 and H_2 must form for the reaction to reach equilibrium. This also means that some CO and H_2O must react. But how much? If we knew the answer, we could calculate the equilibrium concentrations. Therefore, the changes in concentration are our unknown quantities.

Let us allow x to represent the amount of CO per litre that reacts. Notice that we could just as easily have chosen x to be the amount of H_2O per litre that reacts or the amount of CO_2 or H_2 per litre that forms. There is nothing special about having chosen CO to define x. The change in the concentration of CO is then - x (it is negative because the approach of the system to equilibrium decreases the CO concentration). Because CO and H_2O react in a 1 : 1 mole ratio, the change in the H_2O concentration is also - x. Since 1 mole each of CO_2 and H_2 is formed from 1 mole of CO, the CO_2 and H_2O concentrations both increase by x (their changes are + x).

*Equilibrium concentration:*We obtain the equilibrium concentrations as:

$$\begin{pmatrix}\text{equilibrium}\\ \text{concertration}\end{pmatrix} = \begin{pmatrix}\text{initial}\\ \text{concentration}\end{pmatrix} + \begin{pmatrix}\text{change in}\\ \text{concentration}\end{pmatrix}$$

Solution

Here is the completed concentration table.

	CO(g)	+	H_2O(g)	⇌	CO_2(g)	+	H_2(g)
Initial concentration (mol L^{-1})	0.100		0.100		0		0
Change in concentration (mol L^{-1})	-*x*		-*x*		+*x*		+*x*
Equilibrium concentration (mol L^{-1})	0.100 - *x*		0.100 - *x*		*x*		*x*

Note that the last line in the table tells us that the equilibrium CO and H_2O concentrations are equal to the amount per litre that was present initially minus the amount per litre that has reacted. The equilibrium concentrations of CO_2 and H_2 equal the amount per litre of each that forms, since no CO_2 or H_2 is present initially.

Next, we substitute the quantities from the 'Equilibrium concentration' row into the equilibrium constant expression and solve for *x*:

$$\begin{aligned} K_c &= \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = 4.06 \\ &= \frac{(x)(x)}{(0.100-x)(0.100-x)} = 4.06 \end{aligned}$$

which we can write as:

$$\frac{x^2}{(0.100-x)^2} = 4.06$$

In this problem, we can solve the equation for *x*r most easily by taking the square root of both sides:

$$\frac{x}{(0.100-x)} = \sqrt{4.06} = 2.01$$

Rearranging gives:

$$\begin{aligned} x &= 2.01(0.100-x) \\ &= 0.021 - 2.01x \end{aligned}$$

Collecting terms in *x*gives:

$$\begin{aligned} x + 2.01x &= 0.201 \\ 3.01x &= 0.201 \\ x &= 0.0668 \end{aligned}$$

Now that we know the value of *x*, we can calculate the equilibrium concentrations from the last row of the table.

$$\begin{aligned} [CO] &= 0.100 - x = 0.100 - 0.0668 = 0.033\text{M} \\ [H_2O] &= 0.100 - x = 0.100 - 0.0668 = 0.033\text{M} \\ [CO_2] &= x = 0.0668\ \text{M} \\ [H_2] &= x = 0.0668\ \text{M} \end{aligned}$$

Is our answer reasonable?

First, we should check that all concentrations are positive numbers. They are. One way to check the answers is to substitute the equilibrium concentrations we've found into the equilibrium constant expression and evaluate the reaction quotient. If our answers are correct, Q_c should equal K_c. Let us do this:

$$Q_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]}$$

$$= \frac{(0.0668)^2}{(0.033)^2} = 4.1$$

Rounding K_c to two significant figures gives 4.1, so the calculated concentrations are correct.

WORKED EXAMPLE 9.14

Using K_c to Calculate Equilibrium Concentrations — 2

In worked example 9.13, it was stated that the reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

has K_c = 4.06 at 500 °C. Suppose 0.0600 mol of CO and 0.0600 mol of H_2O are mixed with 0.100 mol of CO_2 and 0.100 mol of H_2 in a 1.00 L reaction vessel. Determine the concentrations of all the substances when the mixture reaches equilibrium at this temperature.

Analysis

We will proceed in much the same way as in worked example 9.13. However, this time, determining the algebraic signs of *x*f will not be quite so simple because none of the initial concentrations is 0. The best way to determine the algebraic signs is to use the initial concentrations to calculate the initial reaction quotient. Then we can compare Q_c and K_c, and then by reasoning we will determine which way the reaction must proceed to make Q_c equal to K_c.

Solution

The equilibrium constant expression for the reaction is:

$$K_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]}$$

Let's use the initial concentrations, shown in the concentration table below, to determine the value of the reaction quotient immediately after mixing.

$$Q_c = \frac{(0.100)(0.100)}{(0.0600)(0.0600)} = 2.78 < K_c$$

As indicated, Q_c is less than K_c, so the system is not at equilibrium. To reach equilibrium, Q_c must become larger, which requires an increase in the concentrations of CO_2 and H_2 and a corresponding decrease in the concentrations of CO and H_2O. This means that, for CO_2 and H_2, the change must be positive, and, for CO and H_2O, the change must be negative.

Here is the completed concentration table.

	CO(g)	+	**H_2O(g)**	⇌	**CO_2(g)**	+	**H_2(g)**
Initial concentration (mol L^{-1})	0.0600		0.0600		0.100		0.100
Change in concentration (mol L^{-1})	-*x*		-*x*		+*x*		+*x*
Equilibrium concentration (mol	0.0600 -		0.0600		0.100 +		0.100 +

L^{-1})	x	$-x$	x	x

Substituting equilibrium quantities into the equilibrium constant expression gives us:

$$\begin{aligned} K_c &= \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} \\ &= \frac{(0.100+x)^2}{(0.0600-x)^2} \\ &= 4.06 \end{aligned}$$

Taking the square root of both sides yields:

$$\frac{0.100+x}{0.0600-x} = 2.01$$

To solve for x, we first multiply each side by (0.0600 - x) to obtain:

$$\begin{aligned} 0.100+x &= 2.01(0.0600-x) \\ &= 0.121-2.01x \end{aligned}$$

Collecting terms in x to one side and the constants to the other gives:

$$\begin{aligned} x+2.01x &= 0.121-0.100 \\ 3.01x &= 0.021 \\ x &= 0.0070 \end{aligned}$$

Now we can calculate the equilibrium concentrations:

$$\begin{aligned} [CO] &= [H_2O] = (0.0600-x) = 0.0600-0.0070 = 0.0530\ M \\ [CO_2] &= [H_2] = (0.100+x) = 0.100+0.0070 = 0.107\ M \end{aligned}$$

Is our answer reasonable?

As a check, we can evaluate the reaction quotient using the calculated equilibrium concentrations.

$$\begin{aligned} Q &= \frac{(0.107)^2}{(0.0530)^2} \\ &= 4.08 \end{aligned}$$

This is acceptably close to the value of K_c. (It is not *exactly* equal to K_c because of the rounding of answers during the calculations.)

In worked examples 9.13 and 9.14, we were able to simplify the solution by taking the square root of both sides of the algebraic equation obtained by substituting equilibrium concentrations into the equilibrium constant expression. Such simplifications are not always possible, however, as illustrated in worked example 9.15.

WORKED EXAMPLE 9.15

Using K_c to Calculate Equilibrium Concentrations — 3

At a certain temperature, K_c = 4.50 for the reaction:

$$N_2O_4(g) \rightleftharpoons 2NO(g)$$

If 0.300 mol of N_2O_4 is placed into a 2.00 L container at this temperature, calculate the equilibrium concentrations of both gases.

Analysis

As in worked example 9.14, we first write the equilibrium constant expression:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 4.50$$

We will need to find algebraic expressions for the equilibrium concentrations and substitute them into the equilibrium constant expression. To obtain these, we set up the concentration table for the reaction.

*Initial concentration:*The initial concentration of N_2O_4 is 0.300 mol/2.00 L = 0.150 M. Since no NO_2 was placed in the reaction vessel, its initial concentration is exactly 0. *Change in concentration:* There is initially no NO_2 in the reaction mixture, so we know its concentration must increase. This means the N_2O_4 concentration must decrease as some of the NO_2 is formed. Let's allow *x* to represent the amount of N_2O_4 per litre that reacts, so the change in the N_2O_4 concentration is - *x*. Because of the stoichiometry of the reaction, the NO_2 concentration must increase by 2*x* so its change in concentration is 2*x Equilibrium concentration:* As before, we add the change to the initial concentration in each column to obtain expressions for the equilibrium concentrations.

Solution

Here is the concentration table.

	$N_2O_4(g)$ $\rightleftharpoons$	$2NO_2(g)$
Initial concentration (mol L^{-1})	0.150	0
Change in concentration (mol L^{-1})	-x	+2x
Equilibrium concentration (mol L^{-1})	0.150-x	2x

Now we substitute the equilibrium quantities into the equilibrium constant expression:

$$\begin{aligned} K_c &= \frac{[NO_2]^2}{[N_2O_4]} = 4.50 \\ &= \frac{(2x)^2}{0.150 - x} = 4.50 \\ &= \frac{4x^2}{(0.150 - x)} = 4.50 \end{aligned}$$

This time the left side of the equation is not a perfect square, so we cannot just take the square root of both sides as in worked example 9.14. However, because the equation involves terms in x^2 and *x* and a constant, we can use the quadratic formula. For a quadratic equation of the form $ax^2 + bx + c = 0$:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Expanding the above equation, we get:

$$\begin{aligned} 4x^2 &= 4.50(0.150 - x) \\ &= 0.675 - 4.50x \end{aligned}$$

Arranging terms in the standard order gives:

$$4x^2 + 4.50x - 0.675 = 0$$

Therefore, the quantities we will substitute into the quadratic formula are: $a = 4$, $b = 4.50$ and $c = -0.675$. Making these substitutions gives:

$$x = \frac{-4.50 \pm \sqrt{(4.50)^2 - 4(4)(-0.675)}}{2(4)}$$
$$= \frac{-4.450 \pm \sqrt{31.05}}{8}$$
$$= \frac{-4.50 \pm 5.57}{8}$$

Because of the ± term, there are two values of *x*f that satisfy the equation: *x*= 0.134 and *x*= -1.26. However, only the first value, *x*= 0.134, makes any sense chemically (see below). Using this value, the equilibrium concentrations are:

$$[N_2O_4] = 0.150 - 0.134 = 0.016\ M$$
$$[NO_2] = 2(0.134) = 0.268\ M$$

Notice that, if we had used the negative root, -1.26, the equilibrium concentration of NO_2 would be negative. Negative concentrations are impossible, so *x* = -1.26 is not acceptable *for chemical reasons*. In general, whenever you use the quadratic equation in a chemical calculation, one root will be satisfactory and the other will lead to an answer that does not make sense chemically.

Is our answer reasonable?

Once again, we can evaluate the reaction quotient using the calculated equilibrium values. When we do this, we obtain *Q* = 4.49, which is acceptably close to the given value of K_c.

PRACTICE EXERCISE 9.19

During an experiment, 0.200 mol of H_2 and 0.200 mol of I_2 were placed into a 1.00 L vessel where the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

came to equilibrium. For this reaction, K_c = 49.5 at the temperature of the experiment. What were the equilibrium concentrations of H_2, I_2 and HI?

Equilibrium problems can be much more complex than worked example 9.15. However, when *K* is either very large or very small, simplifying assumptions can be made that allow an approximate solution to be obtained. This is illustrated in worked example 9.16.

WORKED EXAMPLE 9.16

Simplifying Approximations in Equilibrium Calculations

The thermal decomposition of water to its elements occurs only to a very small extent, even at high temperatures; at 1000 °C, $K_c = 7.3 \times 10^{-18}$ for the reaction:

$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$$

If water at an initial concentration of 0.100 m is allowed to react at 1000 °C, what will be the H_2 concentration when the reaction reaches equilibrium?

Analysis

We begin, as always, by writing the equilibrium constant expression, K_c:

$$K_c = \frac{[H_2]^2[O_2]}{[H_2O]^2} = 7.3 \times 10^{-18}$$

and we then set up the concentration table and proceed as we have done before. However, we will find that we can make simplifying assumptions in this problem because of the extremely small value of the equilibrium constant.

Solution

Here is the concentration table.

	$2H_2O(g)$ $\rightleftharpoons$	$2H_2(g)$ +	$O_2(g)$
Initial concentration (mol L^{-1})	0.100	0	0
Change in concentration (mol L^{-1})	-2*x*	+2*x*	+*x*
Equilibrium concentration (mol L^{-1})	0.100-2*x*	2*x*	*x*

We now substitute the equilibrium concentrations into the equilibrium constant expression:

$$K_c = \frac{[H_2]^2[O_2]}{[H_2O]^2} = \frac{(2x)^2(x)}{(0.100-2x)^2} = \frac{4x^3}{0.100-2x^2} = 7.3 \times 10^{-18}$$

This is a cubic equation and the mathematics required to solve such equations exactly are well beyond the scope of this book. However, in this case, the magnitude of K_c allows us to make simplifications to this equation that allow its straightforward solution. Because K_c is so incredibly small, we know that, at equilibrium, not much H_2O will have reacted. This means that, to a very good approximation, the concentration of H_2O at equilibrium equals the initial concentration of H_2O. In other words, the term *x* in the concentration table is tiny, so 0.100 - 2*x* 2≈ 0.100. Making this assumption simplifies the cubic expression as follows.

$$K_c = \frac{4x^2}{(0.100-2x)^2} \approx \frac{4x^3}{(0.100)^2} = 7.3 \times 10^{-18}$$

Hence:

$$\begin{aligned} 4x^3 &= (0.100)^2 \times (7.3 \times 10^{-18}) \\ &= 7.3 \times 10^{-20} \\ x^3 &= 1.8 \times 10^{-20} \\ x &= \sqrt[3]{1.8 \times 10^{-20}} \\ &= 2.6 \times 10^{-7} \end{aligned}$$

We can now obtain the H_2 concentration, which is equal to 2*x* (from the concentration table).

$$\begin{aligned} [H_2] &= 2 \times (2.6 \times 10^{-7}) \\ &= 5.2 \times 10^{-7}\,\text{M} \end{aligned}$$

Is our answer reasonable?

We must first show that the assumption we made was justified. We do this by showing that (0.100 - 2*x*) is indeed essentially equal to 0.100.

$$0.100 - 2x = 0.100 - (5.2 \times 10^{-7}) = 0.099\,999\,48$$

When we round 0.099 999 48 to three significant figures, it is 0.100. This shows that our assumption is justified.

We can now show that our answer is reasonable. The tiny value of K_c leads us to expect that the equilibrium concentration of hydrogen is very small, which it is. We can also substitute our equilibrium values into the expression for Q_c (remember that $[O_2] = x$) and confirm that $Q_c = K_c$. It should also be noted that the exact solution of the original cubic equation using a calculator gives $x = 2.6 \times 10^{-7}$, again showing that our assumption leads to a reasonable answer.

PRACTICE EXERCISE 9.20

In air at 25 °C and 1.013×10^5 Pa, the N_2 concentration is 0.033 M and the O_2 concentration is 0.008 10 M. The reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

has $K_c = 4.8 \times 10^{-31}$ at 25 °C. Taking the N_2 and O_2 concentrations given above as initial values, calculate the equilibrium NO concentration that should exist in our atmosphere from this reaction at 25 °C.

The simplifying assumption made in worked example 9.16 is valid because a very small number was subtracted from a much larger one. We could also have neglected x (or $2x$) if it were a very small number that was being added to a much larger one. Remember that you can neglect x only if it is added or subtracted; you can never neglect x if it occurs as a multiplying or dividing factor.

As an arbitrary rule of thumb, you can expect these simplifying assumptions to be valid if the concentration from which x is subtracted, or to which x is added, is at least 400 times greater than K. For instance, in worked example 9.16, $2x$ was subtracted from 0.100. Since 0.100 is much larger than $400 \times (7.3 \times 10^{-18})$, we expect the assumption $0.100 - 2x \approx 0.100$ to be valid. However, even though the simplifying assumption is expected to be valid, always check to see if it really is after finishing the calculation. If the assumption proves invalid, then some other way to solve the algebra must be found.

Chemical Connections

Equilibria and CO_2 Sequestration

Associate Professor Marcel Maeder, University of Newcastle

On the first page of this chapter, we discussed the increasing CO_2 levels in the atmosphere and how these can adversely affect the equilibria that occur in the Earth's oceans. It is apparent that, if we cannot reduce CO_2 emissions, we must at least find a way of sequestering the emitted CO_2 so that it we can reduce its effect on the Earth's delicate ecosystems.

One potentially promising way of reducing the CO_2 output is post-combustion capture (PCC), which captures CO_2 from coal-fired power plants and then sequesters it. The essence of this process is the separation of CO_2 from the other flue gases, which are mainly N_2, O_2 and H_2O and some minor contaminants such as SO_2. Equilibria involving CO_2 play a crucial role in these separation processes.

CO_2 is absorbed into an aqueous solution of an organic amine, RNH_2, and is then transformed into carbonic acid, H_2CO_3. This donates a proton to the amine, forming mainly hydrogen-carbonate, HCO_3^-, and protonated amine, RNH_3^+. The relevant equilibria are:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) + RNH_2(aq) \rightleftharpoons HCO_3^-(aq) + RNH_3^+(aq)$$

There can be parallel reactions, in particular the formation of other organic compounds called carbamates which complicate the matter, but the principles are the same. Crucially, these equilibria, like the majority of equilibria, are temperature dependent, and at high temperature some of the absorbed CO_2 is released from the amine solution. This is the principle of PCC.

The PCC process is shown schematically in figure 9.17; the flue gas from the power plant is passed upwards through the absorber column through which the amine solution is flowing down. CO_2 is absorbed while the other gases, which do not react with the amine, escape at the top of the column. The saturated amine solution is pumped into the stripper column where at higher temperature some of the CO_2 is released in a pure form, ready for sequestration, and the depleted amine solution is pumped back into the absorber. Figure 9.18 shows the CSIRO PCC pilot plant at the Tarong power station in Queensland.

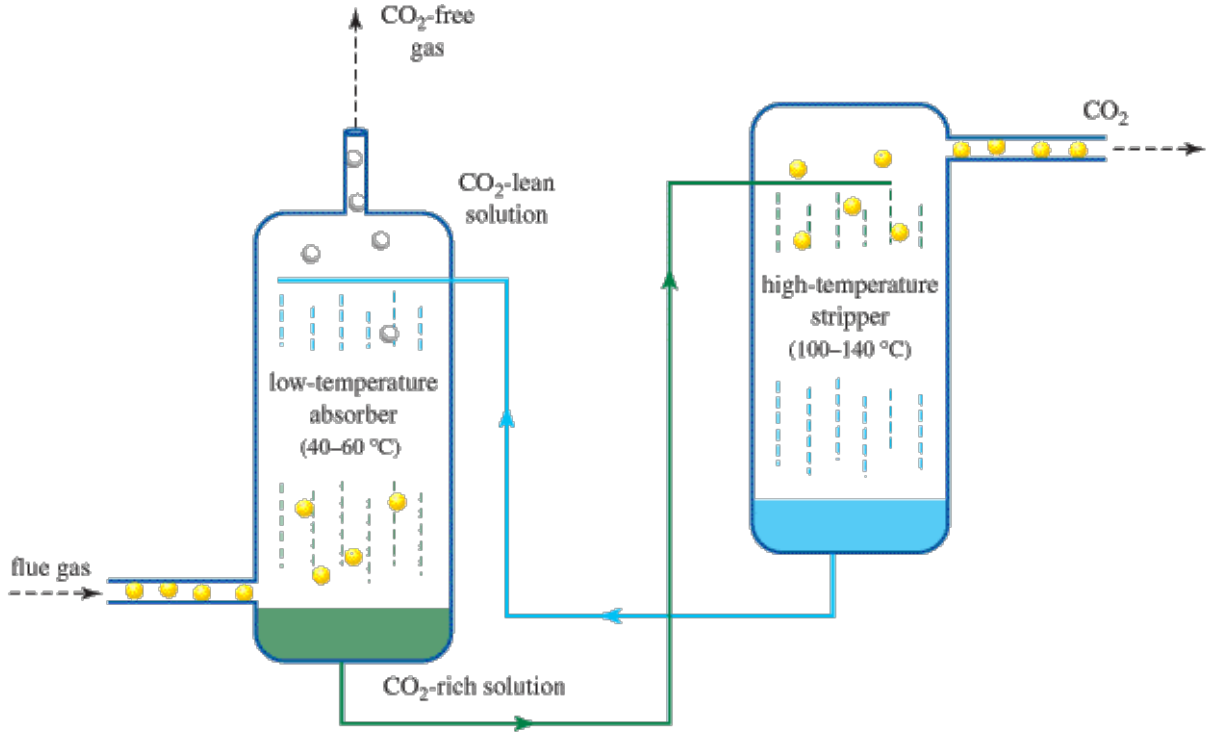


FIGURE 9.17 Schematic of the PCC process.



FIGURE 9.18 The CSIRO PCC pilot plant at the Tarong power station in Queensland.

It is obvious that this process is very energy intensive, and it is crucial that the energy consumption is minimised in order to make PCC a viable process. For this reason, it is important to fully understand the kinetics and thermodynamics as well as the temperature dependence of the complete process. This is not easy, as the reactions can be fast and spectroscopic detection is difficult. Appropriate experimentation together with the computational analysis are developed at the Newcastle research group in collaboration with the CSIRO Energy Technology division.

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SUMMARY

Chemical Equilibrium

Chemical equilibrium occurs when the chemical composition of a system does not change with time. When the forward and reverse reactions in a chemical system occur at equal rates, a dynamic equilibrium exists and the concentrations of the reactants and products remain constant. For a given overall chemical composition, the amounts of reactants and products that are present at equilibrium are the same regardless of whether the equilibrium is approached from the direction of pure 'reactants', pure 'products' or any mixture of them.

The Equilibrium Constant, *K*, and the Reaction Quotient, *Q*

The equilibrium constant expression is a fraction. The concentrations of the products at equilibrium, each divided by $c^{\ominus}$ raised to a power equal to its stoichiometric coefficient in the balanced chemical equation, are multiplied together in the top line (numerator). The bottom line (denominator) is constructed in the same way from the concentrations of the reactants at equilibrium, each divided by $c^{\ominus}$ and raised to a power equal to its stoichio-metric coefficient. The numerical value of the equilibrium constant expression is the equilibrium constant, K_c. If partial pressures of gases, divided by $p^{\ominus}$ and raised to their stoichiometric coefficients, are used in the equilibrium constant expression, K_p is obtained. The thermodynamic equilibrium constant is obtained when activities, rather than pressures or concentrations, are used in the equilibrium constant expression. The equilibrium constant is constant at constant temperature. The magnitude of the equilibrium constant reflects the extent to which the forward reaction has proceeded to completion when equilibrium is reached.

The reaction quotient, *Q*, has the same form as *K*, but the concentrations or pressures are nonequilibrium values. Pure solids and pure liquids do not appear in the expressions for *K* and *Q*.

When an equation is multiplied by a factor *n* to obtain a new equation, we raise its *K* to the power of *n* to obtain *K* for the new equation. When two equations are added, we multiply their values of *K* to obtain the new *K*. When an equation is reversed, we take the reciprocal of its *K* to obtain the new *K*.

The values of K_p and K_c are equal only if the same number of moles of gas are represented on both sides of the chemical equation. When the numbers of moles of gas are different, K_p is related to K_c by the equation:

$$K_p = K_c \left(\frac{1000RT}{p^{\ominus}} \right)^{\Delta n_g}$$

where R = 8.314 J mol^{-1} K^{-1}, T = absolute temperature and Δn_g is the difference between the number of moles of gaseous products and the number of moles of gaseous reactants in the balanced equation.

An equilibrium where all substances are in the same phase is called a homogeneous equilibrium, while one with substances in more than one phase is a heterogeneous equilibrium. The equilibrium constant expression for a heterogeneous equilibrium omits concentration terms for pure liquids and pure solids.

Equilibrium and Gibbs Energy

Gibbs energy diagrams for chemical reactions show the variation in Gibbs energy of a system as a reaction mixture proceeds from pure reactants to pure products. These diagrams show a minimum, due to the Gibbs energy of mixing of reactants and products, and this minimum corresponds to the equilibrium composition of the reaction mixture. The position of the minimum with respect to the proportion of products to reactants is related to the sign and magnitude of $\Delta_r G^{\ominus}$ for the forward

reaction: if $\Delta_r G^\ominus$ is large and negative, the forward reaction proceeds essentially to completion and the equilibrium mixture consists predominantly of products; if $\Delta_r G^\ominus$ is large and positive, the forward reaction proceeds only to a very small extent and negligible amounts of products are present at equilibrium. $\Delta_r G^\ominus$ is related to the equilibrium constant for a chemical reaction by the equation:

$$\Delta_r G^\ominus = -RT\ln K$$

The spontaneity of any change in composition of a reaction mixture is given by the sign of $\Delta_r G$ for that change. $\Delta_r G$ is related to $\Delta_r G^\ominus$ by the equation:

$$\Delta_r G = \Delta_r G^\ominus - RT\ln Q$$

How Systems at Equilibrium Respond to Change

The response of a system at equilibrium to a chemical or physical change can be predicted by determining the effect of such a change on the value of Q, the reaction quotient for the forward reaction. Any change that affects Q instantaneously removes the system from equilibrium because $Q \neq K$; the way in which Q must change (increase or decrease) to again make $Q = K$ determines the direction of spontaneous change in the reaction mixture. Temperature alone can change the value of K for a chemical equilibrium, and the direction in which spontaneous change must occur to re-establish equilibrium in these cases may be determined by the sign of $\Delta_r H^\ominus$ for the forward reaction, via the van't Hoff equation:

$$\frac{\mathrm{d}\ln k}{dT} = \frac{\Delta_r H^\ominus}{RT^2}$$

Pure solids, pure liquids, inert gases and catalysts do not appear in the expression for Q so addition of these can have no effect on the position of equilibrium.

Equilibrium Calculations

Given a set of equilibrium concentration or pressure conditions, we can calculate the value of the equilibrium constant for a reaction, and we can also use the given value of an equilibrium constant to calculate equilibrium concentrations or pressures. We can use a concentration table to assist in such calculations.

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Equilibrium constant expression *(section 9.2)*

This expression defines the relationship between the equilibrium concentrations or partial pressures of the reactants and products in a chemical reaction. For the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{and} \quad K_p = \frac{\left(\frac{p_C}{p^\ominus}\right)^C \left(\frac{p_D}{p^\ominus}\right)^d}{\left(\frac{p_A}{p^\ominus}\right)^a \left(\frac{p_B}{p^\ominus}\right)^b}$$

Reaction quotient expression *(section 9.2)*

This expression has the same form as the equilibrium constant expression, and is used to characterise systems that are not at equilibrium. The concentrations or partial pressures in the expression can have any value. For the reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$Q_c = \frac{[C]^c[C]^d}{[A]^a[B]^b} \quad \text{and} \quad Q_p = \frac{\left(\frac{p_C}{p^\ominus}\right)^c \left(\frac{p_D}{p^\ominus}\right)^d}{\left(\frac{p_A}{p^\ominus}\right)^a \left(\frac{p_B}{p^\ominus}\right)^b}$$

Comparison of *Q* and *K* *(section 9.2)*

At equilibrium, $Q = K$. If the system is disturbed such that $Q > K$, the reaction must shift towards reactants to restore equilibrium; if $Q < K$, the reaction must shift towards products to restore equilibrium.

$$K_p = K_c \left(\frac{1000RT}{p^\ominus}\right)^{\Delta n_g}$$ *(section 9.2)*

This equation converts between the value of K_p and K_c; Δn_g is the change in the number of moles of gas, which is calculated using the coefficients of gaseous products and reactants.

Manipulation of equilibrium equations *(section 9.2)*

1. When the direction of an equation is reversed, the new equilibrium constant is the reciprocal of the original.
2. When the coefficients are multiplied by a factor, the equilibrium constant is raised to a power equal to that factor.
3. When chemical equilibria are added, their equilibrium constants are multiplied.

Magnitude of the equilibrium constant *(section 9.2)*

1. When K_c is very large, the equilibrium position lies towards the products.
2. When $K_c \approx 1$, the concentrations of reactants and products are similar at equilibrium.
3. When K_c is very small, the equilibrium position lies towards the reactants.

Value of $\Delta_r G^\ominus$ for a reaction *(section 9.3)*

The magnitude and sign of $\Delta_r G^\ominus$ indicate qualitatively whether or not a significant amount of products will form. If $\Delta_r G^\ominus$ is reasonably large and negative, the reaction will proceed largely towards products. If $\Delta_r G^\ominus$ is reasonably large and positive, the equilibrium mixture will contain mainly reactants.

$\Delta_r G = \Delta_r G^\ominus - RT\ln K$ *(section 9.3)*

This equation relates the reaction quotient, Q, to $\Delta_r G$, which enables us to determine whether a reaction is at equilibrium and, if not, the direction of spontaneous change required to reach equilibrium.

$\Delta_r G^\ominus = -RT\ln K$ *(section 9.3)*

This equation relates $\Delta_r G^\ominus$ to the equilibrium constant, K.

Concentration table *(section 9.5)*

This may be used in problems involving equilibria to determine the concentrations of reactants and products at equilibrium.

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REVIEW QUESTIONS

Chemical Equilibrium

9.1 Sketch a graph showing how the concentrations of the reactants and products of a typical chemical reaction vary with time during the course of the reaction. Assume no products are present at the start of the reaction.

9.2 What is meant when we say that chemical reactions are reversible?

The Equilibrium Constant, *K*, and Reaction Quotient, *Q*

9.3 How is the term 'reaction quotient' defined?

9.4 Under what conditions are the values of *Q* and *K* the same?

9.5 When a chemical equation and its equilibrium constant are given, why is it not necessary to also specify the form of the equilibrium constant expression?

9.6 At 225 °C, $K_p = 6.3 \times 10^{-3}$ for the reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Would we expect this reaction to go nearly to completion?

9.7 Here are some reactions and their equilibrium constants.

(a) $2CH_4(g) \rightleftharpoons C_2H_6(g) + H_2(g) \quad K_c = 9.5 \times 10^{-13}$

(b) $CH_4OH(g) + H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \quad K_c = 3.6 \times 10^{20}$

(c) $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g) \quad K_c = 2.0 \times 10^{9}$

Arrange these reactions in order of their increasing tendency to go towards completion.

9.8 State the equation relating K_p to K_c and define all terms.

9.9 Use the ideal gas law to show that the partial pressure of a gas is directly proportional to its molar concentration at constant temperature. What is the proportionality constant?

9.10 What is the difference between a heterogeneous equilibrium and a homogeneous equilibrium?

9.11 Why do we omit the concentrations of pure liquids and solids from the equilibrium constant expressions of heterogeneous reactions?

Equilibrium and Gibbs Energy

9.12 Sketch a graph to show how Gibbs energy changes during a phase change such as the melting of a solid.

9.13 Sketch the shape of the Gibbs energy curve for a chemical reaction that has a positive $\Delta_r G^{\ominus}$. Indicate the composition of the reaction mixture when it is at equilibrium.

9.14 Many reactions that have large, negative values of $\Delta_r G^{\ominus}$ are not actually observed to occur at 25 °C and 10^5 Pa. Why?

9.15 Suppose a reaction has a negative $\Delta_r S^{\ominus}$. Will more or less product be present at equilibrium as the temperature is raised? Assume that $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ are independent of temperature.

9.16 Write the equation that relates the Gibbs energy change to the value of the reaction quotient for a reaction.

9.17 How is the equilibrium constant related to the standard Gibbs energy change for a reaction? (Write the equation.)

9.18 What is a 'thermodynamic equilibrium constant'?

9.19 What is the value of $\Delta_r G^{\ominus}$ for a reaction for which $K = 1$?

How Systems at Equilibrium Respond to Change

9.20 How will the equilibrium:

$$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

be affected by the following?

(a) addition of $CH_4(g)$

(b) addition of $H_2(g)$

(c) removal of $CS_2(g)$

(d) decreasing the volume of the container

(e) increasing the temperature (the forward reaction is endothermic)

9.21 The reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ has $\Delta_r H^{\ominus} = -18\ \text{kJ mol}^{-1}$. How will the amount of CH_3OH present at equilibrium be affected by the following?

(a) adding CO(g)

(b) removing $H_2(g)$

(c) decreasing the volume of the container

(d) adding a catalyst

(e) increasing the temperature

9.22 Consider the equilibrium:

$$N_2O(g) + NO_2(g) \rightleftharpoons 3NO(g) \quad \Delta_r H^{\ominus} = +155.7\ \text{kJ mol}^{-1}$$

In which direction will this equilibrium be shifted by the following changes?

(a) addition of $N_2O(g)$

(b) removal of $NO_2(g)$

(c) addition of NO(g)

(d) increasing the temperature of the reaction mixture

(e) addition of helium gas to the reaction mixture at constant volume

(f) decreasing the volume of the container at constant temperature

9.23 In questions 9.21 and 9.22, which change(s) will alter the value of K?

9.24 Consider the equilibrium $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ for which $\Delta_r H^{\ominus} = -77.07\ \text{kJ mol}^{-1}$. How will the amount of Cl_2 at equilibrium be affected by the following?

(a) removal of NO(g)

(b) addition of NOCl(g)

(c) raising the temperature

(d) decreasing the volume of the container

Equilibrium Calculations

9.25 In order to study the following reaction:

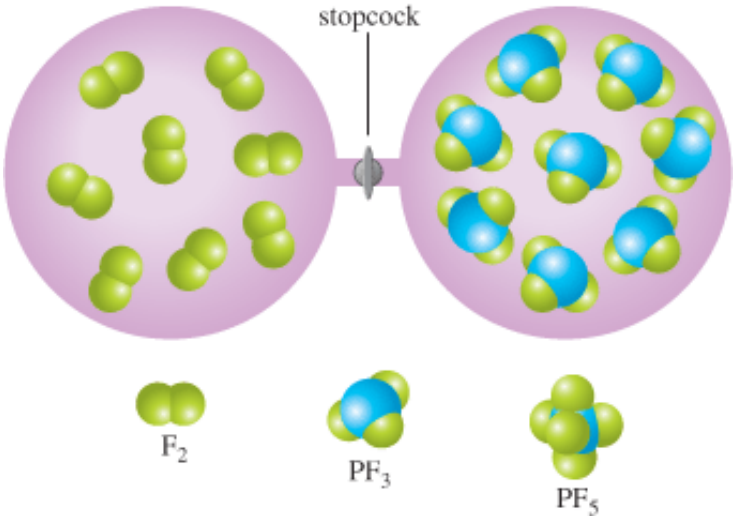
$$NO(g) + NO_2(g) + H_2O(g) \rightleftharpoons 2HNO_2(g)$$

a mixture of NO(g), $NO_2(g)$ and $H_2O(g)$ was prepared in a 10.0 L glass bulb at 20 °C with the

following initial concentrations: [NO] = [NO_2] = 2.59 × 10^{-3} M, [H_2O] = 9.44 × q0^{-4} M and [HNO_2] = 0.0 M. When equilibrium was reached, [HNO_2] was 4.0 × 10^{-4} M. Explain in detail how to calculate the equilibrium constant, K_c, for this reaction.

9.26 Two 1.00 L bulbs are filled with F_2(g) and PF_3(g) to a pressure of 5.00 × 10^4 Pa, as illustrated in the figure below. At a particular temperature, K_p = 4.0 for the reaction of these gases to form PF_5(g):

$$F_2(g) + PF_3(g) \rightleftharpoons PF_5(g)$$



(a) The stopcock between the bulbs is opened and the pressure falls. Sketch this apparatus showing the gas composition once the pressure is stable.

(b) List any chemical reactions that continue to occur once the pressure is stable.

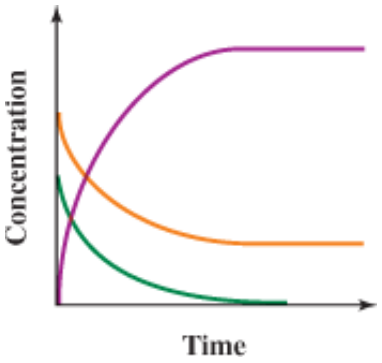
(c) Suppose all the gas in the left bulb is forced into the bulb on the right and then the stopcock is closed. Make a second sketch to show the composition of the gas mixture after equilibrium is reached. Comment on how the composition of the one-bulb system differs from that of the two-bulb system.

9.27 Cl_2 reacts with Br_2 in CCl_4 solution to form BrCl according to the equation:

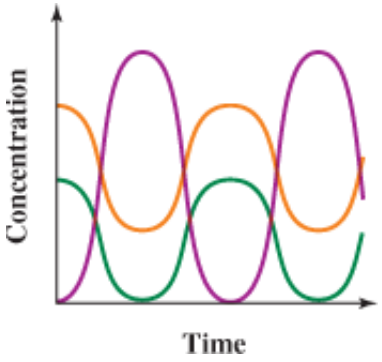
$$Br_2 + Cl_2 \rightleftharpoons 2BrCl \quad K_c = 2$$

If the initial concentrations were [Br_2] = 0.6 M, [Cl_2] = 0.4 M and [BrCl] = 0.0 M, which of the following concentration versus time graphs could represent this reaction? Explain why you rejected each of the other four graphs.

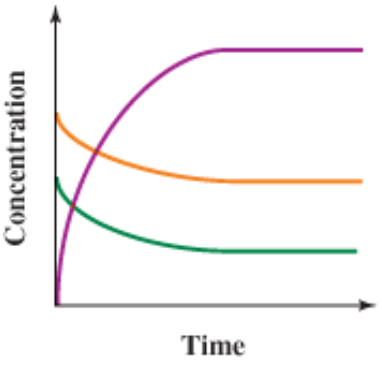
(a)



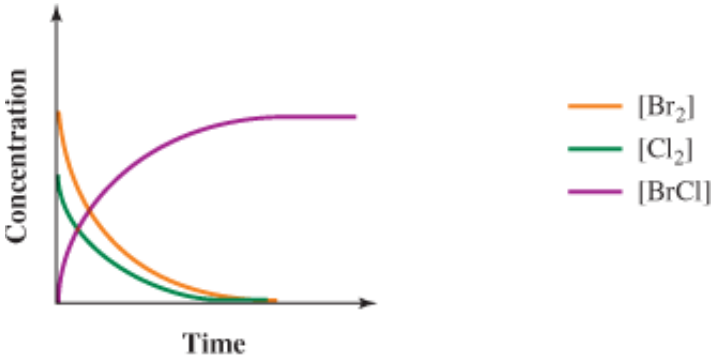
(b)



(c)

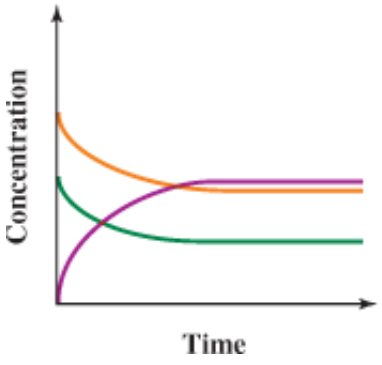


(d)



(d)

(e)



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9.28 Write the equilibrium constant expression for each of the following reactions in terms of molar concentrations.

(a) $2PCl_3(g) + O_2(g) \rightleftharpoons 2POCl_3(g)$

(b) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

(c) $N_2H_4(g) + 2O_2(g) \rightleftharpoons 2NO(g) + 2H_2O(g)$

(d) $N_2H_4(g) + 6H_2O_2(g) \rightleftharpoons 2NO_2(g) + 8H_2O(g)$

(e) $SOCl_2(g) + H_2O(g) \rightleftharpoons SO_2(g) + 2HCl(g)$

(f) $3Cl_2(g) + NH_3(g) \rightleftharpoons NCl_3(g) + 3HCl(g)$

(g) $PCl_3(g) + PBr_3(g) \rightleftharpoons PCl_2Br(g) + PClBr_2(g)$

(h) $NO(g) + NO_2(g) + H_2O(g) \rightleftharpoons 2HNO_2(g)$

(i) $H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$

(j) $Br_2(g) + 5F_2(g) \rightleftharpoons 2BrF_5(g)$

9.29 Write the equilibrium constant expression for the reactions in question 9.28 in terms of partial pressures.

9.30 Write the equilibrium constant expression for each of the following reactions in aqueous solution.

(a) $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$

(b) $Cd^{2}+(aq) + 4SCN^-(aq) \rightleftharpoons [Cd(SCN)_4]^{2}-(aq)$

(c) $HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$

(d) $CO_3^{2}-(aq) + HSO_4^-(aq) \rightleftharpoons HCO_3^-(aq) + SO_4^{2}-(aq)$

9.31 At 25 °C, $K_c = 1 \times 10^{-85}$ for the reaction:

$$7IO_3^-(aq) + 9H_2O(l) + 7H^+(aq) \rightleftharpoons I_2(aq) + 5H_5IO_6(aq)$$

What is the value of K_c for the following reaction?

$$I_2(aq) + 5H_5IO_6(aq) \rightleftharpoons 7IO_3^-(aq) + 9H_2O(l) + 7H^+(aq)$$

9.32 Use the following equilibria:

$$2CH_4(g) \rightleftharpoons C_2H_6(g) + H_2(g) \quad K_c = 9.5 \times 10^{-13}$$
$$CH_4(g) + H_2O(g) \rightleftharpoons CH_3OH(g) + H_2(g) \quad K_c = 2.8 \times 10^{-21}$$

to calculate K_c for the reaction:

$$2CH_3OH(g) + H_2(g) \rightleftharpoons C_2H_6(g) + 2H_2O(g)$$

9.33 Write the equilibrium constant expression for each of the following reactions in terms of molar concentrations.

(a) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

(b) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)$

How does K_c for reaction (a) compare with K_c for reaction (b)?

9.34 Write the equilibrium constant expression for the reaction:

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

How does K_c for this reaction compare with K_c for reaction (a) in question 9.33?

9.35 A 345 mL container holds NH_3 at a pressure of 9.93×10^4 Pa and a temperature of 45 °C. What is the molar concentration of ammonia in the container?

9.36 The concentration of water vapour is 0.0200 M in a certain container at 145 °C. What is the partial pressure of H_2O in the container?

9.37 For which of the following reactions does $K_p = K_c$?

(a) $2H_2(g) + C_2H_2(g) \rightleftharpoons C_2H_6(g)$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(c) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

(d) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

(e) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

(f) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

9.38 The reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ has $K_p = 6.3 \times 10^{-3}$ at 225 °C. What is the value of K_c at this temperature?

9.39 The reaction $HCOOH(g) \rightleftharpoons CO(g) + H_2O(g)$ has $K_p = 1.6 \times 10^6$ at 400 °C. What is the value of K_c for this reaction at this temperature?

9.40 The reaction $N_2O(g) + NO_2(g) \rightleftharpoons 3NO(g)$ has $K_c = 4.2 \times 10^{-4}$ at 500 °C. What is the value of K_p at this temperature?

9.41 One possible way of removing NO from the exhaust of a petrol engine is to cause it to react with CO in the presence of a suitable catalyst:

$$2NO(g) + 2CO(g) \rightleftharpoons N_2(g) + 2CO_2(g)$$

At 300 °C, this reaction has $K_c = 2.2 \times 10^{59}$. What is K_p at 300 °C?

9.42 At 773 °C, the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ has $K_c = 4.0 \times 10^{-1}$. What is K_p at this temperature?

9.43 The reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ has $K_p = 4.6 \times 10^{-2}$ at 395 °C. What is K_c at this temperature?

9.44 Calculate the molar concentration of water in (a) 18.0 mL of H_2O, (b) 100.0 mL of H_2O and (c) 1.00 L of H_2O. Assume that the density of water is 1.00 g mL^{-1}.

9.45 The density of solid sodium chloride is 2.164 g cm^{-3}. What is the molar concentration of NaCl in a 12.0 cm^3 sample of pure NaCl? What is the molar concentration of NaCl in a 25.0 g sample of pure NaCl?

9.46 Write the equilibrium constant expression, K_c, for each of the following heterogeneous reactions.

(a) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$

(b) $2NaHSO_3(s) \rightleftharpoons Na_2SO_3(s) + H_2O(g) + SO_2(g)$

(c) $2C(s) + 2H_2O(g) \rightleftharpoons CH_4(g) + CO_2(g)$

(d) $CaCO_3(s) + 2HF(g) \rightleftharpoons CaF_2(s) + H_2O(g) + CO_2(g)$

(e) $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

9.47 The heterogeneous reaction:

$$2HCl(g) + I_2(s) \rightleftharpoons 2HI(g) + Cl(g)$$

has $K_c = 1.6 \times 10^{-34}$ at 25 °C. Suppose 0.100 mol each of HCl and solid I_2 are placed in a 1.00 L container. Calculate the equilibrium concentrations of HI and Cl_2 in the container.

9.48 At 25 °C, $K_c = 360$ for the reaction:

$$AgCl(s) + Br^-(aq) \rightleftharpoons AgBr(s) + Cl^-(aq)$$

If solid AgCl is added to a solution containing 0.10 M Br^-, calculate the equilibrium concentrations of Br^- and Cl^-.

9.49 Calculate the value of the thermodynamic equilibrium constant for the following reactions at 25 °C. (Refer to the data in appendix A.)

(a) $2PCl_3(g) + O_2(g) \rightleftharpoons 2POCl_3(g)$

(b) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

(c) $N_2H_4(g) + 2O_2(g) \rightleftharpoons 2NO(g) + 2H_2O(g)$

(d) $N_2H_4(g) + 6H_2O_2(g) \rightleftharpoons 2NO_2(g) + 8H_2O(g)$

9.50 The reaction $NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$ has $\Delta_r G^\ominus{}_{1273\ K} = -9.67\ kJ\ mol^{-1}$. A 1.00 L reaction vessel at 1273 K contains 0.0200 mol NO_2, 0.040 mol NO, 0.015 mol N_2O and 0.0350 mol O_2. Is the reaction mixture at equilibrium? If not, in which direction will spontaneous change occur to reach equilibrium?

9.51 The reaction $CO(g) + H_2O(g) \rightleftharpoons HCOOH(g)$ has $\Delta_r G^\ominus{}_{673\ K} = +79.8\ kJ\ mol^{-1}$. If a mixture at 400 °C contains 0.040 mol CO, 0.022 mol H_2O and 3.8×10^{-3} mol HCOOH in a 2.50 L container, is the reaction mixture at equilibrium? If not, in which direction will spontaneous change occur?

9.52 A reaction that can convert coal to methane (the chief component of natural gas) is:

$$C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$$

for which $\Delta_r G^\ominus = -50.79\ kJ\ mol^{-1}$. What is the value of K_p for this reaction at 25 °C? Does this value of K_p suggest that it is worth studying this reaction as a means of methane production?

9.53 One of the important reactions in living cells from which the organism draws energy is the reaction of adenosine triphosphate (ATP) with water to give adenosine diphosphate (ADP) and a free phosphate ion:

$$ATP(aq) + H_2O(l) \rightleftharpoons ADP(aq) + PO_4^{3-}(aq)$$

The value of $\Delta_r G^\ominus$ for this reaction at 37 °C (normal human body temperature) is -33 kJ mol^{-1}. Calculate the value of the equilibrium constant for the reaction at this temperature.

9.54 What is the value of the equilibrium constant for a reaction for which $\Delta_r G^\ominus = 0$? What would happen to the composition of the system if we begin the reaction with the pure products?

9.55 Methanol, a potential replacement for petrol as a fuel in cars, can be made from H_2 and CO by the reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

At 500 K, this reaction has $K_p = 6.25 \times 10^{-3}$. Calculate $\Delta_r G^\ominus{}_{500}$ for this reaction.

9.56 Refer to the data in table 8.6 on p. 329 to determine $\Delta_r G^\ominus$ for the reaction:

$$2NO(g) + 2CO(g) \rightleftharpoons N_2(g) + 2CO_2(g)$$

What is the value of K_p for this reaction at 25 °C?

9.57 Use the data in appendix A to calculate $\Delta_r G^\circ_{773\ K}$ for the following reaction:

$$2NO(g) + 2CO(g) \rightleftharpoons N_2(g) + 2CO_2(g)$$

What is the value of K_p for the reaction at this temperature?

9.58 At a certain temperature, $K_c = 0.18$ for the equilibrium:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

Suppose a reaction vessel at this temperature contained these three gases at the following concentrations: $[PCl_3] = 0.0420$ M, $[Cl_2] = 0.0240$ M, $[PCl_5] = 0.005\ 00$ M.

(a) Is the system in a state of equilibrium?

(b) If not, in which direction will a spontaneous change occur to restore equilibrium?

9.59 At 460 °C, the reaction:

$$SO_2(g) + NO_2(g) \rightleftharpoons NO_2(g) + SO_3(g)$$

has $K_c = 85.0$. A reaction flask at 460 °C contains these gases at the following concentrations: $[SO_2] = 0.002\ 50$ m, $[NO_2] = 0.003\ 50$ m, $[NO] = 0.0250$ m, $[SO_3] = 0.0400$ m.

(a) Is the reaction at equilibrium?

(b) If not, in which direction will a spontaneous change occur to restore equilibrium?

9.60 At a certain temperature, the reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

has $K_c = 0.500$. If a reaction mixture at equilibrium contains 0.180 m CO and 0.220 m H_2, what is the concentration of CH_3OH?

9.61 $K_c = 64$ for the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

at a certain temperature. Suppose it was found that an equilibrium mixture of these gases contained 0.360 M NH_3 and 0.0192 M N_2. What was the equilibrium concentration of H_2 in the mixture?

9.62 At 773 °C, a mixture of CO(g), H_2(g) and CH_3OH(g) was allowed to come to equilibrium. The following equilibrium concentrations were then measured: [CO] = 0.105 M, $[H_2] = 0.250$ M, $[CH_3OH] = 0.002\ 61$ M. Calculate K_c for the reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

9.63 Ethene, C_2H_4, and water react under appropriate conditions to give ethanol. The reaction is:

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$$

An equilibrium mixture of these gases at a certain temperature had the following concentrations: $[C_2H_4] = 0.0148$ M, $[H_2O] = 0.0336$ M, $[C_2H_5OH] = 0.180$ M. What is the value of K_c?

9.64 At a high temperature, 2.00 mol of HBr was placed in a 4.00 L container where it decomposed according to the equation:

$$2HBr(g) \rightleftharpoons {}_2(g) + Br_2(g)$$

At equilibrium, the concentration of Br_2 was measured to be 0.0955 M. What is K_c for this reaction at this temperature?

9.65 A 0.050 mol sample of formaldehyde vapour, CH_2O, was placed in a heated 500 mL vessel and some of it decomposed. The reaction is:

$$HCHO(g) \rightleftharpoons H_2(g) + CO(g)$$

At equilibrium, the HCHO(g) concentration was 0.066 mol L^{-1}. Calculate the value of K_c for this reaction.

9.66 The reaction $NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$ reached equilibrium at a certain high temperature. Originally, the reaction vessel contained the following initial concentrations: $[N_2O]$ = 0.184 M, $[O_2]$ = 0.377 M, $[NO_2]$ = 0.0560 M, [NO] = 0.294 M. The concentration of NO_2, the only coloured gas in the mixture, was monitored by following the intensity of the colour. At equilibrium, the NO_2 concentration was 0.118 M. What is the value of K_c for this reaction at this temperature?

9.67 At 25 °C, 0.0560 mol O_2 and 0.020 mol N_2O were placed in a 1.00 L container where the following equilibrium was then established:

$$2NO_2(g) + 3O_2(g) \rightleftharpoons 4N_2O(g)$$

At equilibrium, the NO_2 concentration was 0.020 M. What is the value of K_c for this reaction?

9.68 At 25 °C, K_c = 0.145 for the following reaction in the solvent CCl_4:

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

If the initial concentration of BrCl in the solution is 0.050 M, calculate the equilibrium concentrations of Br_2 and Cl_2.

9.69 At 25 °C, K_c = 0.145 for the following reaction in the solvent CCl_4:

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

If the initial concentrations of Br_2 and Cl_2 are both 0.0250 M, calculate their equilibrium concentrations.

9.70 The equilibrium constant, K_c, for the reaction:

$$SO_3(g) + NO(g) \rightleftharpoons NO_2(g) + SO_2(g)$$

was found to be 0.500 at a certain temperature. If 0.240 mol of SO_3 and 0.240 mol of NO are placed in a 2.00 L container and allowed to react, calculate the equilibrium concentration of each gas.

9.71 For the reaction in question 9.70, a reaction mixture is prepared in which 0.120 mol NO_2 and 0.120 mol of SO_2 are placed in a 1.00 L vessel. What are the concentrations of all four gases at equilibrium? How do these equilibrium values compare with those calculated in question 9.70? Account for your observation.

9.72 At a certain temperature, the reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

has K_c = 0.400. Exactly 1.00 mol of each gas was placed in a 100 L vessel and the mixture underwent reaction. What was the equilibrium concentration of each gas?

9.73 The reaction $2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$ has $K_c = 3.2 \rightleftharpoons 10^{-34}$ at 25 °C. If a reaction vessel initially contains 0.0500 mol L^{-1} of HCl, what are the concentrations of H_2 and Cl_2 at equilibrium?

9.74 At 200 °C, $K_c = 1.4 \times 10^{-10}$ for the reaction:

$$N_2O(g) + NO_2(g) \rightleftharpoons 3NO(g)$$

If 0.200 mol of N_2O and 0.400 mol NO_2 are placed in a 4.00 L container, what is the NO

concentration at equilibrium?

9.75 At 2000 °C, the decomposition of CO_2:

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

has $K_c = 6.4 \times 10^{-7}$. If a 1.00 L container holding 1.0×10^{-2} mol of CO_2 is heated to 2000 °C, what is the concentration of CO at equilibrium?

9.76 At 500 °C, the decomposition of water into hydrogen and oxygen:

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

has $K_c = 6.0 \times 10^{-28}$. What amounts of H_2 and O_2 are present at equilibrium in a 5.00 L reaction vessel at this temperature if the container originally held 0.015 mol H_2O?

9.77 At a certain temperature, $K_c = 0.18$ for the equilibrium:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

If 0.026 mol of PCl_5 is placed in a 2.00 L vessel at this temperature, what is the concentration of PCl_3 at equilibrium?

9.78 At 460 °C, the reaction:

$$SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$$

has $K_c = 85.0$. Suppose 0.100 mol of SO_2, 0.0600 mol of NO_2, 0.0800 mol of NO and 0.120 mol of SO_3 are placed in a 10.0 L container at this temperature. What are the concentrations of all the gases when the system reaches equilibrium?

9.79 At a certain temperature, $K_c = 0.500$ for the reaction:

$$SO_3(g) + NO(g) \rightleftharpoons NO_2(g) + SO_2(g)$$

If 0.100 mol SO_3 and 0.200 mol NO are placed in a 2.00 L container and allowed to come to equilibrium, what are the NO_2 and SO_2 concentrations?

9.80 At 25 °C, $K_c = 0.145$ for the following reaction in the solvent CCl_4:

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

A solution was prepared with the following initial concentrations: [BrCl] = 0.0400 m, [Br_2] = 0.0300 m, [Cl_2] = 0.0200 m. What are their equilibrium concentrations?

9.81 At a certain temperature, $K_c = 4.3 \times 10^5$ for the reaction:

$$HCOOH(g) \rightleftharpoons CO(g) + H_2O(g)$$

If 0.200 mol of HCOOH is placed in a 1.00 L vessel, what are the concentrations of CO and H_2O when the system reaches equilibrium?

9.82 The reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ has $K_c = 2.0 \times 10^9$ at 25 °C. If 0.100 mol of H_2 and 0.200 mol of Br_2 are placed in a 10.0 L container, what are the equilibrium concentrations of all components at 25 °C?

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9.83 The reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ has $K_p = 0.114$ at 25 °C. In a reaction vessel containing these gases in equilibrium at this temperature, the partial pressure of N_2O_4 was 2.53×10^4 Pa.

(a) What was the partial pressure of the NO_2 in the reaction mixture?

(b) What was the total pressure of the mixture of gases?

9.84 The following reaction in aqueous solution has $K_c = 1 \times 10^{-85}$ at a temperature of 25 °C:

$$7IO_3^-(aq) + 9H_2O(l) + 7H^+(aq) \rightleftharpoons I_2(aq) + 5H_5IO_6(aq)$$

What is the equilibrium constant expression for this reaction?

9.85 At a certain temperature, $K_c = 0.914$ for the reaction:

$$NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$$

A mixture was prepared containing 0.200 mol NO_2, 0.300 mol NO, 0.150 mol N_2O and 0.250 mol O_2 in a 4.00 L container. What are the equilibrium concentrations of each gas?

9.86 At 400 °C, $K_c = 2.9 \times 10^4$ for the reaction:

$$HCOOH(g) \rightleftharpoons CO(g) + H_2O(g)$$

A mixture was prepared with the following initial concentrations: [CO] = 0.20 m, [H_2O] = 0.30 m. No formic acid, HCOOH, was initially present. What was the equilibrium concentration of HCOOH?

9.87 At 27 °C, $K_p = 1.5 \times 10^{18}$ for the reaction:

$$3NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$$

If 0.030 mol of NO is placed in a 1.00 L vessel and equilibrium is established, what are the equilibrium concentrations of NO, N_2O and NO_2?

9.88 Consider the equilibrium:

$$2NaHSO_3(s) \rightleftharpoons Na_2SO_3(s) + H_2O(g) + SO_2(g)$$

How is the position of equilibrium affected by the following?

(a) adding $NaHSO_3$ to the reaction vessel

(b) removing Na_2SO_3 from the reaction vessel

(c) adding H_2O to the reaction vessel

(d) increasing the volume of the reaction vessel

9.89 At a certain temperature, $K_c = 0.914$ for the reaction:

$$NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$$

A mixture was prepared containing 0.200 mol of each gas in a 5.00 L container. Calculate the equilibrium concentration of each gas. How will the concentrations change if 0.050 mol of NO_2 is added to the equilibrium mixture?

9.90 At a certain temperature, $K_c = 0.914$ for the reaction:

$$NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$$

Equal amounts of NO and NO_2 are placed in a 5.00 L container until the N_2O concentration at equilibrium is 0.050 m. What amounts of NO and NO_2 must be placed in the container?

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KEY TERMS

activities
chemical equilibrium
concentration table
dynamic equilibrium
equilibrium constant (K)
equilibrium constant expression
Gibbs energy diagrams
heterogeneous equilibrium
heterogeneous reaction
homogeneous equilibrium
homogeneous reaction
Le Châtelier's principle
reaction quotient *(Q)*
reaction quotient expression
thermodynamic equilibrium constants
van't Hoff equation

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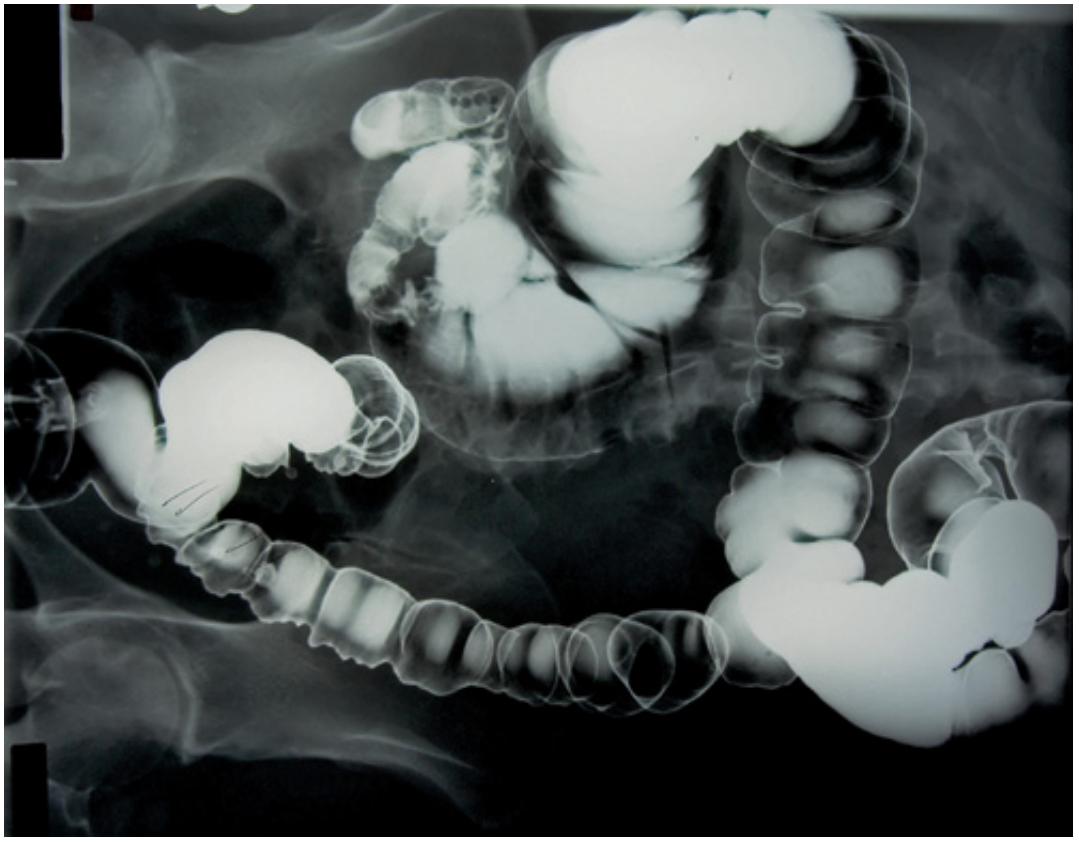
CHAPTER

10 Solutions and Solubility

The discovery of X-rays in 1895 enabled doctors to take images of the inside of the living human body for the first time, and this technique is still used over one hundred years later. It relies on the absorption of X-rays by constituents of the body. While objects such as bone give clear images, soft tissue is more difficult to see. Therefore, to create an X-ray image of areas such as the gastrointestinal tract, it is necessary to use a contrast agent which absorbs X-rays well and which can be delivered specifically to the required part of the body. Barium sulfate, $BaSO_4$, is one such contrast agent. This is ingested by the patient in the form of a barium meal, thereby coating the gastrointestinal tract, and an X-ray is taken shortly thereafter. This photo is an example of an X-ray of the gastrointestinal tract using $BaSO_4$ as a contrast agent.

It may surprise you to learn that the Ba^{2+} ion is highly toxic, and that swallowing a barium salt would generally end in death. However, barium sulfate is only slightly soluble in aqueous solution, meaning that the concentration of Ba^{2+} never approaches toxic levels.

In this chapter, we will examine various aspects of solutions and solubility. In addition to outlining the different possible types of solutions, we will investigate the energetics behind the formation of solutions, quantify the solubility of slightly soluble salts using the solubility product, K_{sp}, and show that physical properties such as the freezing and boiling points of solutions depend on the number of solute particles in the solution.



KEY TOPICS

10.1 Introduction to solutions and solubility
10.2 Gaseous solutions
10.3 Liquid solutions
10.4 Quantification of solubility: the solubility product
10.5 Colligative properties of solutions

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10.1 Introduction to Solutions and Solubility

The ability of chemical substances to mix with each other is a very important aspect of chemistry. We are familiar with many examples from everyday life; for example, dissolving instant coffee in a cup of hot water, adding detergent to water and cleaning a used paintbrush with turpentine are all situations where we require two substances to mix completely. However, there are also substances that we cannot get to mix no matter how hard we try, the prime example being oil and water (so we don't use water to clean a paintbrush covered in oil-based paint). Many aspects of chemical synthesis, in particular the purification of products following a chemical reaction, rely on the fact that particular substances don't mix. An understanding of the principles involved in the formation of solutions is important in many areas of chemistry. In this chapter, we will focus on the energetics of formation of solutions and the quantification of physical properties of solutions.

A **solution** can be defined as a homogeneous mixture of two or more pure substances ('homogeneous' means that all regions of the solution have exactly the same composition). Despite the fact that we often think of a solution as involving some type of liquid, we can have gaseous solutions comprising two or more gases (e.g. air) and even solid solutions comprising two or more solids (e.g. alloys such as brass and pewter) in addition to the 'usual' solutions containing a gas, liquid or solid dissolved in a liquid. In the case of liquid solutions, we call the liquid the **solvent**, while the dissolved substance is called the **solute**; the solute is present in smaller amounts than the solvent. A solute is said to be **soluble** in a particular solvent if it dissolves completely in that solvent at the specified temperature. We define the **solubility** of the solute in a particular solvent as the maximum amount of the solute that dissolves completely in a given amount of the solvent at a particular temperature, T, and a particular pressure, P, while a **saturated solution** is one in which no more solute will dissolve.

The most common type of saturated solution we will encounter is that illustrated in figure 10.1, in which excess solid solute is in equilibrium with its dissolved form.

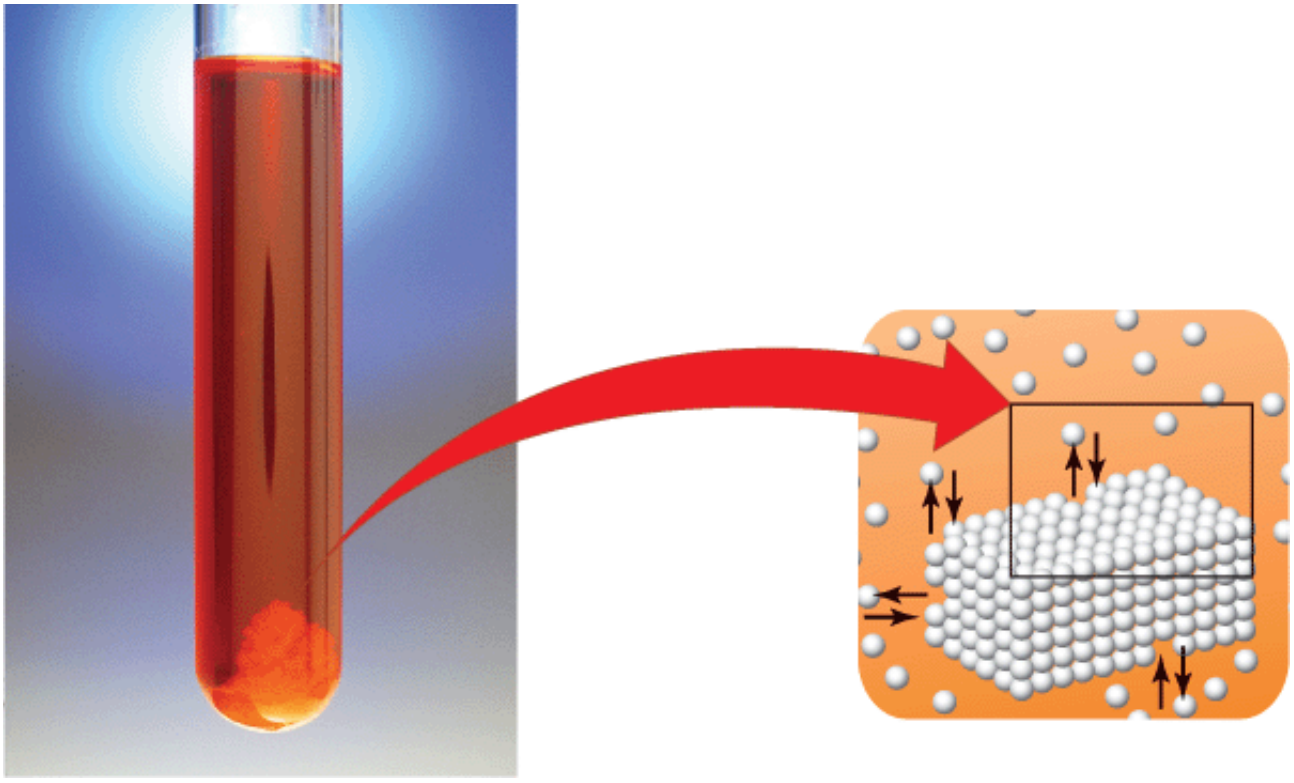


FIGURE 10.1 A saturated solution. In a saturated solution, a dynamic equilibrium exists between the undissolved solute and the dissolved solute in the solution.

The process of dissolving a solute in a solvent to give a homogeneous solution is called **dissolution**. We

therefore talk of the dissolution of a solute in a particular solvent.

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10.2 Gaseous Solutions

We will begin our investigation of solutions by looking at mixing two gases to form a gaseous solution. We start with the situation depicted in figure 10.2, where two different pure gases are separated by a divider. When we remove the divider, we find that the two gases mix spontaneously to give a homogeneous gaseous solution. This is not surprising given that the gas molecules are moving randomly at hundreds of metres per second. Even if we cool the two gases, they will still mix, albeit more slowly. In fact, as we saw in chapter 9, all gases mix completely with all other gases in all proportions. The fact that the two gases in figure 10.2 mix spontaneously means that ΔG for the mixing process ($\Delta_{mix}G$) must be negative. Recalling from chapter 8 that:

$$\Delta G = \Delta H - T\Delta S$$

and given that the enthalpy change when two gases are mixed is usually small, it is the large positive $\Delta_{mix}S$ term that ensures that $\Delta_{mix}G$ is negative. The completely mixed state is far more statistically likely and, therefore, of higher entropy than the unmixed state; this leads to a large entropy increase on mixing, and a correspondingly large positive $\Delta_{mix}S$ value. In fact, we say that the mixing process is entropy driven. When we consider the gases at the molecular level (or indeed the atomic level for monatomic gases such as He, Ne, Ar, Kr, Xe and Rn), we can see that there is no impediment to mixing the gases, as the intermolecular forces between individual gas molecules are tiny, and the gas molecules are far apart. However, when we consider condensed-phase solutions (i.e. solutions involving liquids and/or solids), we will see that the magnitude of interatomic or intermolecular attractions in the condensed phase can determine whether or not two substances can mix. In these cases, the enthalpy of mixing becomes important.

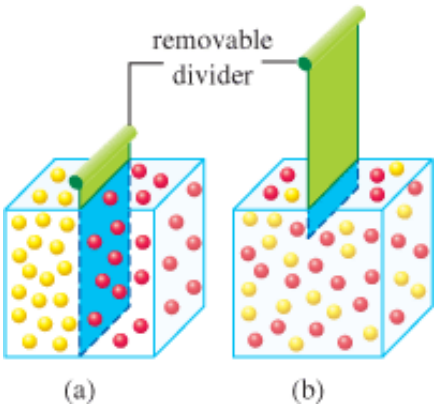


FIGURE 10.2 Mixing gases. When two gases, initially in separate compartments **(a)** suddenly find themselves in the same container **(b)**, they mix spontaneously.

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10.3 Liquid Solutions

As mentioned on the previous page, there are many possible types of solutions. In this section, we will discuss, in detail, the solutions that result from dissolution of a gas, liquid or solid in a liquid.

Gas–liquid Solutions

As can be seen in table 10.1, gases display a wide range of solubilities in water. Molecules such as O_2 and N_2 have very limited solubility at room temperature, while the solubility of the polar molecule ammonia is a quite remarkable 51.8 g per 100 g of water at 20 °C. For a gas to dissolve in a liquid, the gas molecules must be able to disperse themselves evenly throughout the solvent. Such a process differs from that for formation of a gaseous solution in that the intramolecular forces between the solvent molecules are not negligible, and neither therefore is the value of $\Delta_{sol}H$, the enthalpy of solution.

TABLE 10.1 Solubilities of common gases in water

	Temperature		
Gas	0 °C	20 °C	50 °C
nitrogen, N_2	0.0029([a])	0.0019	0.0012
oxygen, O_2	0.0069	0.0043	0.0027
carbon dioxide, CO_2	0.335	0.169	0.076
sulfur dioxide, SO_2	22.8	10.6	4.3
ammonia, NH_3	89.9	51.8	28.4

a Solubilities are in grams of solute per 100 g of water when the gaseous space over the liquid is saturated with the gas and the total pressure is 10^5 Pa.

The enthalpy change when a gas dissolves in a liquid has essentially two contributions, as shown in figure 10.3 on the next page.

1. ***Energy is required to open 'pockets' in the solvent that can hold gas molecules.*** The solvent must be expanded slightly to accommodate the molecules of the gas. This is an endothermic process since attractions between solvent molecules must be overcome. Water is a special case — it already contains open holes in its network of loose hydrogen bonds around room temperature. For water, very little energy is required to create pockets that can hold gas molecules.
2. ***Energy is released when gas molecules enter these pockets.*** Intermolecular attractions between the dissolved gas molecules and the surrounding solvent molecules lower the total energy, and energy is released as heat. The stronger the attractions are, the more heat is released. Water can form hydrogen bonds with some gases, such as NH_3, whereas many organic solvents cannot. More heat is released when such a gas molecule is placed in a pocket in water than in organic solvents.

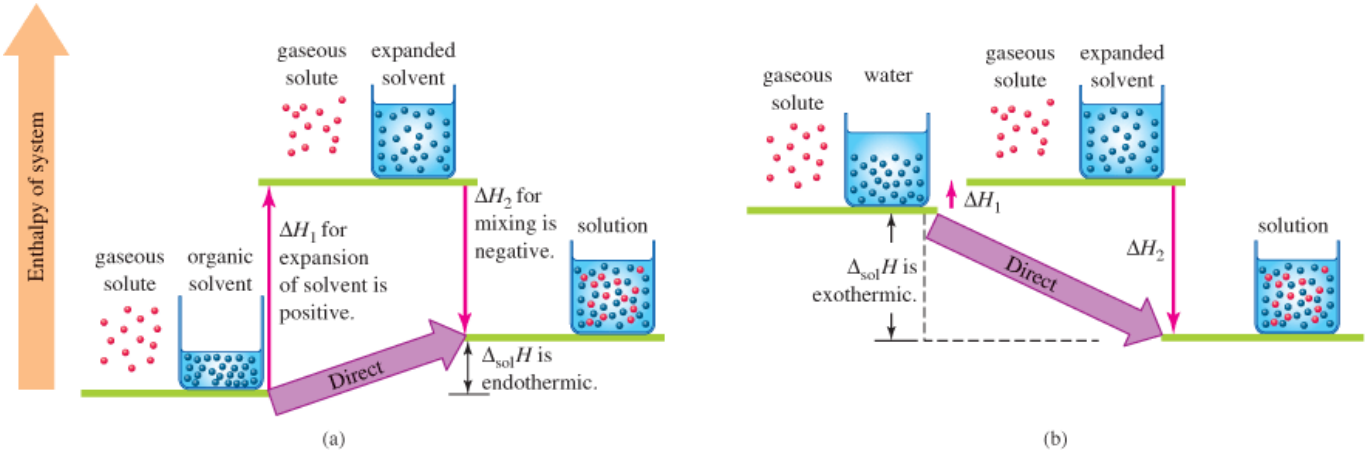


FIGURE 10.3 A molecular model of gas solubility:

(a) A gas dissolves in an organic solvent. Energy is absorbed to open 'pockets' in the solvent that can hold the gas molecules. In the second step, energy is released when the gas molecules enter the pockets, where they are attracted to the solvent molecules. Here, the solution process is shown to be endothermic.

(b) Around room temperature, water's loose network of hydrogen bonds already contains pockets that can accommodate gas molecules, so little energy is needed to prepare the solvent to accept the gas. In the second step, energy is released as the gas molecules take their place in the pockets where they experience attractions to the water molecules. In this case, the solution process is exothermic.

Enthalpies of solution for gases in organic solvents are often endothermic because the energy required to open up pockets is greater than the energy released by attractions formed between the gas and solvent molecules. Enthalpies of solution for gases in water are often exothermic because water already contains pockets to hold the gas molecules, and energy is released when water and gas molecules attract each other.

While we stated earlier that gaseous solutions form mainly because of the large entropy of the completely mixed state, the situation is not so straightforward with solutions of a gas in a liquid. Liquid water has a surprisingly ordered structure, and the addition of gas molecules does not necessarily disrupt this structure — in fact, there is experimental evidence that entropy *decreases*on formation of some gas–water solutions. Thus the solubility of a particular gas in water is a subtle balance of enthalpic and entropic effects, and it is often difficult to determine which factor predominates.

We can also see from table 10.1 that the solubility of gases in water varies significantly with temperature, with all the examples given becoming less soluble as the temperature increases. The decreasing solubility of O_2 with increasing temperature has obvious implications for aquatic life, given the gradual warming of the Earth's oceans.

If we write the dissolution process as an equilibrium between the undissolved gas and the dissolved gas:

$$\text{gas}_{\text{undissolved}} \rightleftharpoons \text{gas}_{\text{dissolved}}$$

we can see that the equilibrium constant for this process decreases with increasing temperature for the examples in table 10.1. Recalling the relationship between ΔH and K from chapter 9 (p. 368), we can conclude that the dissolution process for these gases is exothermic. However, not all gases become less soluble as the temperature increases; for example, the solubilities of H_2, N_2, CO, He and Ne in common organic solvents, such as toluene and acetone, actually increase with increasing temperature. You can see from these examples that predicting solubilities even in simple systems is fraught with difficulty!

The solubility of a gas in a liquid is affected not only by temperature but also by pressure. For example, the gases in air, chiefly nitrogen and oxygen, while not very soluble in water under ordinary pressures, become increasingly soluble at elevated pressures (see figure 10.4).

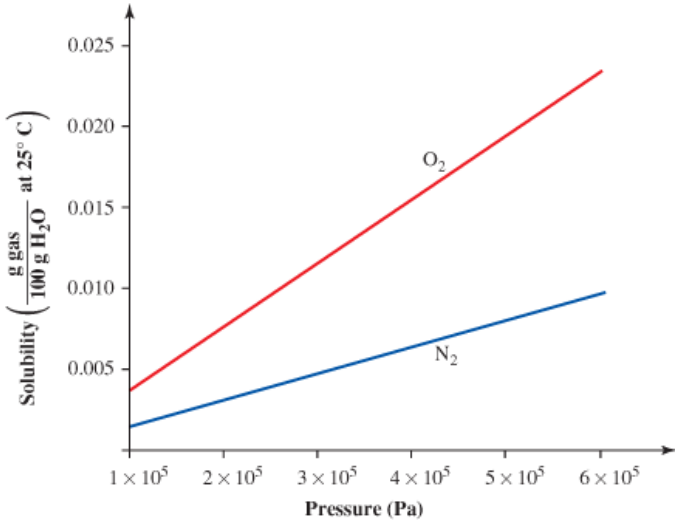


FIGURE 10.4 Solubility in water versus pressure for nitrogen and oxygen. The amount of gas that dissolves increases as the pressure is raised.

We can rationalise this observation by again considering the equilibrium:

$$\text{gas}_{\text{undissolved}} \rightleftharpoons \text{gas}_{\text{dissolved}}$$

and looking at the effect of increasing the pressure on the position of this equilibrium. The reaction quotient expression for this equilibrium can be written in a form that involves both the pressure of the undissolved gas and the concentration of the dissolved gas:

$$Q = \frac{[\text{gas}_{\text{dissloved}}]}{\frac{p(\text{gas}_{\text{undissloved}})}{p^{\ominus}}}$$

We can see from this that Q is inversely proportional to $p(\text{gas}_{\text{undissolved}})$. Thus, if we increase the pressure of the undissolved gas at constant temperature, we decrease Q so that $Q < K$. To restore equilibrium and make $Q = K$, the equilibrium position shifts towards the right-hand side to increase Q by increasing $[\text{gas}_{\text{dissolved}}]$. Of course, the converse is also true; if we decrease the pressure above a gas–liquid solution, we increase Q, and some of the dissolved gas leaves the solution in order to decrease Q and restore equilibrium. We see this most often whenever we open a bottle of anything fizzy; when the top is removed, bubbles of CO_2 emerge from the solution in response to the sudden lowering of pressure (figure 10.5).



FIGURE 10.5 Bottled carbonated beverages fizz when the bottle is opened because the sudden drop in pressure causes a sudden drop in gas solubility.

To see how pressure affects gas solubility on a molecular level, imagine a closed container with a piston, partly filled with a solution of a gas in a liquid. Figure 10.6a shows the system at equilibrium; gas molecules move at equal rates between the dissolved and undissolved states. Gas molecules enter the solution at a rate proportional to the frequency with which they collide with the surface of the solution. This frequency increases when we increase the pressure of the gas (figure 10.6b) because the gas molecules are squeezed closer together. Because liquids and liquid solutions are incompressible, the increased pressure alone has no effect on the frequency with which gas molecules can leave the solution. That means that increasing the pressure favours dissolution of the gas.

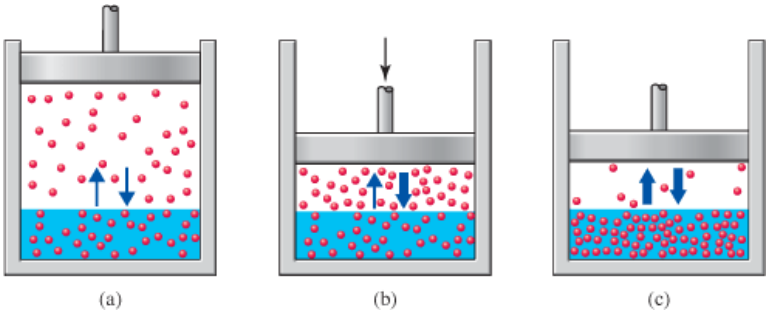


FIGURE 10.6 How pressure increases the solubility of a gas in a liquid:
(a) At some specific pressure, equilibrium exists between the vapour phase and the solution.
(b) An increase in pressure puts stress on the equilibrium. More gas molecules are dissolving than are leaving the solution.
(c) More gas has dissolved and equilibrium is restored.

As more gas dissolves, however, the rate of the forward process to give dissolved gas steadily slows and the reverse rate increases. It increases because, at a higher concentration of dissolved gas, there are simply more gas molecules in solution at each unit of surface area. Their frequency of escape is proportional to this concentration. But the dissolution process dominates until enough additional gas has dissolved to equalise the opposing rates. We again have equilibrium (figure 10.6c), but now more gas molecules are dissolved in the solution than initially.

Henry's Law

For gases *that do not react with the solvent*, Henry's law gives the relationship between gas pressure and gas solubility. **Henry's law** states that the concentration of a gas dissolved in a liquid at any given temperature is directly proportional to the partial pressure of the gas above the solution:

$$c_{\text{gas}} = k_{\text{H}} p_{\text{gas}} \text{ (at constant temperarture)}$$

In the equation, c_{gas} is the concentration of the dissolved gas and p_{gas} is the partial pressure (pp. 226–7) of the gas above the solution. The proportionality constant, k_{H}, called the *Henry's law constant*, is unique to each gas. The equation is true only at low concentrations and pressures and, as we said, for gases that do not react with the solvent.

An alternative (and commonly used) expression of Henry's law is:

$$\frac{c_1}{p_1} = \frac{c_2}{p_2}$$

where c_1 and p_1 refer to initial conditions and c_2 and p_2 to final conditions.

WORKED EXAMPLE 10.1

Using Henry's Law

At 20 °C, the solubility of N_2 in water, expressed in terms of mass of dissolved gas per volume of solution, is 0.0150 g L^{-1} when the partial pressure of nitrogen is 7.63×10^4 Pa. Use these data to calculate the Henry's Law constant for N_2 in water at this temperature. What is the solubility of N_2 in water at 20 °C when its partial pressure is 1.05×10^5 Pa?

Analysis

This problem deals with the effect of gas pressure on gas solubility, so Henry's law applies. We must first convert the solubility of N_2 in g L^{-1} to a solubility in mol L^{-1} to calculate the Henry's Law constant. We then use this to calculate the solubility at the higher pressure.

Solution

We use stoichiometry to determine the solubility of N_2 in mol L^{-1}. We know that 0.0150 g of N_2 will dissolve in 1.00 L of water. Therefore:

$$n_{N_2} = \frac{m}{M} = \frac{0.0150\,\text{g}}{28.02\,\text{g mol}^{-1}} = 5.35 \times 10^{-4}\,\text{mol}$$

This is the amount of N_2 that will dissolved in 1.00 L. Thus the solubility of N_2 is5.35×10^{-4} mol L^{-1}.

Gathering data, we now have $c_{gas} = 5.35 \times 10^{-4}$ mol L^{-1} and $p_{gas} = 7.63 \times 10^4$ Pa. We use these to calculate k_H by rearranging $c_{gas} = k_H p_{gas}$:

$$k_H = \frac{c_{gas}}{p_{gas}} = \frac{5.35 \times 10^{-4}\,\text{mol L}^{-1}}{7.63 \times 10^4\,\text{Pa}} = 7.01 \times 10^{-9}\,\text{mol L}^{-1}\,\text{Pa}^{-1}$$

We now use this calculated value of k_H to determine the solubility at higher pressure:

$$C_{gas} = k_H p_{gas} = 7.01 \times 10^{-9}\,\text{mol L}^{-1}\,\text{Pa}^{-1} \times 1.05^5\,\text{Pa} = 7.36 \times 10^{-4}\,\text{mol L}^{-1}$$

Therefore the solubility of N_2 at 1.05×10^5 Pa is 7.36×10^{-4} mol L^{-1}.

Is our answer reasonable?

As Henry's Law states that gas solubility is proportional to gas pressure, we would expect N_2 to be more soluble at higher pressure. Our answer shows this to be the case.

PRACTICE EXERCISE 10.1

At 1.0×10^5 Pa pressure and 20 °C, the solubility of oxygen in water is 0.00134 mol L^{-1}. Use these data to calculate k_H for O_2 under these conditions. Given that air comprises 21% O_2, what mass of O_2 would be dissolved in water when the water is saturated with air?

Liquid–liquid Solutions

The formation of a Liquid–Liquid solution requires that we overcome the attractive forces present between the molecules of the two pure liquids to get the liquids to mix completely. This is an even more complicated situation than formation of a gas–liquid solution, yet we can predict the ability of any two liquids to mix, with some confidence, simply by considering the polarities of the two liquids. For example, we find that ethanol and water mix completely in all proportions — we say they are **miscible** — while hexane and water are essentially **immiscible** and form two layers on addition of one liquid to the other (figure 10.7).

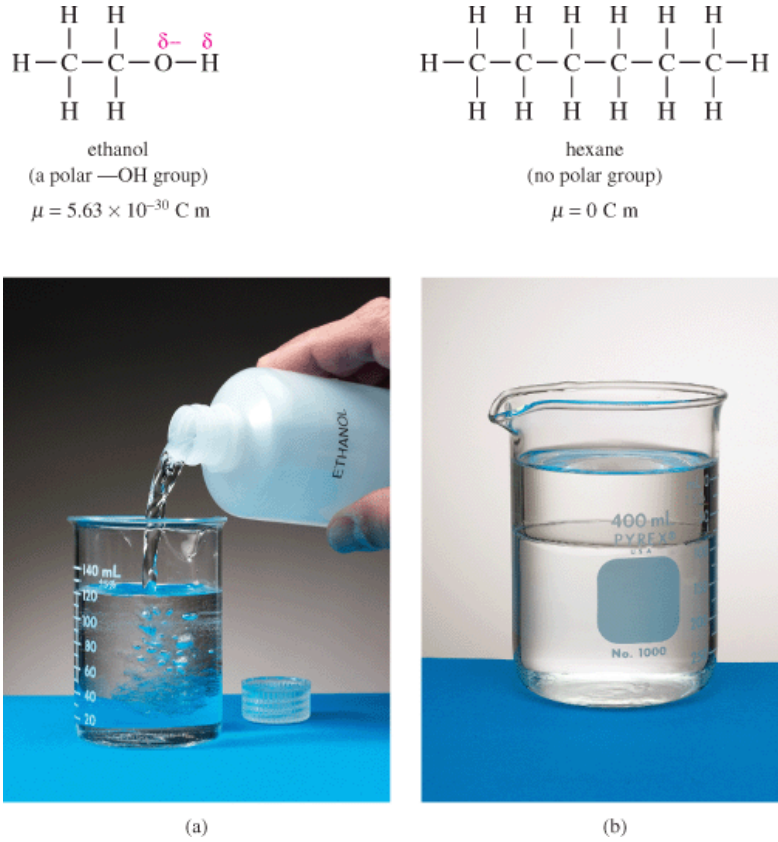


FIGURE 10.7 Like dissolves like.

(a) Ethanol is soluble in water because the mixed ethanol–water attractions are not significantly weaker than the water–water or ethanol–ethanol attractions.

(b) Hexane is not soluble in water because the mixed hexane–water attraction is much weaker than the water–water and hexane–hexane attractions. The stronger attractions in the pure liquids constitute an energy barrier to mixing.

Both water and ethanol are polar molecules, while hexane is essentially nonpolar; these facts are central to explaining the behaviour of these liquids on mixing. The —OH functional group in the ethanol molecule leads to extensive hydrogen bonding interactions between ethanol mol ecules and between ethanol and water molecules (figure 10.8). Thus, the intermolecular attractive forces in the two pure liquids can be compensated for on mixing by the hydrogen bonding interactions between the ethanol and water molecules; the system, therefore, adopts the entropically favoured mixed state. Conversely, hexane molecules are nonpolar and so cannot interact strongly with water molecules; this means that the energy required to disrupt the hydrogen bonding network in water cannot be compensated for by water–hexane interactions on mixing. Even if we could disperse water molecules in hexane, each time two water molecules collided, they would tend to ‘stick together’ through hydrogen bonding interactions. This would continue to occur until all the water mol ecules had stuck together and the system would eventually become two phases.

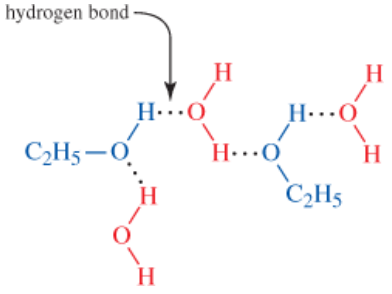


FIGURE 10.8 Hydrogen bonds in aqueous ethanol. Ethanol molecules form hydrogen bonds to water molecules.

We can use similar arguments to explain why nonpolar liquids tend to mix with each other. The intermolecular interactions in the pure liquids are low, so there is no energetic impediment to mixing.

In general, when two liquids are of similar polarity, they tend to be miscible, whereas liquids of widely differing polarities are often found to be immiscible. This **like-dissolves-like rule** works well in predicting solubilities, but, as always, there are exceptions. The presence of a polar —OH functional group does not guarantee that all alcohols are water soluble; while methanol, CH_3OH, ethanol, CH_3CH_2OH, and propan-1-ol, $CH_3CH_2CH_2OH$, are miscible with water in all proportions, butan-1-ol, $CH_3CH_2CH_2CH_2OH$, is only partially miscible and pentan-1-ol, $CH_3CH_2CH_2CH_2CH_2OH$, is immiscible.

The differing miscibilities of the above alcohols with water cannot be explained in terms of differing polarities as they all have very similar dipole

moments (˜5.6 × 10^{-30} C m). We must therefore consider the relative energetic magnitudes of the hydrogen bonding interactions between the polar —OH functional groups and water, and the dispersion forces between the nonpolar hydrocarbon tails of neighbouring alcohol molecules. For methanol, ethanol and propan-1-ol, the hydrogen bonding interactions between the —OH groups and water dominate, leading to water miscibility. However, as the hydrocarbon tails on the alcohol molecules increase in length beyond three carbon atoms, the dispersion forces between these become significant. This causes the alcohol molecules to cluster together as a single phase, leading to immiscibility with water.

We can use similar arguments to explain the solubilities of alcohols in nonpolar solvents. For example, even though long-chain alcohols are appreciably polar molecules, they are miscible with hexane because of the dispersion forces between the hydrocarbon chain on the alcohol and the hexane molecules. These dispersion forces diminish as the chain length of the alcohol decreases, and we find that the shortest chain alcohol, methanol, is immiscible with hexane.

The long-chain alcohols discussed above are examples of molecules with both polar and nonpolar regions; we might therefore expect the different regions of such molecules to display different affinities towards both polar and nonpolar solvents. Indeed, we make use of this behaviour every day when we use soaps and detergents to make oils and water mix. Both detergents and soaps consist of molecules called surfactants (a contraction of the term ‘surface active agents’), which comprise polar and nonpolar parts; the polar parts generally result from a full positive or negative charge. The structure of a common surfactant found in shampoos and tooth-pastes, sodium lauryl sulfate, is shown in figure 10.9. As the polar group is negatively charged, we call this an anionic surfactant. When added to a mixture of two immiscible liquids, the polar end of a surfactant molecule preferentially orients itself in the polar liquid, while the nonpolar end is situated in the nonpolar liquid. This helps bring the two immiscible phases together. This process will be discussed in more detail in chapter 23.

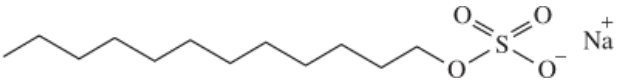


FIGURE 10.9 The structure of sodium lauryl sulfate.

Liquid–solid Solutions

In moving to solutions of solids in liquids, the basic principles remain the same. We will look first at what happens when sodium chloride, a crystalline salt, dissolves in water.

Figure 10.10 depicts a section of a crystal of NaCl in contact with water. The dipoles of water molecules orient themselves so that the negative ends of some point towards Na^+ ions and the positive ends of others point at Cl^- ions. In other words, *ion–dipole* attractions occur that tend to tug and pull ions from the crystal. At the corners and edges of the crystal, ions are held by fewer neighbours within the solid so they are more readily dislodged than those elsewhere on the crystal's surface. As water molecules dislodge these ions, new corners and edges are exposed, and the crystal continues to dissolve.

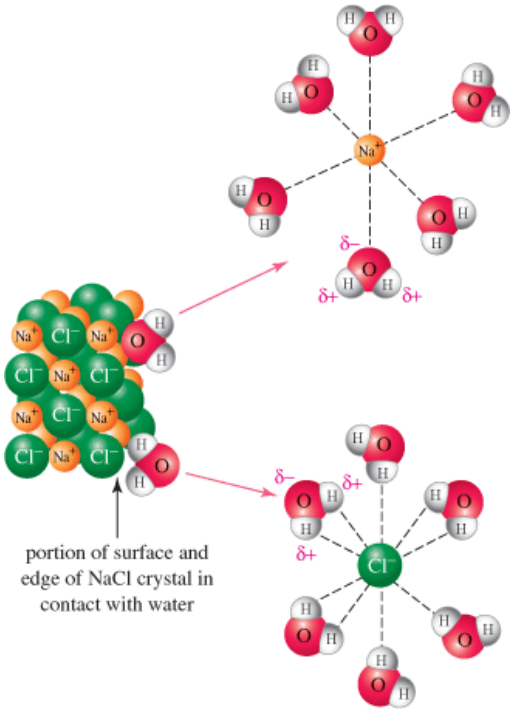


FIGURE 10.10 Hydration of ions involves a complex redirection of forces of attraction and repulsion. Before the solution forms, water molecules are attracted only to each other, and Na^+ and Cl^- ions are attracted only to each other in the crystal. In the solution, the ions have water molecules to take the places of their oppositely charged counterparts; in addition, water molecules are attracted to ions even more than they are to other water molecules.

As they are freed, the ions become completely surrounded by water molecules (figure 10.10). This phenomenon is called the **hydration** of ions. The *general* term for the surrounding of a solute particle by solvent molecules is **solvation**, so hydration is just a special case of solvation.

Ionic compounds can dissolve in water when the attractions between water dipoles and ions overcome both the attractions of the ions for each other within the crystal and the attractive forces between water molecules in bulk water. Similar events explain why solids composed of polar molecules, such as those of sugar, dissolve in water (see figure 10.11 on the next page). Attractions between the solvent and solute dipoles help to dislodge molecules from the crystal and bring them into solution. Again we see that 'like dissolves like'; a polar solute dissolves in a polar solvent.

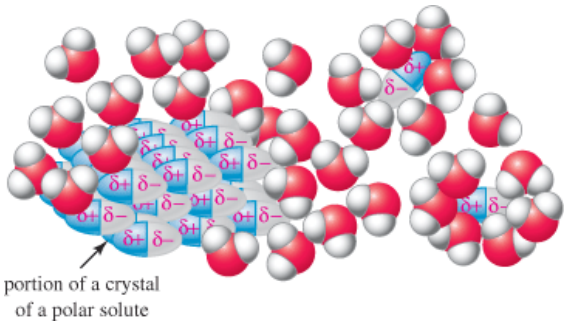


FIGURE 10.11 Hydration of a polar molecule. A polar solid dissolves in water because its molecules are attracted to the very polar water molecules, causing the solute molecules to become hydrated. Notice that the water molecules orient themselves so their positive ends are near the negative ends of the solute dipoles and their negative ends are near the positive ends of the solute dipoles.

The same reasoning explains why nonpolar solids, such as wax, are soluble in nonpolar sol-vents, such as benzene. Wax is a solid mixture of long-chain hydrocarbons held together by dispersion forces.

The attractions between the molecules of the solvent (benzene) and the solute (wax) are also due to dispersion forces of comparable strength.

When intermolecular attractive forces within solute and solvent are sufficiently different, the two do not form a solution. For example, ionic solids or very polar molecular solids (such as sugar) are **insoluble** in nonpolar solvents such as benzene and hexane. The molecules of these hydrocarbon solvents are unable to attract ions or very polar molecules with enough force to overcome the much stronger attractions that the ions or polar molecules experience in the solid state.

We have already seen that, while the enthalpy changes on mixing in simple gaseous solutions are minimal, the same is not necessarily true in Liquid–Liquid solutions. The enthalpy changes on formation of a solution containing a dissolved ionic solid can be substantial and we will now consider these changes in some detail. Recalling from chapter 8 that enthalpy is a state function, and therefore does not depend on the way in which we get from the initial state to the final state, we can model the dissolution of an ionic solute in a solvent as a hypothetical two-step process, as shown in figure 10.12.

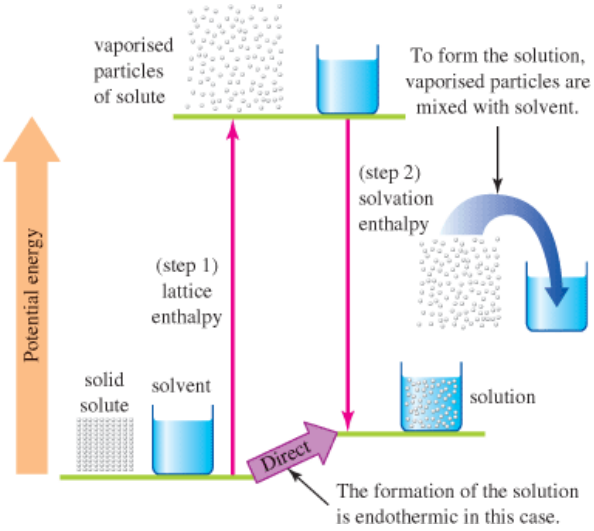


FIGURE 10.12 Enthalpy diagram for a solid dissolving in a liquid. In the real world, the solution is formed directly, as indicated by the purple arrow. We can analyse the enthalpy change by imagining the two separate steps, because enthalpy changes are state functions and so are independent of the path. The enthalpy change along the direct path is the algebraic sum of those for step 1 and step 2.

As you can see from figure 10.12, the first step is endothermic. The particles in the solid attract each other, and so energy must be supplied to separate them. The amount of energy required is the **lattice enthalpy**. Recall from chapter 8 that the lattice enthalpy is the enthalpy required to separate 1 mole of a crystalline compound into gaseous particles. For ionic compounds, the gaseous particles are ions; for molecular compounds, they are molecules. For example, the lattice enthalpy of potassium iodide, KI, is the enthalpy change for the process:

$$KI(s) \longrightarrow K^+(g) + I^-(g) \quad \Delta H = +632\ kJ\ mol^{-1}$$

In the second step, gaseous solute particles enter the solvent and are solvated. This step is exothermic. The enthalpy change when gaseous solute particles (obtained from 1 mole of solute) are dissolved in a solvent is called the **solvation enthalpy**. If the solvent is water, the solvation enthalpy can also be called the **hydration enthalpy**. For example, the hydration enthalpy of KI is the enthalpy change for the process:

$$K^+(g) + I^-(g) \rightarrow K^+(aq) + I^-(aq) \quad \Delta H = -619\ kJ mol^{-1}$$

The **enthalpy of solution ($\Delta_{sol}H$)** is the enthalpy change when 1 mole of a crystalline substance is dissolved in a solvent; it is equal to the enthalpy difference between the endothermic step 1 and the exothermic step 2 For example, the enthalpy of solution of KI calculated from the data given on the previous page is the sum of the enthalpy changes for steps 1 and 2, namely:

$$KI(s) \rightarrow K^+(aq) + I^-(aq) \quad \Delta_{sol}H = -619 kJ mol^{-1} + 632 kJ mol^{-1} = 13 kJ mol^{-1}$$

This process is shown in detail in figure 10.13.

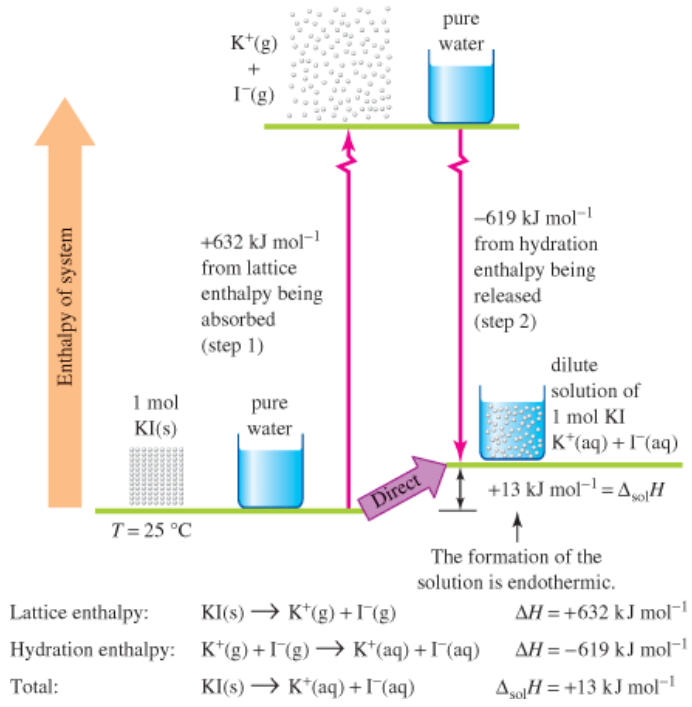


FIGURE 10.13 Enthalpy of solution — the formation of aqueous potassium iodide.

When the energy required for step 1 exceeds the energy released in step 2, the solution forms endothermically; when more energy is released in step 2 than is needed for step 1, the solution forms exothermically.

We can test this analysis by comparing the experimental enthalpies of solution of some salts in water with those calculated from lattice and hydration enthalpies (table 10.2). The calculations are described in figures 10.13 and 10.14 using enthalpy diagrams for the formation of aqueous solutions of two salts, KI and NaBr.

TABLE 10.2 Lattice enthalpies, hydration enthalpies and enthalpies of solution for some group 1 metal halides at 25 °C

			$\Delta_{sol}H$[(a)]	
Calculated	Lattice enthalpy (kJ mol^{-1})	Hydration enthalpy (kJ mol^{-1})	Calculated $\Delta_{sol}H$ (kJ mol^{-1})[(b)]	Measured $\Delta_{sol}H$ (kJ mol^{-1})
LiCl	+833	-883	-50	-37.0
NaCl	+766	-770	-4	+3.9
KCl	+690	-686	+4	+17.2
LiBr	+787	-854	-67	-49.0
NaBr	+728	-741	-13	-0.602
KBr	+665	-657	+8	+19.9
KI	+632	-619	+13	+20.33

(a) Enthalpies of solution refer to the formation of extremely dilute solutions.

(b) Calculated $\Delta_{sol}H$ = lattice enthalpy + hydration enthalpy.

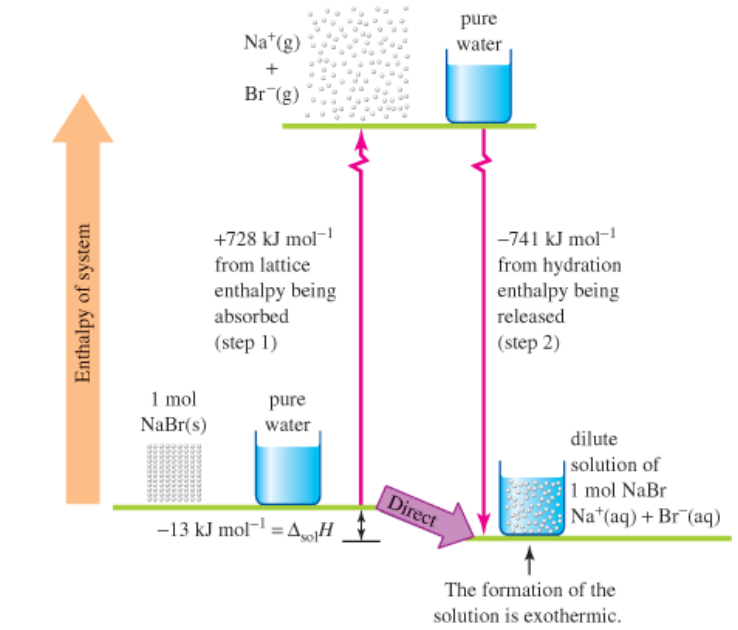


FIGURE 10.14 Enthalpy of solution — the formation of aqueous sodium bromide.

The agreement between calculated and measured values in table 10.2 is not particularly close. This is partly because precise lattice and hydration enthalpies are not known and partly because the model used in our analysis is evidently too simple. Notice however that, when 'theory' predicts relatively large enthalpies of solution, the experimental values are also relatively large and both values have the same sign (except for NaCl, where the values are close to 0 and fall either side of it). Notice also that the changes in values show the same trends when we compare the three chloride salts — LiCl, NaCl and KCl — and the three bromide salts — LiBr, NaBr and KBr.

Temperature can have a significant effect on the solubility of a solid solute in a liquid. Figure 10.15 shows a plot of solubility versus temperature for a number of ionic salts; it is obvious that all but one of these examples become more soluble as the temperature increases, which we might expect intuitively (there are few genuine examples of salts that become less soluble as the temperature increases).

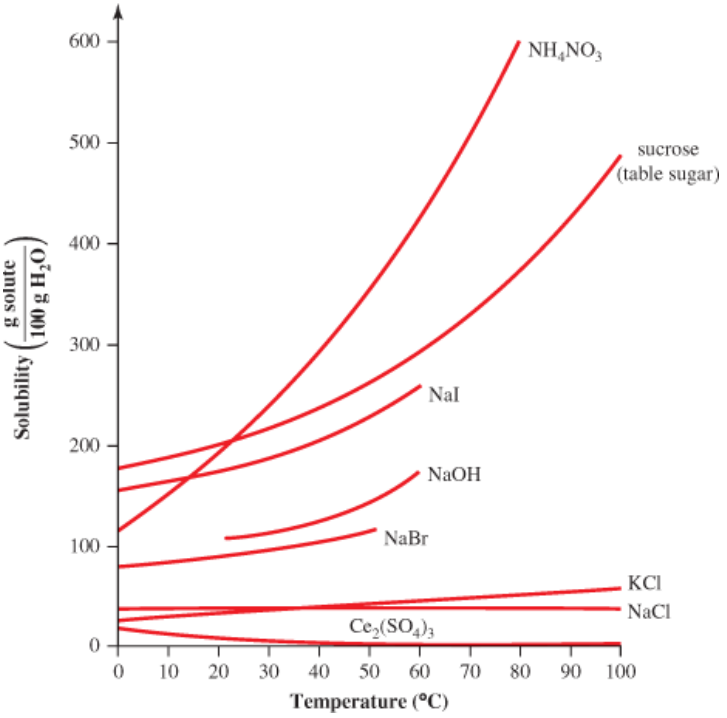


FIGURE 10.15 Solubility in water versus temperature for several substances. Most substances become more soluble when the temperature of the solution increases, but the amount of this increased solubility varies considerably.

However, not everything is as straightforward as we would wish. Many of you will have dissolved solid NaOH in water and noticed that the solution gets quite hot as the solid dissolves, meaning that the process is exothermic. From the van't Hoff equation (chapter 9, p. 368) we might therefore predict that the equilibrium constant for the dissolution of NaOH should decrease as the temperature increases; hence, NaOH should become less soluble with increasing temperature. As you can see in figure 10.15, the opposite trend is observed, and this can be explained by the nature of solid NaOH in a saturated solution. NaOH generally exists as an anhydrous solid — in other words, the crystalline solid contains no water molecules — and, as we have stated earlier, this dissolves exothermically. However, when we prepare a saturated solution of NaOH by adding excess NaOH to water, analysis of the solid phase shows it to consist not of anhydrous NaOH, but rather the solid *hydrate*, $NaOH{\cdot}H_2O$, in which one water molecule is associated with each NaOH unit. In fact, this species dissolves endothermically, so it is more soluble at higher temperatures. You should also appreciate that the van't Hoff equation uses $\Delta H^{\ominus}$ values, so $\Delta_{sol}H$ data measured under nonstandard conditions are of limited use in predicting the variation of solubilities with temperature.

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10.4 Quantification of Solubility: the Solubility Product

Ionic salts are generally classified as being either soluble or insoluble in water. The word 'insoluble' suggests that salts classified as such do not dissolve at all in water, but this is not the case. If we mix aqueous solutions containing equal amounts of the soluble salts silver nitrate and sodium chloride (figure 10.16), we see immediate precipitation of the 'insoluble' salt AgCl, according to the equation:

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

However, if we carefully analyse the solution above the precipitate, we find that it contains very small amounts of both $Ag^+(aq)$ and $Cl^-(aq)$ ions; this means that AgCl does in fact have a very limited solubility (about 0.19 milligrams per 100 mL at 25.0 °C) in aqueous solution. We would classify AgCl as a slightly soluble salt. As is the case with any saturated solution in contact with the undissolved solid, a dynamic equilibrium exists, with the rate of dissolution of AgCl(s) being the same as the rate of precipitation of $Ag^+(aq)$ and $Cl^-(aq)$. We can, therefore, quantify the solubility of AgCl(s) with reference to the magnitude of the equilibrium constant for the dissolution equilibrium:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The equilibrium constant for the dissolution of a slightly soluble salt is called the **solubility product** and is abbreviated K_{sp}. For the above equilibrium, we write K_{sp} as:

$$K_{sp} = [Ag^+][Cl^-]$$

Recall from chapter 9 that pure solids *never* appear in an equilibrium constant. Therefore, as we will see on the next page, the expression for K_{sp} for any ionic solid always consists only of the product of the aqueous ions raised to their stoichiometric powers. We can derive an expression for the solubility product of any salt $M_aX_b(s)$ by considering the equilibrium constant for its dissolution in water:

$$M_aX_b(s) \rightleftharpoons aM^{b+}(aq) + bX^{a-}(aq)$$

$$K_{sp} = [M^{b+}]\,[X^{a-}]^b$$

For AgCl, $K_{sp} = 1.8 \times 10^{-10}$ at 25.0 °C, meaning that the solubility of AgCl in water is indeed small *but not zero*. Salts that we generally classify as slightly soluble have K_{sp} values of the order of 10^{-5} or less, and table 10.3 gives K_{sp} data for a variety of such salts (a more comprehensive list is given in appendix C). In general, the smaller the value of K_{sp}, the less soluble is the salt. However, you should appreciate that direct comparison of K_{sp} values can be made only for salts with the same ratio of anions to cations. For example, CaF_2 is more soluble on a molar basis than AgCl in water, even though K_{sp} for CaF_2 is smaller than that for AgCl. This is because the equilibrium constant expressions for the two salts do not have identical forms; the equation for dissolution of CaF_2 is:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F-(aq)$$

and this leads to the equilibrium constant expression:

$$K_{sp} = \left[Ca^{2+}\right][F^-]^2$$

which obviously differs from that on the previous page for AgCl. We will explore this in more detail on the following pages.



FIGURE 10.16 Precipitation of AgCl(s) on mixing aqueous solutions of $AgNO_3$ and NaCl.

TABLE 10.3 Solubility products for selected slightly soluble salts at 25 °C

Salt		Dissolvedions	K_{sp}
halides			
$PbCl_2(s)$	⇄	$Pb^{2}+(aq) + 2Cl^{-}(aq)$	1.7×10^{-5}
$PbBr_2(s)$	⇄	$Pb^{2+}(aq) + 2Br^{-}(aq)$	2.1×10^{-6}
$PbF_2(s)$	⇄	$Pb^{2+}(aq) + 2F^{-}(aq)$	3.6×10^{-8}
$PbI_2(s)$	⇄	$Ag^{+}(aq) + Cl^{-}(aq)$	7.9×10^{-9}
$AgCl(s)$	⇄	$Pb^{2+}(aq) + 2I^{-}(aq)$	1.8×10^{-10}
$CaF_2(s)$	⇄	$Ca^{2+}(aq) + 2F^{-}(aq)$	3.9×10^{-11}
$AgBr(s)$	⇄	$Ag^{+}(aq) + Br^{-}(aq)$	5.0×10^{-13}
$AgI(s)$	⇄	$Ag^{+}(aq) + I^{-}(aq)$	8.3×10^{-17}
hydroxides			
$Ca(OH)_2(s)$	⇄	$Ca^{2+}(aq) + 2OH^{-}(aq)$	6.5×10^{-6}
$Mg(OH)_2(s)$	⇄	$Mg^{2+}(aq) + 2OH^{-}(aq)$	7.1×10^{-12}
$Fe(OH)_2(s)$	⇄	$Fe^{2+}(aq) + 2OH^{-}(aq)$	7.9×10^{-16}
$Zn(OH)_2(s)$	⇄	$Zn^{2+}(aq) + 2OH^{-}(aq)$	$3.0 \times 10^{-16(a)}$
$Al(OH)_3(s)$	⇄	$Al^{3}+(aq) + 3OH^{-}(aq)$	$3 \times 10^{-34(b)}$
$Fe(OH)_3(s)$	⇄	$Fe^{3+}(aq) + 3OH^{-}(aq)$	1.6×10^{-39}
carbonates			
	⇄		

$NiCO_3(s)$		$Ni^{2+}(aq) + CO_3^{2-}(aq)$	1.3×10^{-7}
$MgCO_3(s)$	⇄	$Mg^{2+}(aq) + CO_3^{2-}(aq)$	3.5×10^{-8}
$BaCO_3(s)$	⇄	$Ba^{2+}(aq) + CO_3^{2-}(aq)$	5.0×10^{-9}
$CaCO_3(s)$	⇄	$Ca^{2+}(aq) + CO_3^{2-}(aq)$	$4.5 \times 10^{-9(c)}$
$SrCO_3(s)$	⇄	$Sr^{2+}(aq) + CO_3^{2-}(aq)$	9.3×10^{-10}
$CoCO_3(s)$	⇄	$Co^{2+}(aq) + CO_3^{2-}(aq)$	1.0×10^{-10}
$ZnCO_3(s)$	⇄	$Zn^{2+}(aq) + CO_3^{2-}(aq)$	1.0×10^{-10}
$Ag_2CO_3(s)$	⇄	$2Ag^{+}(aq) + CO_3^{2-}(aq)$	8.1×10^{-12}
chromates			
$Ag_2CrO_4(s)$	⇄	$2Ag^{+}(aq) + CrO_4^{2-}(aq)$	1.2×10^{-12}
$PbCrO_4(s)$	⇄	$Pb^{2+}(aq) + CrO_4^{2-}(aq)$	2.5×10^{-13}
sulfates			
$CaSO_4(s)$	⇄	$Ca^{2+}(aq) + SO_4^{2-}(aq)$	2.4×10^{-5}
$PbSO_4(s)$	⇄	$Pb^{2+}(aq) + SO_4^{2-}(aq)$	6.3×10^{-7}
$SrSO_4(s)$	⇄	$Sr^{2+}(aq) + SO_4^{2-}(aq)$	3.2×10^{-7}
$BaSO_4(s)$	⇄	$Ba^{2+}(aq) + SO_4^{2-}(aq)$	1.1×10^{-10}
oxalates			
$MgC_2O_4(s)$	⇄	$Mg^{2+}(aq) + C_2O_4^{2-}(aq)$	8.6×10^{-5}
$FeC_2O_4(s)$	⇄	$Fe^{2+}(aq) + C_2O_4^{2-}(aq)$	2.1×10^{-7}
$BaC_2O_4(s)$	⇄	$Ba^{2+}(aq) + C_2O_4^{2-}(aq)$	1.2×10^{-7}
$CaC_2O_4(s)$	⇄	$Ca^{2+}(aq) + C_2O_4^{2-}(aq)$	2.3×10^{-9}
$PbC_2O_4(s)$	⇄	$Pb^{2+}(aq) + C_2O_4^{2-}(aq)$	2.7×10^{-11}

A more comprehensive list is given in appendix C.
(a) Exists in more than one solid form; data given for the amorphous form
(b) Exists in more than one solid form; data given for the alpha form
(c) Exists in more than one solid form; data given for the calcite form

The Relationship Between K_{sp} and Solubility

One way to determine the value of K_{sp} for a slightly soluble salt is to measure its solubility,i.e. how much of the salt is required to make a saturated solution of a specified volume. The molar concentration of a salt in its saturated solution is called the **molar solubility (s)**; this equals the amount of salt dissolved in 1 litre of the saturated solution at the specified temperature.The molar solubility can be used

to calculate K_{sp}, assuming that all of the salt that dissolves is 100% dissociated into its ions. This assumption works reasonably well for slightly soluble salts made of univalent ions, such as silver bromide. For simplicity, and to illustrate the nature of calculations involving solubility equilibria, we will work on the assumption that all salts behave as though they are 100% dissociated. This is not entirely true, especially for salts of polyvalent ions, so the accuracy of our calculations is limited.

WORKED EXAMPLE 10.2

Calculating K_{sp} from Solubility Data

In the time before digital photography, silver bromide, AgBr, was the light-sensitive compound used in nearly all photographic film. The solubility of AgBr in water is 1.3×10^{-4} g L^{-1} at 25 °C. Calculate K_{sp} for AgBr at this temperature.

Analysis

We begin by writing the balanced chemical equation for the dissolution of AgBr and use this to determine the expression for the solubility product, K_{sp}:

$$\begin{aligned} \mathrm{AgBr(s)} &\rightleftharpoons \mathrm{Ag^+(aq) + Br^-(aq)} \\ K_{sp} &= [\mathrm{Ag^+}]\,[\mathrm{Br^-}] \end{aligned}$$

To calculate K_{sp}, we require the concentrations of Ag^+ and Br^- in the saturated solution expressed in mol L^{-1}, so we must convert the given value of 1.3×10^{-4} g L^{-1} to mol L^{-1}. We then insert these values into the above expression for K_{sp}.

Solution

We know that 1.3×10^{-4} g of AgBr is dissolved in every litre of the saturated solution, so we convert 1.3×10^{-4} g of AgBr to amount in moles:

$$n = \frac{m}{M} = \frac{1.3 \times 10^{-4}\,\mathrm{g}}{187.77\,\mathrm{g\,mol^{-1}}} = 6.9 \times 10^{-7}\,\mathrm{mol}$$

From the balanced chemical equation for the dissolution reaction, we know that, when 6.9×10^{-7} mol of AgBr(s) dissolves in water, it produces 6.9×10^{-7} mol of Ag^+(aq) ions and 6.9×10^{-7} mol of Br^-(aq) ions. Hence, the molar concentrations of Ag^+ and Br^- are both 6.9×10^{-7} mol L^{-1}. Inserting these values into the expression for K_{sp} gives:

$$K_{sp} = \left[\mathrm{Ag^+}\right][\mathrm{Br^-}] = \left(6.9 \times 10^{-7}\,\mathrm{mol\,L^{-1}}\right)\left(6.9 \times 10^{-7}\,\mathrm{mol\,L^{-1}}\right) = 4.8 \times 10^{13}\,\mathrm{at\,25\,^\circ C}$$

As is usual with equilibrium constants, K_{sp} is dimensionless.

Is our answer reasonable?

We have divided roughly 1×10^{-4} by a number that is about 2×10^{2}, which gives a value of about 5×10^{-7}, so our molar solubility seems reasonable. (Also, we know AgBr has a very low solubility in water, so we expect the molar solubility to be very small.) The amount of each ion formed per litre must equal the amount of AgBr that dissolves. Finally, if we round

6.9×10^{-7} to 7×10^{-7} and square it, we obtain $49 \times 10^{-14} = 4.9 \times 10^{-13}$. Our answer of 4.8×10^{-13} therefore seems reasonable.

PRACTICE EXERCISE 10.2

The solubility of thallium(I) iodide, TlI, in water at 20 °C is 1.8×10^{-5} mol L^{-1}. Calculate K_{sp} for TlI assuming that it is 100% dissociated in the solution.

PRACTICE EXERCISE 10.3

The concentration of $Pb^{2}+$, i.e. $[Pb^{2+}]$, in a saturated solution of PbF_2 at 25 °C is 2.15×10^{-3} mol L^{-1}. Calculate the value of K_{sp} for PbF_2.

Obviously, if we can calculate K_{sp} from molar solubility data, we should also be able to calculate the molar solubility from K_{sp}. Worked example 10.3 shows how this is done.

WORKED EXAMPLE 10.3

Calculating Molar Solubility from K_{sp}

Calculate the molar solubility of lead iodide, PbI_2, given that $K_{sp}(PbI_2) = 7.9 \times 10^{-9}$ at 25 °C.

Analysis

We start, as usual, by writing the balanced chemical equation for the dissolution of $PbI_2(s)$ and write the K_{sp} expression from this:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^{-}(aq)$$

$$K_{sp} = \left[Pb^{2+}\right][I^{-}]^2$$

In this case, we know the value of K_{sp} and must determine $[Pb^{2+}]$ and $[I^-]$. However, we have one equation containing two unknowns. To solve this, we must make use of the stoichiometric relationship between $[Pb^{2+}]$ and $[I^-]$ in the saturated solution.

Solution

As this is an equilibrium problem, we can solve it using a concentration table in a similar

manner to the examples in chapter 9 (pp. 371–8). We set up the concentration table in the usual fashion, recognising that the initial concentrations of the ions will be 0 m. As the salt dissolves, *s* moles of PbI_2 will dissolve to increase the concentrations of Pb^{2+} and I^- by *s* and 2*s*, respectively. Note that we use *s* rather than *x* in this concentration table, as *s* is defined as the molar solubility; in other words the amount of the salt dissolved in 1 litre of solution.

Here is the concentration table.

	$PbI_2(s)$ $\rightleftharpoons$	$Pb^{2+}(aq)$ +	$2I^-(aq)$
Initial concentration (m)		0	0
Change in concentration (m)		+*s*	+2*s*
Equilibrium concentration (m)		*s*	2*s*

We now substitute the equilibrium concentrations into the equilibrium constant expression, K_{sp}.

$$\begin{aligned} K_{sp} &= [pb^{2+}][I^-]^2 \\ &= (s)(2s)^2 \\ &= (s)(4s^2) \\ &= 4s^3 \end{aligned}$$

We have now gone from one equation with two unknowns to one equation with a single unknown, *s*, which we can solve:

$$\begin{aligned} 4s^3 &= 7.9 \times 10^{-9} \\ s^3 &= \frac{7.9 \times 10^{-9}}{4} \\ &= 2.0 \times 10^{-9} \\ s &= 1.3 \times 10^{-3} \end{aligned}$$

Thus, the molar solubility of $PbI_2(s)$ in water at 25 °C is 1.3×10^{-3} mol L^{-1}.

Is our answer reasonable?

A molar solubility of 10^{-3} mol L^{-1} is low, implying that the salt is not very soluble and that our answer is at least reasonable. We can quickly check our answer by carrying out the reverse calculation, cubing *s* and multiplying the answer by 4. This should equal K_{sp} (allowing for rounding errors).

PRACTICE EXERCISE 10.4

Use the K_{sp} data in table 10.3 to calculate the molar solubility of (a) AgBr and (b) Ag_2CO_3 in water at 25 °C.

We have seen in worked example 10.3 that solubility, s, can be related to K_{sp}. The exact nature of this relationship depends on the chemical formula of the salt. As we showed for a 1: 2 electro-lyte (with the formula MX_2 or M_2X), $K_{sp} = 4s^3$. You should be able to derive the corresponding expressions for a 1: 1 electrolyte MX ($K_{sp} = s^2$), a 1: 3 electrolyte (MX_3 or M_3X, $K_{sp} = 27s^4$) and a 2: 3 electrolyte (M_2X_3 or M_3X_2, $K_{sp} = 108s^5$).

The Commonion Effect

Until now, we have considered the solubility only of slightly soluble ionic salts in pure water. Does the solubility of such salts differ if the solvent is not pure water but a solution that already contains one of the ions in the slightly soluble salt? Likewise, what happens if we take a saturated solution of a slightly soluble salt and add a solution of another salt that has one ion in common with the first salt?

We can answer these questions with reference to a saturated solution of $PbCl_2(s)$ ($K_{sp} = 1.7 \times 10^{-5}$) at equilibrium. To this saturated solution we add a small volume of a concentrated solution of $Pb(NO_3)_2$, a soluble lead salt, and look at the effect on the equilibrium position by comparing Q_{sp} and K_{sp}. We begin by writing the balanced chemical equation for the dissolution of $PbCl_2$ and derive the expression for K_{sp} from this, recalling that the expressions for K_{sp} and Q_{sp} have the same form. (In chapter 9, we called Q the reaction quotient. In the case of Q_{sp}, that name is rather incongruous, given that the expression for Q_{sp} is never a fraction. In some texts, Q_{sp} is called the **ionic product**.)

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$K_{sp} = \left[Pb^{2+}\right][Cl^-]^2$$

Adding a small volume of concentrated $Pb(NO_3)_2(aq)$ to the saturated solution instantaneously increases $[Pb^{2+}]$ and therefore Q_{sp}. This means that $Q_{sp} > K_{sp}$ and therefore, to restore equilibrium, Q_{sp} must be decreased. The system achieves this by precipitating $PbCl_2(s)$, which reduces both $[Pb^{2+}]$ and $[Cl^-]$, thereby decreasing Q_{sp} to the point where the equilibrium condition $Q_{sp} = K_{sp}$ is again satisfied. If we were to analyse the saturated solution at this point, we would find $[Cl^-]$ to be less than it was in the original solution. As all the Cl^- in solution comes from dissolution of $PbCl_2$, this means that $PbCl_2(s)$ is *less soluble* in the presence of another source of Pb^{2+}. This is a manifestation of the **common ion effect**, which states that any ionic salt is less soluble in the presence of a **common ion**, an ion that is a component of the salt.

We have shown above that $PbCl_2$ is less soluble in the presence of Pb^{2+} than it is in pure water, and we can also show by the same reasoning that it is less soluble in the presence of another source of Cl^-. The common ion effect is not limited to solutions of slightly soluble salts; for example, figure 10.17 shows that even the relatively soluble salt NaCl can be precipitated from solution on addition of concentrated HCl, a source of the common ion Cl^-. The addition or presence of a common ion *always* lowers the solubility of a salt providing that no further chemical reaction is possible. An example of a situation where a chemical reaction occurs is provided by the slightly soluble salt AgCl(s), which can react with excess Cl^- to form the complex anion $[AgCl_2^-]$, which, in turn, forms soluble salts with a variety of cations.



FIGURE 10.17 The common ion effect. The test tube shown here initially held a saturated solution of NaCl, where the equilibrium $NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$ had been established. Addition of a few drops of concentrated HCl, with a high concentration of the common ion Cl^-, forced the equilibrium to shift to the left. This caused some white crystals of solid NaCl to precipitate.

WORKED EXAMPLE 10.4

Calculations Involving the Common Ion Effect

What is the molar solubility of PbI_2 in a 0.10 M NaI solution at 25 °C?

Analysis

As usual, we begin with the balanced chemical equation and the expression for K_{sp} derived from it:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

$$K_{sp} = [Pb^{2+}][I^-]^2 = 7.9 \times 10^{-9} \text{ (from table 10.3)}$$

In this case, we construct a concentration table as we did in chapter 9 (p. 372). The initial concentration of Pb^{2+} is 0; we assume that NaI dissociates completely so the initial concentration of I^- is 0.10 M. As in worked example 10.3, we represent the molar solubility of $PbI_2(s)$ in the NaI solution as s mol L^{-1}. Therefore, when the $PbI_2(s)$ dissolves, $[Pb^{2+}]$ changes by $+s$ mol L^{-1} and $[I^-]$ by $+2s$ mol L^{-1}. We can then calculate the equilibrium concentrations of Pb^{2+} and I^- by summing the initial concentrations and the changes. Here is the concentration table.

	$PbI_2(s)$ $\rightleftharpoons$	$Pb^{2+}(aq)$ +	$2I^-(aq)$
Initial concentration (m)		0	0.10
Change in concentration (m)		$+s$	$+2s$
Equilibrium concentration (m)		s	$0.10 + 2s$

Solution

Substituting equilibrium values into the K_{sp} expression gives:

$$K_{sp} = [Pb^{2+}][I^-]^2 = s(0.10 + 2s)^2 = 7.9 \times 10^{-9}$$

A brief inspection reveals that solving this expression for *s* will be difficult if we cannot simplify the maths. Fortunately, a simplification is possible, because the small value of K_{sp} for PbI_2 tells us that the salt has a very low solubility. We also know that the presence of the common ion I^- makes PbI_2 even less soluble. This means very little of the salt will dissolve, so *s* (or even 2*s*) is quite small. Let's assume that 2*s* is much smaller than 0.10, in a similar fashion to simplifications we made in worked example 9.16 on pp. 378–9. If this is so:

$$0.10 + 2s \approx 0.10 \text{(assuming 2s is negligible compared with 0.10)}$$

Substituting 0.10 M for the I^- concentration gives:

$$\begin{aligned} K_{sp} &= s(0.10)^2 = 7.9 \times 10^{-9} \\ s &= \frac{7.9 \times 10^{-9}}{(0.10)^2} \\ &= 7.9 \times 10^{-7} \text{M} \end{aligned}$$

Thus, the molar solubility of PbI_2 in 0.10 M NaI solution is 7.9×10^{-7} M.

Is our answer reasonable?

Check the entries in the table. The initial concentrations come from the NaI solution, which contains no Pb^{2+} but does contain 0.10 M I^-. By letting *s* equal the molar solubility, the coefficients of *s* in the 'Change in concentration' row equal the coefficients in the equation for the equilibrium. We should also check to see if our simplifying assumption is valid. Notice that 2*s*, which equals 1.6×10^{-6}, is indeed vastly smaller than 0.10, just as we anticipated. (If we add 1.6×10^{-6} to 0.10 and round correctly, we obtain 0.10.)

In worked example 10.3 we found that the molar solubility of PbI_2 in *pure* water is 1.3×10^{-3} M. In water that contains 0.10 M NaI (worked example 10.4), the solubility of PbI_2 is 7.9×10^{-7} M, well over 1000 times smaller. As we said, the common ion effect can cause huge reductions in the solubilities of slightly soluble compounds.

PRACTICE EXERCISE 10.5

Calculate the molar solubility of AgI in 0.20 M NaI solution at 25 °C. Compare the answer with the calculated molar solubility of AgI in pure water.

PRACTICE EXERCISE 10.6

Calculate the molar solubility of $Fe(OH)_3$ in a solution where the OH^- concentration is initially0.050 M at 25 °C. Assume that any dissolved $Fe(OH)_3$ dissociates completely into its ions Fe^{3+} and $3OH^-$.

Will a Precipitate Form?

We can use K_{sp} values to predict whether a precipitate will form when solutions containing ionic salts are mixed. We calculate Q_{sp} by determining the molar concentration of the appropriate ions immediately after mixing and compare this value with K_{sp}. If $Q_{sp} > K_{sp}$ at the instant the solutions are mixed, the equilibrium position will move to the left to make $Q_{sp} = K_{sp}$. This will result in the formation of a precipitate. Conversely, if $Q_{sp} < K_{sp}$ on mixing the solutions, the equilibrium position will move to the right, the dissolved ions will be favoured, and no precipitate will form.

WORKED EXAMPLE 10.5

Predicting Whether a Precipitate Will form

Will a precipitate of AgCl(s) form on mixing 50.0 mL of 1.0×10^{-4} M NaCl(aq) with50.0 mL of 1.0×10^{-6} M $AgNO_3$(aq) at 25 °C?

Analysis

We have to calculate Q_{sp} for the solution immediately after mixing and compare its value with K_{sp} for AgCl. Thus, we require the molar concentrations of Ag^+(aq) and Cl^-(aq), remembering that there is a dilution factor on mixing the two solutions.

Solution

We begin by writing the balanced chemical equation for the dissolution of AgCl(s) and deriving the expression for K_{sp} from it:

$$\begin{aligned} AgCl(s) &\rightleftharpoons Ag^+(aq) + Cl^-(aq) \\ K_{sp} = [Ag^+][Cl^-] &= 1.8 \times 10^{-10} \text{ (from table 10.3)} \end{aligned}$$

We then calculate the molar concentrations of Ag^+ and Cl^- in the final mixed solution by determining the amount of each and dividing it by the volume of the final solution:

$$n_{Ag^+} = cV = (1.0 \times 10^{-6}\,\text{mol L}^{-1}) \times (50.0 \times 10^{-3}\,\text{L}) = 5.0 \times 10^{-8}\,\text{mol}$$

$$n_{Cl^-} = cV = (1.0 \times 10^{-4}\,\text{mol L}^{-1}) \times (50.0 \times 10^{-3}\,\text{L}) = 5.0 \times 10^{-6}\,\text{mol}$$

$$[Ag^+]_{\text{final}} = \frac{5.0 \times 10^{-8}\,\text{mol}}{100 \times 10^{-3}\,\text{L}} = 5.0 \times 10^{-7}\,\text{mol L}^{-1}$$

$$[Cl^-]_{\text{final}} = \frac{5.0 \times 10^{-6}\,\text{mol}}{100 \times 10^{-3}\,\text{L}} = 5.0 \times 10^{-5}\,\text{mol L}^{-1}$$

We now substitute these values into the expression for Q_{sp}:

$$Q_{sp} = [Ag^+][Cl^-] = (5.0 \times 10^{-7}\,\text{mol L}^{-1}) \times (5.0 \times 10^{-5}\,\text{mol L}^{-1}) = 2.5 \times 10^{-11}$$

Thus $Q_{sp} < K_{sp}$, so we predict that no precipitate of AgCl(s) will form when the solutions are mixed.

Is our answer reasonable?

As this is essentially a stoichiometric problem, it is hard to tell whether the answer makes sense. In cases like these, you should check your arithmetic and ensure you have transcribed the correct numbers into your calculations. The most common mistake to make in this type of problem is to forget to take account of the final volume of the mixed solution. We have used the correct numbers, and we have factored in the dilution, so our answer should be correct. This example clearly shows that AgCl(s) is not insoluble.

PRACTICE EXERCISE 10.7

Will a precipitate of $PbSO_4$(s) form if we mix 100.0 mL of 1.0×10^{-3} M $Pb(NO_3)_2$(aq) and 100.0 mL of 2.0×10^{-3} M $MgSO_4$(aq) at 25 °C?

PRACTICE EXERCISE 10.8

Will a precipitate of $PbCl_2$(s) form if we mix 50.0 mL of 0.10 M $Pb(NO_3)_2$(aq) and 20.0 mL of 0.040 M NaCl(aq) at 25 °C?

Chemistry Research

Scale — Crystals Causing Problems for Industry

Dr Franca Jones and Professor Mark Ogden, Curtin University

Next time you are about to boil the kettle, have a look inside. More often than not, you will see a build-up of solid material on and around the heating element. This is *scale* — an undesirable solid (usually crystalline) material (figure 10.18). While cleaning out the kettle is an easy task, imagine having to remove tonnes of crystalline solid from a huge industrial plant, or trying to unclog a borehole delivering oil from below the seabed. These are the challenges faced by industry when trying to deal with the very costly problem of scale formation.



FIGURE 10.18 Scale inside a metal pipe.

Consider a solution flowing through a pipe. The *thermodynamics* of a system tells us *if* crystal growth *f*will occur (see Chemistry Research on p. 334). If the solution is supersaturated (in other words, $Q_{sp} > K_{sp}$), we expect crystallis ation to occur — but will it take place before our solution gets to the end of the pipe? This is where the *kinetics* (see chapter 15) of the process is important; the *rate* of crystallisation determines how rapidly our pipe may be blocked by scale formation.

Chemists can tackle this problem by changing the thermodynamics of the system or by controlling the kinetics.If we have a supersaturated solution of calcium sulfate, the solution can be stabilised by adding enough EDTA (ethylenediaminetetraacetic acid, see figure 13.4) to form a complex with most of the calcium cations. This method alters the thermodynamics of the system to ensure no crystallisation occurs. Unfortunately, this requires as many moles of EDTA as there is excess calcium, and is too expensive for most industrial situations. A viable alternative is to change the rate of crystal growth by introducing a compound designed to dock on to the crystal surface; by blocking the active growth sites on the crystal surface, the additive compound slows down the rate at which the crystal can grow. The surface is usually only a very small fraction of the total material present, and the most active sites for crystal growth are a small fraction of the crystal surface, and hence a very small amount of compound can have a huge impact on the crystal growth processes.

Curtin University is studying the design and impact of molecules that will control crystal growth. Using computational chemistry in combination with experi-mental work, molecules can be designed to bind to crystals, and even to specific crystal faces. For example, additives such as the ethylenediaminetetraphosphonate anion can substitute for sulfate anions at the surface of a barium sulfate crystal; the system can be modelled in the computer (figure 10.19) to determine the most favourable binding sites. Experimentally, we usually observe changes in the crystal shape — a clear sign that the additive is binding to the crystal surface and changing the relative rates of growth of different crystal faces (figures 10.20 and 10.21). The additive also slows crystal growth and helps to stop those pipes getting blocked.

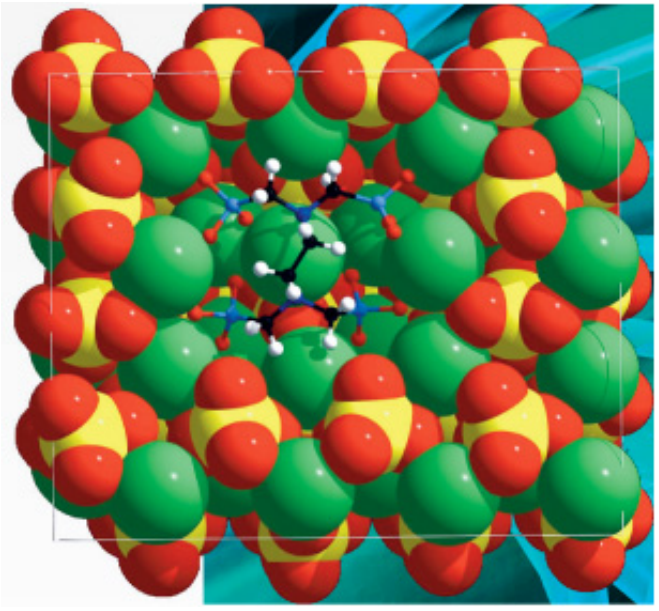


FIGURE 10.19 A computational model of an ethylenediaminetetraphosphonate anion docked into the surface of a barium sulfate crystal. The anionic additive substitutes for sulfate anions at the surface.

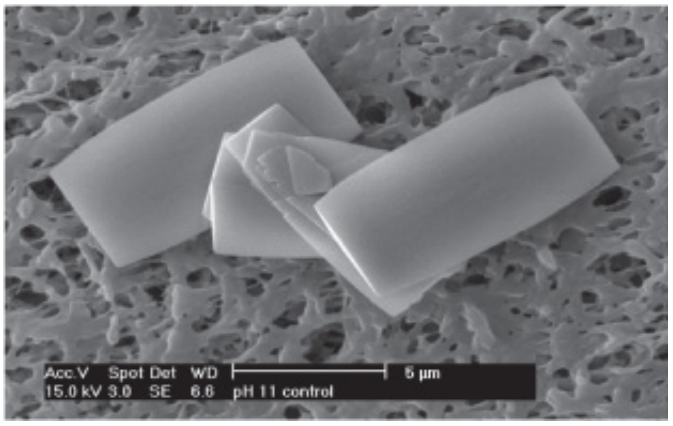


FIGURE 10.20 Scanning electron micrograph of barium sulfate crystals grown in the absence of any additives.

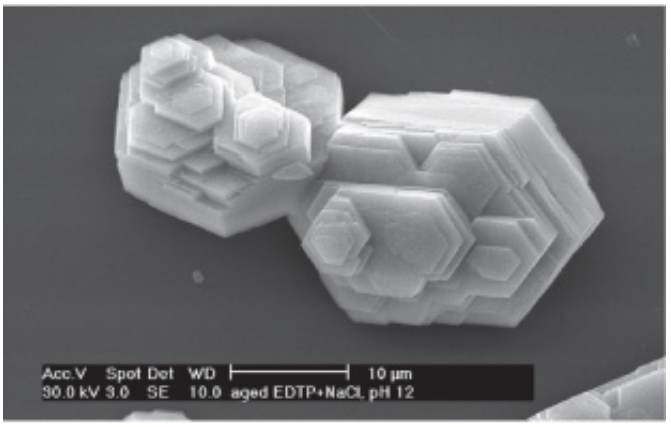


FIGURE 10.21 Scanning electron micrograph of barium sulfate crystals grown in the presence of ethylenediaminetetraphosphonate anion.

But that's just the start. Well-designed additive molecules can be used to allow the crystallisation of a desired product by blocking the growth of an impurity. It is exciting that controlling how nanometre-sized molecules interact with a growing crystal can help control the fate of a kilometre-sized industrial plant. The right balance of thermodynamics and kinetics makes all the difference!

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10.5 Colligative Properties of Solutions

When we prepare a solution by dissolving a small amount of a **nonvolatile** solute in a solvent, we find that particular properties of the resulting solution differ quite significantly from those of the pure solvent. For example, the boiling point of the solution is higher than that of the pure solvent and the freezing point is lower. Interestingly, the magnitudes of the boiling point elevation and the freezing point depression do not necessarily depend on the identity of the solute; if we prepared separate aqueous solutions of NaCl and NaBr by dissolving 1 mole of each salt in 1 kg of water, we would find that the boiling points (about 101 °C) and freezing points (about -3.4 °C) of both solutions would be the same. Properties such as vapour pressure, boiling point elevation, freezing point depression and osmotic pressure, which depend only on the *number* of solute particles in the solution, are called **colligative properties** and can be very useful in elucidating the exact nature of solute particles in a solution.

The word 'colligative' is derived from the Latin *colligare* meaning 'to bind together'. Such a derivation is appropriate as colligative properties do in fact arise from the attractive interactions between solute particles and solvent molecules.

Colligative properties are important in everyday situations. Adding antifreeze to a car's radiator lowers the freezing point of the coolant solution to well below 0 °C; this reduces the probability of damage to the engine caused by the expansion that occurs on formation of ice. Antifreeze also raises the boiling point of the radiator coolant. Reverse osmosis, a process that relies on colligative properties, is used extensively in the food industry as a method of concentrating heat-sensitive materials, such as fruit and vegetable juices, as it requires only the application of pressure. It is also used for desalination of sea water and to remove acetic acid from fermenting wine.

To be able to quantify the effects of colligative properties, we must first look at ways in which we can express the composition of solutions.

Molarity

The most common method of expressing the concentration of a solution, and the one we have used throughout the book thus far, is in mol L^{-1}; i.e. the amount of substance in a particular volume of solution. This is more properly called the **molar concentration** or **molarity** of a solution and has the symbol *c*:

$$\text{molarity}\,(c) = \frac{\text{amount of solute (mol)}}{\text{volume of solution (L)}}$$

However, because solutions (usually) increase their volume when the temperature is raised, and vice versa, the molarity of a solution changes as the temperature changes. For example, a saline solution of known molarity prepared at 25 °C has a different molarity when it is warmed to body temperature; this makes molarity a less than ideal measure of concentration in situations involving colligative properties.

Molality

Molality is the preferred method of expressing solution composition in situations that involve colligative properties, as these properties are proportional to molality. We define the **molal concentration** or **molality** of a solution as the amount of solute per kilogram of solvent, and use the symbol *b*:

$$\text{molarity}\,(b) = \frac{\text{amount of solute (mol)}}{\text{mass of solvent (Kg)}}$$

The molality of a solution is temperature independent as mass does not depend on temperature. The molarity and molality of aqueous solutions are numerically different but, as aqueous solutions become more and more dilute, the numerical value of the molarity approaches that of the molality.

WORKED EXAMPLE 10.6

Calculation to Prepare a Solution of a Given Molality

What mass of NaCl would have to be dissolved in 500.0 g of water to prepare a solution of molality 0.150 mol kg^{-1}?

Analysis

Rearranging the equation for molality given above, we obtain:

$$\text{amount of solute (mol)} = \text{molality (mol kg}^{-1}) \times \text{mass of solvent (kg)}$$

Knowing the amount of solute, NaCl, we then relate amount to mass through the molar mass of NaCl.

Solution

$$\begin{aligned} \text{amount of NaCl} &= \text{molality} \times \text{mass of solvent} \\ &= 0.150\,\text{mol kg}^{1} \times 0.5000\,\text{kg} \\ &= 0.0750\,\text{mol} \end{aligned}$$

$$m = nM = 0.0750\,\text{mol} \times 58.44\,\text{g mol}^{-1} = 4.38\,\text{g}$$

Therefore, 4.38 g of NaCl needs to be dissolved in 500.0 g of water to give a solution of mol ality 0.150 mol kg^{-1}.

Is our answer reasonable?

If we round the molar mass of NaCl to 60, 0.1 mol is 6 g and 0.2 mol is 12 g. We also notice that 0.150 mol kg^{-1} is halfway between 0.1 and 0.2 mol kg^{-1}. So, for 1 kilogram of water, we'd need halfway between 6 g (0.1 mol) and 12 g (0.2 mol) of NaCl. For half as much water (500 g), we cut these limits in two, so we need halfway between 3 and 6 g of NaCl. Our answer is in this range.

PRACTICE EXERCISE 10.9

Water freezes at a lower temperature when it contains solutes. To study the effect of methanol on the freezing point of water, we might begin by preparing a series of solutions of known molali-ties. Calculate the mass of methanol, CH_3OH, needed to prepare a 0.250 mol kg^{-1} solution using 2000 g of water.

PRACTICE EXERCISE 10.10

If we prepare a solution by dissolving 4.00 g of NaOH in 250 g of water, what is the molality of the solution?

Mole Fraction

In chapter 6 we introduced the mole fraction as a method of expressing the composition of gas mixtures. We can also use it for liquid solutions. We define the **mole fraction (x)** of a particular component of a solution as the amount of that component divided by the total amount of material in the solution. For example, the mole fraction of A, x_A, in a solution containing substances A, B and C would be defined as:

$$x_A = \frac{n_A}{n_A + n_B + n_C}$$

Mole fraction is also temperature independent.

We will now see how these alternative measures of solution composition are used when quantifying colligative properties.

Raoult's Law

As mentioned earlier, the boiling point of a solution containing a nonvolatile solute is higher than that of the pure solvent. The boiling point of a solvent is the temperature at which the vapour pressure of the solvent is equal to the atmospheric pressure; therefore, the observation of a higher boiling point must mean that the solution has a lower vapour pressure than the pure solvent, as it now takes greater energy input to raise the vapour pressure of the solution to equal the atmospheric pressure. Providing that the solution is sufficiently dilute (i.e. $x_{solvent}$ is close to 1), **Raoult's law** describes the relationship between the vapour pressure of the solution ($p_{solution}$), the mole fraction of solvent in the solution (*x*solvent) and the vapour pressure of the pure solvent $(p^*_{solvent})$ in a simple two-component system:

$$p_{solution} = x_{solvent} p^*_{solvent} \text{ (at constant temperature)}$$

This equation describes a straight line and so a plot of $p_{solution}$ versus $x_{solvent}$ is linear, as shown in figure 10.22. Because $x_{solvent}$ and x_{solute} are related in a two-component system:

$$x_{solvent} = 1 - x_{solute}$$

we can also write Raoult's law in terms of x_{solute}:

$$\begin{aligned} p_{solution} &= (1 - x_{solute}) p^*_{solvent} \\ &= p^*_{solvent} - x_{solute} p^*_{solvent} \end{aligned}$$

This expression can be rearranged to give the following relationship for the *pressure difference*(Δp) between the pure solvent and the solution:

$$\Delta p = x_{solute} p^*_{solvent}$$

$$\text{where } \Delta p = p^*_{solvent} - p_{solution}.$$

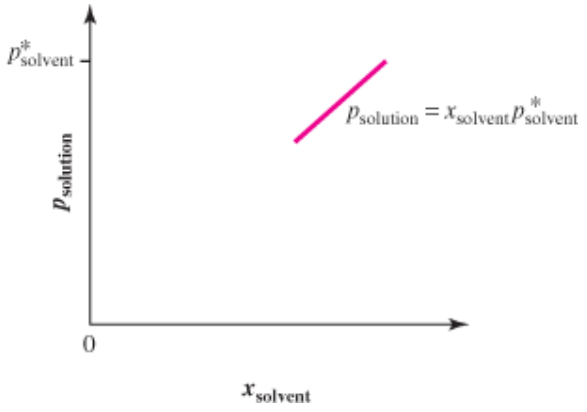


FIGURE 10.22 A Raoult's law plot. When the vapour pressure of a solution is plotted against the mole fraction of the solvent, a straight line results. It should be stressed that such behaviour is observed only in dilute solutions, i.e. those in which $x_{solvent}$ is close to 1.

WORKED EXAMPLE 10.7

Calculation Using Raoult's Law

What is the vapour pressure of a solution of 10.0 g of candle wax in 40.0 g of tetrachloromethane, CCl_4, at 23 °C? The molecular formula of candle wax is $C_{22}H_{46}$ and the vapour pressure of pure CCl_4 at 23 °C is

1.32×10^4 Pa.

Analysis

We use Raoult's law so we must calculate the mole fraction of solvent, *x*solvent, from the data given by calculating the amount of both $C_{22}H_{46}$ and CCl_4.

Solution

$$n_{CCl_4} = \frac{m}{M} = \frac{40.0\,g}{153.81\,g\,mol^{-1}} = 0.26\,mol$$

$$n_{C_{22}H_{46}} = \frac{m}{M} = \frac{10.0\,g}{310.59\,g\,mol^{-1}} = 0.0322\,mol$$

Therefore, n_{total} = 0.260 mol + 0.0322 mol = 0.292 mol. We can now calculate the mole fraction of solvent:

$$x_{solvent} = \frac{n_{CCl_4}}{n_{total}} = \frac{0.260\,mol}{0.292\,mol} = 0.890$$

We use this value in Raoult's law:

$$p_{solution} = x_{solvent} p^*_{solvent} = 0.890 \times (1.32 \times 10^4\,Pa) = 1.17 \times 10^4\,Pa$$

Hence, dissolving 10.0 g of candle wax in 40.0 g of CCl_4 lowers the vapour pressure by about 11%.

Is our answer reasonable?

The pressure we obtained is less than the vapour pressure of the pure solvent, which is what we would expect from Raoult's law. Barring arithmetic errors, our answer looks sensible.

PRACTICE EXERCISE 10.11

Dibutyl phthalate, $C_{16}H_{22}O_4$ (molar mass 278.34 g mol^{-1}), is an oil sometimes used to soften plastic articles. Its vapour pressure is negligible at room temperature. The vapour pressure of pure octane at 20 °C is 1.38×10^3 Pa. What is the vapour pressure at 20 °C of a solution of20.0 g of dibutyl phthalate in 50.0 g of octane, C_8H_{18} (molar mass 114.22 g mol^{-1})?

While Raoult's law shows that a solution has a lower vapour pressure than the pure solvent, it does not explain why this is the case. If we compare a pure solvent with a solution containing a nonvolatile solute, we see that the surface of the solution comprises a mixture of solvent and solute molecules, while the surface of the solvent consists only of solvent molecules (figure 10.23).

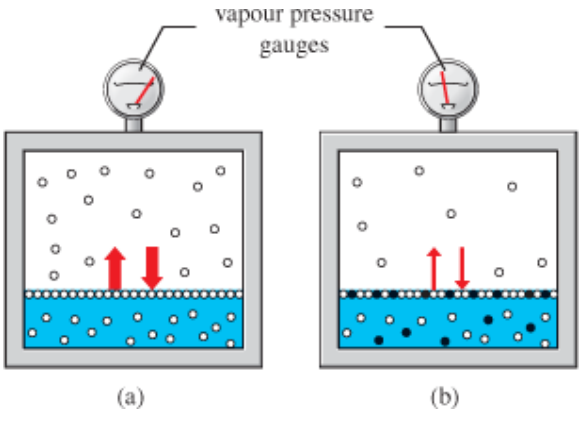


FIGURE 10.23 Effect of a nonvolatile solute on the vapour pressure of a solvent:

(a) Equilibrium between a pure solvent and its vapour. With a high number of solvent molecules at the surface of the liquid, the rate of evaporation is relatively high.

(b) In the solution, some of the solvent molecules at the surface have been replaced by solute molecules so there are fewer solvent molecules available to evaporate from the surface of the solution. This lowers the evaporation rate, so, when equilibrium is established, there are fewer molecules in the vapour. The vapour pressure of the solution is therefore less than that of the pure solvent.

Therefore, there are fewer molecules of solvent at the surface of a solution than of a pure solvent. This means that, in the solution, there are fewer solvent molecules available to evaporate, so we expect the vapour pressure exerted by the solvent molecules to be lower than in the pure solvent.

A solution that obeys Raoult's law is called an **ideal solution**. Such solutions are generally dilute and have very small values of enthalpy of mixing, implying that there are only small interactions between their constituent molecules. We can think of an ideal solution as being analogous to an ideal gas.

Solutions Containing More than One Volatile Component

When two (or more) components of a liquid solution can evaporate, the vapour contains molecules of each. Each volatile component contributes its own partial pressure to the total pressure. By Raoult's law, the partial pressure of a particular component is directly proportional to the component's mole fraction in the solution, and the total vapour pressure is the sum of the partial pressures. To calculate these partial pressures, we use Raoult's law for each component. For component *A:*

$$p_A = x_A p_A^*$$

and for component *B:*

$$p_B = x_B p_B^*$$

The total pressure above a solution of liquids *A* and *B*is then the sum of p_A and p_B.

$$p_{\text{total}} = x_A p_A^* + x_B p_B^* \text{ (at constant temperature)}$$

Figure 10.24 shows how the vapour pressure of an ideal, two-component solution of volatile compounds changes with composition.

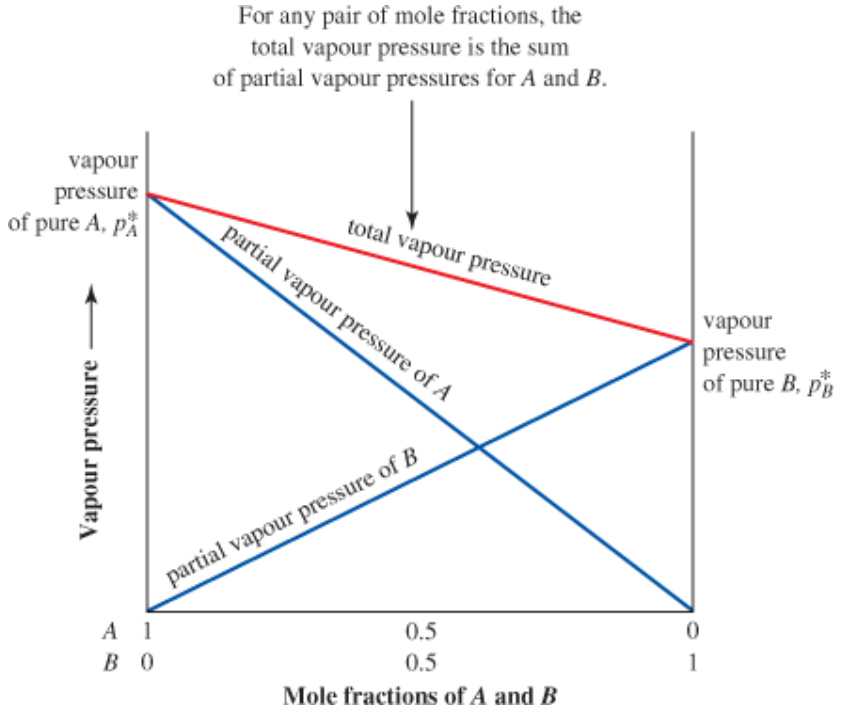


FIGURE 10.24 The vapour pressure of an ideal, twocomponent solution of volatile compounds.

WORKED EXAMPLE 10.8

Calculating the Vapour Pressure of a Solution of Two Volatile Liquids

At 20 °C, acetone has a vapour pressure of 2.13×10^4 Pa. The vapour pressure of water at 20 °C is 2.30×10^3 Pa. Assuming that the mixture obeys Raoult's law, calculate the vapour pressure of a solution of acetone and water containing 80.0 mol % of water.

Analysis

To find p_{total}, we need to calculate the individual partial pressures and then add them.

Solution

A concentration of 80.0 mol % water corresponds to a mole fraction of 0.800 for water and 0.200 for acetone, so:

$$\begin{aligned} p_{acetone} &= 0.200 \times 2.13 \times 10^4 \text{Pa} = 4.26 \times 10^3 \text{Pa} \\ p_{water} &= 0.800 \times 2.30 \times 10^3 \text{Pa} = 1.84 \times 10^3 \text{Pa} \\ p_{total} &= 6.10 \times 10^3 \text{Pa} \end{aligned}$$

Is our answer reasonable?

The vapour pressure of the solution (6.10×10^3 Pa) has to be higher than that of pure water (2.30×10^3 Pa), because of the volatile acetone, but less than that of pure acetone (2.13×10^4 Pa), because of the high mole fraction of water. The answer seems to be reasonable.

PRACTICE EXERCISE 10.12

At 20 °C, the vapour pressure of cyclohexane (a hydrocarbon solvent) is 8.80×10^3 Pa and that of toluene (another solvent) is 2.78×10^3 Pa. What is the vapour pressure of a solution of the two at 20 °C when toluene is present at a mole fraction of 0.700?

Because solutes influence the vapour pressures of solutions, they also affect their boiling and freezing points. The boiling point of a solution of a nonvolatile solute, for example, is higher than that of the pure solvent, and the freezing point of the solution is lower than that of the solvent. We can explain this for aqueous solutions by considering the phase diagram for water (see figure 7.19, p. 263).

Boiling Point Elevation and Freezing Point Depression

We have seen how the presence of a nonvolatile solute in a solution increases the boiling point of the solution relative to that of the pure solvent. Such solutions also have lower freezing points than those of the pure solvents, meaning that the attractive forces between solvent molecules in the solution must be smaller than those in the pure solvent at a given temperature. This is due to the presence of solute molecules and the corresponding solute–solvent interactions, which are not present in the pure solvent.

We can illustrate the changes in boiling and freezing points in solutions using a phase diagram. Figure 10.25 shows a

phase diagram for an aqueous solution containing a nonvolatile solute (red lines) superimposed on the phase diagram for pure water (blue lines). We know that, at any temperature, the aqueous solution has a lower vapour pressure than pure water, so the Liquid–gas equilibrium line lies below that for pure water. This has the effect of lowering the pressure and temperature at the triple point, so the ice–liquid equilibrium line is also displaced. We can see from the phase diagram that the boiling point of the solution is increased by ΔT_b, relative to water, and the freezing point is depressed below 0 °C by ΔT_f. ΔT_b is called the **boiling point elevation** and ΔT_f is called the **freezing point depression** and both are a direct consequence of lowering the vapour pressure in the solution. They are colligative properties as their magnitudes are directly proportional to the number of solute particles in the solution. We can calculate ΔT_b and ΔT_f from the equations:

$$\Delta T_b = K_b b$$
$$\Delta T_f = K_f b$$

where K_b and K_f are the **molal boiling point elevation constant** and the **molal freezing point depression constant**, respectively, and b is the molality of the solution in mol kg^{-1}. K_b and K_f are properties of the solvent only and are independent of the identity of the solute; table 10.4 gives values of K_b and K_f for a number of solvents. These values apply exactly to very dilute solutions only, but we can use them to estimate the freezing points and boiling points of fairly concentrated solutions with reasonable precision.

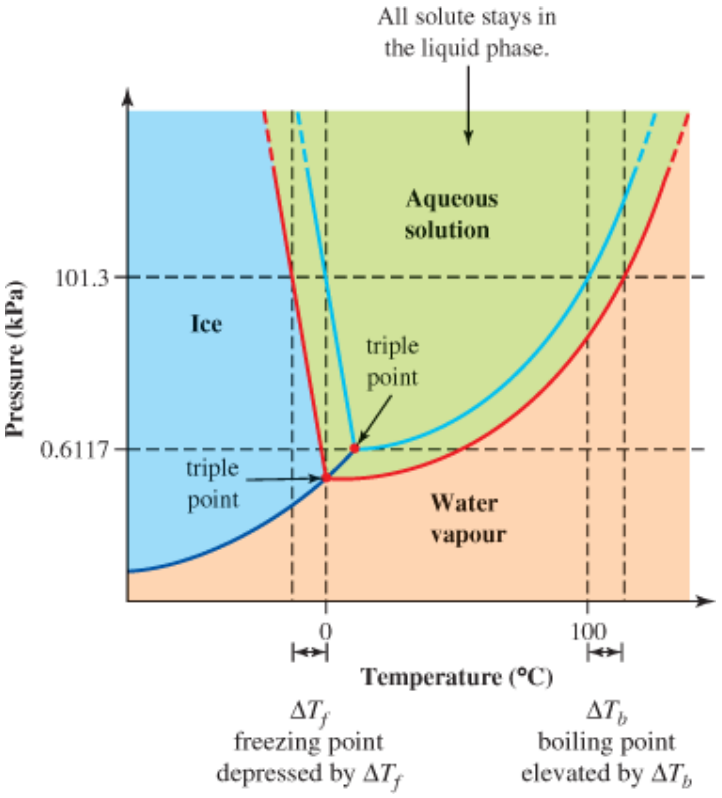


FIGURE 10.25 Phase diagram for an aqueous solution of a nonvolatile solute.

TABLE 10.4 Molal boiling point elevation and freezing point depression constants

Solvent	K_b (K mol^{-1}kg)	K_f (K mol^{-1} kg)
water	0.51	1.86
acetic acid	3.07	3.57
benzene	2.53	5.07
chloroform	3.63	–
camphor	–	37.7
cyclohexane	2.69	20.0

WORKED EXAMPLE 10.9

Estimating a Freezing Point Using a Colligative Property

Estimate the freezing point of a solution made from 10.00 g of urea, $CO(NH_2)_2$ (molar mass 60.06 g mol^{-1}), in 100.0 g of water.

Analysis

$\Delta T_f = K_f b$ relates concentration to freezing point depression. To use the equation, we must first calculate the molality of the solution.

Solution

$$n_{CO(NH_2)_2} = \frac{10.00\,g}{60.06\,g\,mol^{-1}} = 0.1665\,mol$$

This is the amount of $CO(NH_2)_2$ in 100.0 g or 0.1000 kg of water. Therefore:

$$b = \frac{0.1665\,mol}{0.1000\,kg} = 1.665\,mol\,kg^{-1}$$

For our estimate, we must next use $\Delta T_f = K_f b$. From table 10.4, K_f for water is 1.86 K mol^{-1} kg.

$$\Delta T_f = K_f b = (1.86\,K\,mol^{-1}\,Kg)(1.665\,mol\,Kg^{-1}) = 3.10\,K$$

Remembering that a temperature difference of 3.10 K is equal to 3.10 °C, the solution should freeze at 3.10 °C below 0 °C, or at -3.10 °C.

Is our answer reasonable?

For a solution of molality 1 mol kg^{-1}, the freezing point depression is:

$$\Delta T_f = K_f b = (1.86\,K\,mol^{-1}\,kg)(1\,mol\,kg^{-1}) = 1.86\,K$$

Therefore, for every unit of molality, the freezing point must be depressed by about 2 °C. The molality of this solution is between 1 mol kg^{-1} and 2 mol kg^{-1}, so we expect the freezing point depression to be between about 2 °C and 4 °C. It is.

PRACTICE EXERCISE 10.13

At what temperature does a 10% (by mass) aqueous solution of sugar, $C_{12}H_{22}O_{11}$, boil at 1.013×10^5 Pa?

We have described the properties of freezing point depression and boiling point elevation as *colligative*; that is, they depend on the relative *numbers* of particles, rather than their identities. Because the effects are proportional to molal concentrations, experimental values of ΔT_f or ΔT_b can be useful for calculating the molar masses of unknown solutes. We'll see how this works in worked example 10.10.

WORKED EXAMPLE 10.10

Calculating a Molar Mass from Freezing Point Depression Data

A solution made by dissolving 5.65 g of an unknown molecular compound in 110.0 g of benzene froze at 4.39 °C. Given that the normal melting point of benzene is 5.45 °C, calculate the molar mass of the solute.

Analysis

We can use $\Delta T_f = K_f b$ to calculate the amount of solute in the given solution. Then we can divide the mass of solute by the amount of solute to find the molar mass.

Solution From table 10.4, the value of K_f for benzene is 5.07 K mol^{-1} kg. The magnitude of the freezing point depression is:

$$\Delta T_f = 5.45°C - 4.39°C = 1.06°C = 1.06K$$

We now use $\Delta T_f = K_f b$ to find the molality of the solution:

$$\begin{aligned} \Delta T_f &= K_f b \\ b &= \frac{\Delta T_f}{K_f} \\ &= \frac{1.06K}{5.07K\ mol^{-1}Kg} \\ &= 0.209 molKg^{-1} \end{aligned}$$

This means that there is 0.209 mol of solute for every kilogram of benzene in the solution. But we have only 110.0 g or 0.1100 kg of benzene. So the actual amount of solute in the given solution is:

$$0.1100kg \times 0.209 molkg^{-1} = 0.0230 mol$$

We can now obtain the molar mass:

$$M = \frac{m}{n} = \frac{5.65g}{0.0230mol} = 246g\,mol^{-1}$$

The mass of 1 mole of the solute is 246 g.

Is our answer reasonable?

The easiest way to check our answer is to do the reverse calculation, starting with 5.65 g of a compound having a molar mass of 246 g mol^{-1}, and determining the resultant freezing point depression when dissolved in 110.0 g of benzene. If you do this (it's good practice!), you'll find that the answer is correct.

PRACTICE EXERCISE 10.14

A solution made by dissolving 3.46 g of an unknown compound in 85.0 g of benzene froze at 4.13 °C. What is the molar mass of the compound?

Osmosis and Osmotic Pressure

In living things, membranes of various kinds keep mixtures and solutions organised and separated. Yet some substances have to be able to pass through membranes so that nutrients and products of chemical reactions can be distributed correctly. In other words, these membranes must have a selective *permeability*. They must keep some substances from going through while allowing others to pass. Such membranes are said to be *semipermeable*.

The degree of permeability varies with the kind of membrane. Cellophane, for example, is permeable to water and small solute particles — ions or molecules — but impermeable to very large molecules, such as those of starch or proteins. Special membranes can even be prepared that are permeable only to water but not to any solutes.

Depending on the kind of membrane separating solutions of different concentration, two similar phenomena, *dialysis* and *osmosis*, can be observed. Both are functions of the relative populations of particles in the dissolved materials on

either side of the membrane, so they are colligative properties.

When a membrane is capable of allowing both water and small solute particles to pass through, such as membranes found in living systems, the process is called **dialysis**, and the membrane is called a *dialysing membrane*. It does not permit huge molecules to pass through, such as those of proteins and starch. Artificial kidney machines use dialysing membranes to help filter and remove the smaller molecules of wastes from the blood while the larger protein molecules, which cannot pass through the membrane, are retained in the blood.

Osmosis is a net shift of only solvent through a membrane, in a direction from the side less concen trated in *solute* to the side more concentrated. The special membrane required is called an **osmotic membrane**. Such membranes are rare, but they can be made.

The *direction* in which osmosis occurs, namely, the net movement of solvent from the more dilute solution (or pure solvent) into the more concentrated solution, may be explained with the help of figure 10.26. Water molecules move freely across the membrane. The concentration of water in the aqueous solution (*B*) is lower than the concentration in pure water (*A*). More water molecules are available to cross the membrane from *A* to *B*, so the flow of water molecules *into*the solution is somewhat greater than the flow *out of* the solution. In figure 10.26b, the net flow *f* of water into the solution has visibly increased the volume of *B*.

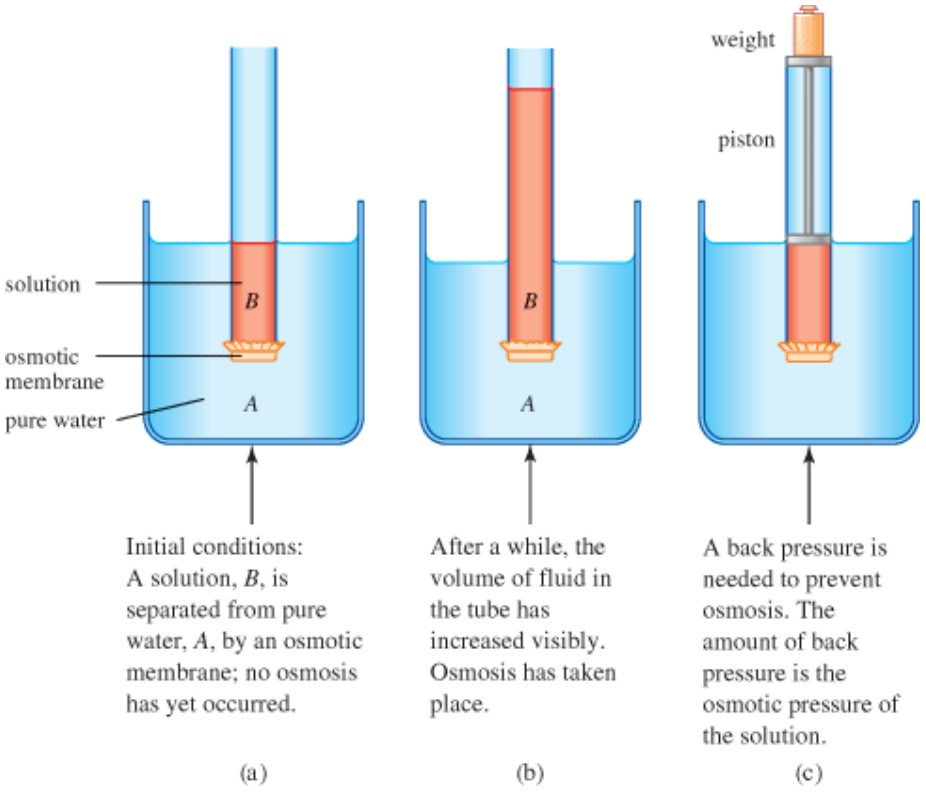


FIGURE 10.26 Osmosis and osmotic pressure.

If we push on the solution, we can force water back through the membrane (from *B* to *A*). The weight of the rising fluid column in figure 10.26b provides a push or opposing pressure that eventually stops osmosis. If we apply further pressure (figure 10.26c), we can force enough water back through the membrane to restore the system to its original condition. The exact opposing pressure needed to prevent any osmotic flow *when one of the liquids is pure solvent* is called the *t* **osmotic pressure** of the solution.

By *exceeding* the osmotic pressure, osmosis can be reversed and we refer to this situation as reverse osmosis. Reverse osmosis allows pure water to be obtained from an aqueous salt solution simply by forcing it through a membrane under high pressure. It is therefore widely used to obtain drinking water from sea water. There are currently three reverse osmosis desalination plants operating in Australia, with a further three under construction.

To further illustrate the principles involved in osmosis, consider the situation in figure 10.27; we have a beaker of water in an enclosed space *already saturated in water vapour*, and we have just added a beaker of an aqueous solution of a nonvolatile solute. Water molecules tend to escape into the vapour phase from both beakers, but their rate of escape from the pure water (larger upward arrow) is greater than their rate of escape from the solution (smaller upward arrow). This must be so because the vapour pressure of pure water is greater than that of the solution, as predicted by

Raoult's law. The rate at which water molecules return to the solution from the saturated vapour state is not diminished by the presence of the solute. At the solution–vapour interface, more water molecules return to the solution than leave it, and this takes water from the vapour state. To keep the vapour phase saturated, more of the pure water must evaporate. The net effect is that water moves from the beaker of pure water into the vapour space and then into the solution. In osmosis, an osmotic membrane instead of beakers separates the liquids, but the same principles are at work.

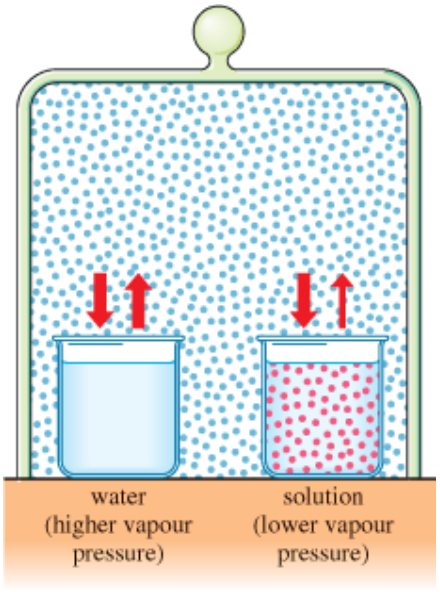


FIGURE 10.27 Principles at work in osmosis. Here, beakers, instead of a semipermeable membrane, separate the pure solvent (water) from an aqueous solution containing a nonvolatile solute. Because the vapour pressure of pure water is greater than the vapour pressure of the aqueous solution, molecules transfer from the beaker of pure water to the aqueous solution.

The higher the concentration of the *solution*, the more water is transferred to it (figure 10.27). In other words, the osmotic pressure of a solution is proportional to the relative concentrations of its solute and solvent.

The symbol used for osmotic pressure is Π, the capital Greek letter *pi*. In a dilute aqueous solution, Π(Pa) is proportional both to temperature, *T(K)*, and molar concentration, *c* (mol m^{-3}):

$$\Pi \propto cT$$

The proportionality constant turns out to be the gas constant, *R*, so for a *dilute* aqueous solution we can write:

$$\Pi = cRT$$

$$\text{As } c = \frac{n}{V}:$$

$$\Pi V = nRT$$

This is the *van't Hoff equation for osmotic pressure* and is analogous to the ideal gas law. Note that we work in terms of concentration rather than molality here to emphasise the similarity of this equation to the ideal gas law. Recall from p. 408 that, provided the solution is sufficiently dilute, the molality and concentration are numerically essentially equal.

Chemical Connections

Desalination

Both Australia and New Zealand are susceptible to drought. Record low rainfalls in the early years of this century led one expert to state that Australia was in the grip of a 1-in-1000-year drought, while New Zealand experienced its worst drought in 100 years in the 1990s. As major cities in both countries rely on regular rainfall for drinking water, drought conditions threaten the very existence of these large population centres. Climate change may also exacerbate the problems associated with drought.

As both countries are surrounded by water, one possible solution lies in the conversion of sea water to drinking water through *desalination*. There are a number of ways in which this can be done, but all of them require significant quantities of energy. The simplest way of desalinating sea water is to boil it and condense the pure water vapour that results. The high heat capacity of water makes this method economically,

environmentally and energetically infeasible on a large scale. However, carrying out the process at low pressure means that the water boils at a lower temperature, so less energy is required to heat the water. Of course, the energy required to lower the pressure also needs to be taken into account in the overall economics of the process. Several desalination plants in the Middle East use a variant of this technology and some have capacities of over 250 million litres per day.

Currently, the most popular method of desalination is *reverse osmosis* (see figure 10.29). As we have seen in this chapter, pure water will flow spontaneously through a semipermeable membrane from a dilute electrolyte solution to a concentrated electrolyte solution, thereby exerting an osmotic pressure. If a pressure greater than this is exerted on the more concentrated solution, the direction of flow can be reversed, and pure water results. The Kurnell desalination plant in Sydney, which was opened in 2010, operates using this principle (figure 10.28). It was designed to provide a minimum of 15% of Sydney's water needs. The electricity required to generate the required high pressures comes from a wind farm, meaning that this plant runs entirely on renewable energy. In addition, researchers at Murdoch University have invented the Solarflow, a portable, solar-powered desalination unit capable of producing 400 litres of water a day using reverse osmosis. Such a unit appears ideal for small communities in remote areas.



FIGURE 10.28 Kurnell desalination plant in Sydney, New South Wales.

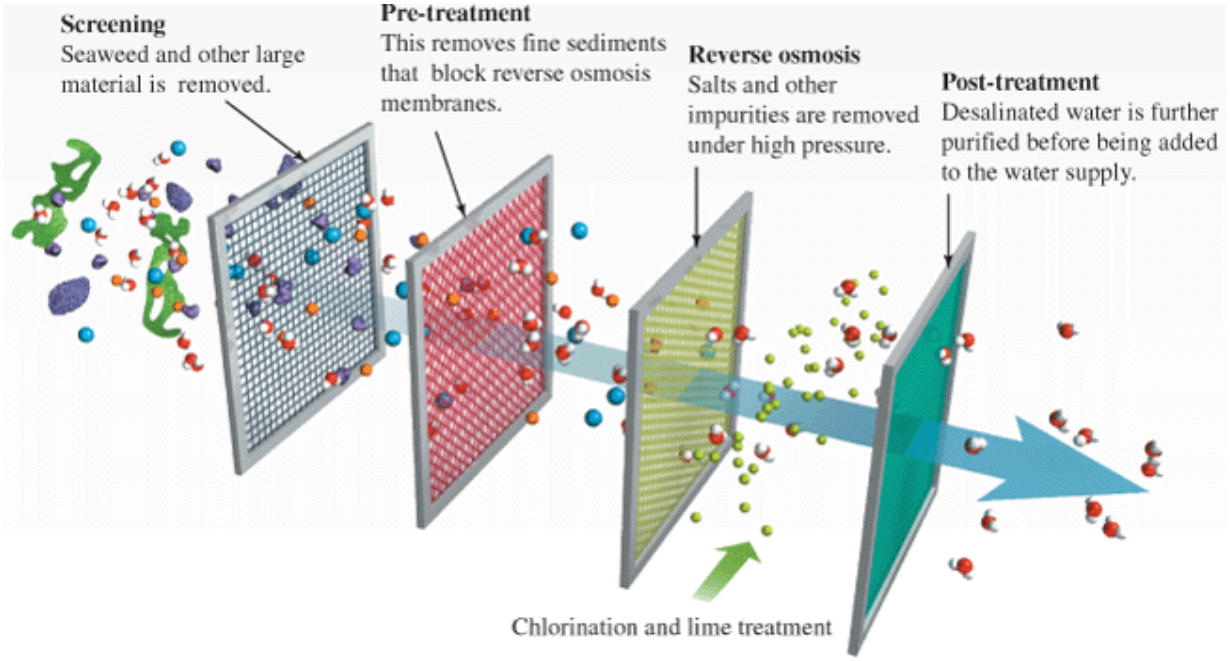


FIGURE 10.29 The four major steps in conversion of sea water to drinking water using reverse osmosis.

One less-than-obvious problem with the use of reverse osmosis plants that must be overcome is the disposal of the concentrated salt solutions that are formed. Pumping these wastes back into the ocean at source can lead to high levels of salt in the local marine environment, especially in shallow and slow-moving estuarine waters, and this can have a harmful effect on marine life. A possible solution is to pump the waste into deep offshore waters where the sea currents disperse the salt; this however does have attendant energy costs. Another solution is the harvesting of salt from the concentrated residues, and this may indeed be economically viable.

Osmotic pressure is of tremendous importance in biology and medicine. Cells are surrounded by membranes that restrict the flow of salts but allow water to pass through freely. To maintain a constant amount of water, the osmotic pressure of solutions on either side of a cell membrane must be identical. For example, a solution that is 0.9% NaCl by mass has the same osmotic pressure as the contents of red blood cells, and red blood cells bathed in this solution can maintain their normal water content. The solution is said to be **isotonic** with red blood cells. Blood plasma is an isotonic solution.

If a cell is placed in a solution with a salt concentration higher than the concentration within the cell, osmosis causes water to flow out of the cell. Such a solution is said to be **hypertonic**. The cell shrinks and dehydrates, and eventually dies. This process kills freshwater fish and plants that are washed out to sea.

On the other hand, water flows into a cell if it is placed into a solution with an osmotic pressure that is much lower than the osmotic pressure of the cell's contents. Such a solution is called a **hypotonic** solution. A cell placed in distilled water, for example, swells and bursts. The effects of isotonic, hypertonic and hypotonic solutions on red blood cells are shown in figure 10.30.

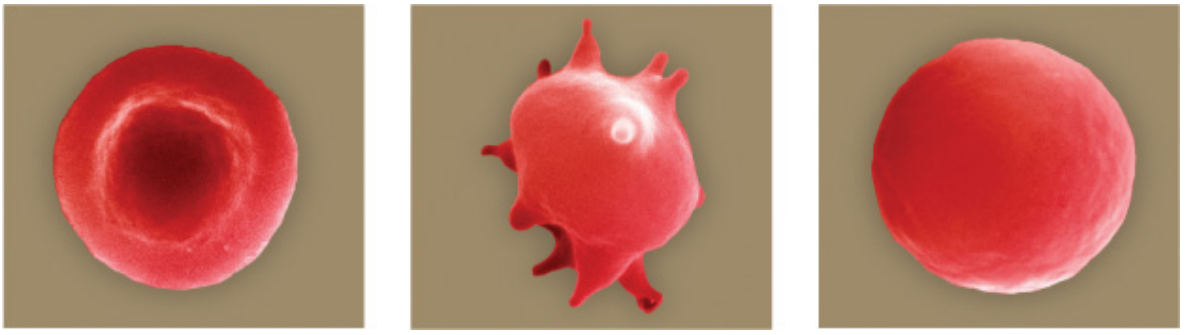


FIGURE 10.30 Effects on red blood cells that have been placed in isotonic, hypertonic and hypotonic solutions, all at the same magnification:

(a) In an isotonic solution (0.9% NaCl by mass), solutions on either side of the cell membrane have the same osmotic pressure, so there is no net flow of water in one direction across the membrane.

(b) In a hypertonic solution (5.0% NaCl by mass), water flows from an area of lower salt concentration (inside the cell) to higher concentration (the hypertonic solution), causing the cell to dehydrate.

(c) In a hypotonic solution (0.1% NaCl by mass), water flows from an area of lower salt concentration (the hypotonic solution) to higher concentration (inside the cell). The cell swells and bursts.

Obviously, the measurement of osmotic pressure can be very important in preparing solutions used to culture tissues or to administer medicines intravenously. Osmotic pressures can be measured by an instrument called an *osmometer*, illustrated and explained in figure 10.31. Osmotic pressures can be very high, even in dilute solutions, as worked

example 10.11 shows.

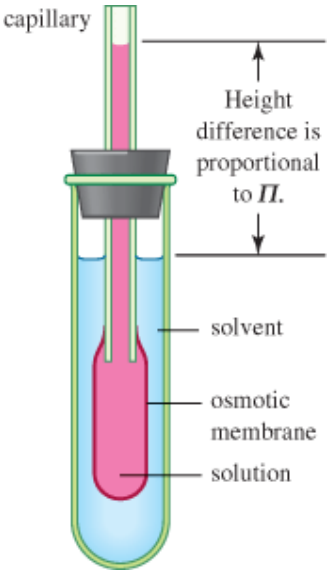


FIGURE 10.31 Simple osmometer. When solvent moves into the solution by osmosis, the level of the solution in the capillary rises.The height reached is related to the osmotic pressure of the solution.

WORKED EXAMPLE 10.11

Calculating Osmotic Pressure

A solution of 1.00×10^{-3} M sugar in water is separated from pure water by an osmotic membrane. What osmotic pressure (in Pa) develops at 25 °C?

Analysis

We can use $\Pi = cRT$. Recall that $R = 8.314$ J mol^{-1} K^{-1}. Remember that, when we use this equation, the concentration must be expressed in mol m^{-3} to give an answer in Pa (1 Pa = 1 J m^{-3}, p. 29).

Solution

We multiply the concentration by 1000 to convert from mol L^{-1} to mol m^{-3}; thus, $c = 1.00$ mol m^{-3}.

$$\Pi = (1.00\,\text{mol m}^{-3})(8.314\,\text{J mol}^{-1}\text{K}^{-1})(298\,\text{K})$$
$$= 2.48 \times 10^{3}\,\text{J m}^{-3} = 2.48 \times 10^{3}\,\text{Pa}$$

Thus, the osmotic pressure of 1.00×10^{-3} M sugar in water is 2.48×10^{3} Pa.

Is our answer reasonable?

The units are the greatest cause of error in calculations like this. Remember to express T in K and c in mol m^{-3}, not mol L^{-1}. This will give an answer in Pa.

PRACTICE EXERCISE 10.15

What is the osmotic pressure of a 0.0115 M glucose solution at body temperature (37 °C)?

In worked example 10.11, you saw that a 1.00×10^{-3} M solution of sugar has an osmotic pres-sure of 2.48×10^{3} Pa. This pressure would support a column of the solution roughly 25 cm high. If the solution had been 100 times as concentrated (0.100 M sugar — still relatively dilute), the height of the column supported would be roughly 25 m.

An osmotic pressure measurement of a dilute solution can be used to determine the molar concentration and, therefore, the molar mass of a molecular solute. Determination of molar mass by osmotic pressure is much more sensitive than determination by freezing point depression or boiling point elevation. Worked example 10.12 shows how experimental measurements of osmotic pressure can be used to determine molar mass.

WORKED EXAMPLE 10.12

Calculating Molar Mass from Osmotic Pressure

An aqueous solution with a volume of 100 mL and containing 0.122 g of an unknown molecular compound has an osmotic pressure of 2.11×10^{3} Pa at 20.0 °C. What is the molar mass of the solute?

Analysis

A molar mass is the ratio of mass to amount. We are given the mass of the solute; to calculate the ratio, we need to find the amount equivalent to this mass.

To find the amount of solute, we must first use $\Pi = cRT$ to find the concentration of the solution in mol m^{-3}. Then we can use the given volume of the solution and the concentration to calculate the amount that corresponds to 0.122 g of solute. Finally, we can calculate the molar mass by dividing the mass of solute by the amount of solute.

Solution

First, calculate the solution's concentration using the osmotic pressure. The temperature,20.0 °C, corresponds to 293 K. Recall that 1 Pa = 1 J m^{-3}.

$$\begin{aligned} \Pi &= cRT \\ c &= \frac{\Pi}{RT} \\ &= \frac{2.11 \times 10^{3}\,\text{Pa}}{8.314\,\text{J mol}^{-1}\text{K}^{-1} \times 293\,\text{K}} \\ &= 0.866\,\text{mol m}^{-3} \\ &= 8.66 \times 10^{-4}\,\text{mol L}^{-1} \end{aligned}$$

Therefore, in 100 mL or 0.100 L of solution, we have:

$$\begin{aligned} n &= cV = 8.66 \times 10^{-4}\,\text{mol L}^{-1} \times 0.100\,\text{L} \\ &= 8.66 \times 10^{-5}\,\text{mol} \end{aligned}$$

The molar mass of the solute is then obtained in the usual way:

$$M = \frac{m}{n} = \frac{0.122\,\text{g}}{8.66 \times 10^{-5}\,\text{mol}} = 1.41 \times 10^{3}\,\text{g mol}^{-1}$$

Is our answer reasonable?

All we can do is double-check the calculation of the amount, which turns out to be a little less than 10^{-4} mol. Dividing the mass, roughly 0.12 g, by 10^{-4} mol gives 0.12×10^{4} g mol^{-1}, or 1.2×10^{3} g mol^{-1}, which is very roughly what we found.

PRACTICE EXERCISE 10.16

A solution of a carbohydrate prepared by dissolving 72.4 mg in 100 mL of solution has an osmotic pressure of 3.29×10^3 Pa at 25.0 °C. What is the molar mass of the compound?

Measurement of Solute Dissociation

The molal freezing point depression constant for water is 1.86 K mol^{-1} kg, and therefore you might think that a 1.00 mol kg^{-1} solution of NaCl would freeze at -1.86 °C. Instead, it freezes at about -3.37 °C. This greater depression of the freezing point by the salt, which is almost twice 1.86 °C, is not hard to understand if we remember that colligative properties depend on the number of solute particles. NaCl(s) undergoes complete **dissociation** into its constituent ions in water according to the equation:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

Therefore, if we dissolve 1 mole of NaCl(s) (58.5 g) in 1 kg of water, the resulting solution has a total molality of *dissolved solute particles* of 2 mol kg^{-1}: 1 mol kg^{-1} of Na^+ ions and 1 mol kg^{-1} of Cl^- ions. Theoretically, a 1.00 mol kg^{-1} NaCl solution should freeze at 2 × (-1.86 °C) or -3.72 °C. (Why it actually freezes a little higher than this, at -3.37 °C, will be discussed shortly.)

If we made up a 1.00 mol kg^{-1} solution of $(NH_4)_2SO_4$, we would have to consider the following dissociation:

$$(NH_4)_2SO_4(s) \rightarrow 2NH_4^+(aq) + SO_4^{2-}(aq)$$

So, 1 mole of $(NH_4)_2SO_4$ gives a total of 3 moles of ions (2 moles of NH_4^+ and 1 mole of SO_4^{2-}). We expect the freezing point of this solution of $(NH_4)_2SO_4$ to be 3 × (-1.86 °C) = -5.58 °C.

You should ensure you understand the distinction between *dissolution* and *dissociation*. A slightly soluble ionic solid such as AgCl dissolves only to a very small extent (i.e. it does not undergo complete dissolution), but the small amount of resulting Ag^+ and Cl^- ions in solution are essentially completely dissociated (i.e. they show little tendency to stick together).

When we want to estimate a colligative property of a solution of an electrolyte, we recalculate the solution's molality assuming that the salt dissociates completely. This is illustrated in worked example 10.13.

WORKED EXAMPLE 10.13

Estimating the Freezing Point of a Salt Solution

Estimate the freezing point of an aqueous solution of 0.106 mol kg^{-1} $MgCl_2$, assuming that it dissociates completely.

Analysis

The equation that relates a change in freezing temperature to molality is:

$$\Delta T_f = K_f b$$

From table 10.4, K_f for water is 1.86 K mol^{-1} kg. We cannot simply use 0.106 mol kg^{-1} for the molarity because $MgCl_2$ is an ionic compound that dissociates in water; we must use the total molality of ions in the equation.

Solution

When $MgCl_2$ dissolves in water, it dissociates as follows:

$$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

Because 1 mole of $MgCl_2$ gives 3 moles of ions, the effective (assumed) molality of what we have called 0.106 mol kg^{-1} $MgCl_2$ is three times as great:

$$\text{effective molality} = 3 \times 0.106\ \text{mol kg}^{-1} = 0.318\ \text{mol kg}^{-1}$$

Now we can use $\Delta T_f = K_f b$:

$$\begin{aligned} \Delta T_f &= (1.86\,\text{K mol}^{-1}\text{kg})(0.318\,\text{mol kg}^{-1}) \\ &= 0.591\ ^\circ\text{C} \end{aligned}$$

The freezing point is depressed below 0.000 °C by 0.591 °C, so we calculate that this solution freezes at -0.591 °C.

Is our answer reasonable?

The molality, as recalculated, is roughly 0.3, so 0.3 of 1.86 (call it 2) is 0.6, which, after we add the unit °C and subtract from 0 °C, gives -0.6 °C, which is close to the answer.

PRACTICE EXERCISE 10.17

Calculate the freezing point of an aqueous solution of 0.237 mol kg^{-1} LiCl on the assumption that it is 100% dissociated. Calculate its freezing point assuming 0% dissociation.

Experiments show that neither the 1.00 mol kg^{-1} $(NH_4)_2SO_4$ nor the 1.00 mol kg^{-1} NaCl solution described above and on the previous page freezes at as low a temperature as calculated. Our assumption that an electrolyte separates *completely* into its ions is incorrect. Some oppositely charged ions exist as very closely associated pairs, called **ion pairs**, which behave as single 'molecules'. Clusters larger than two ions probably exist also. The formation of ion pairs and clusters makes the actual *particle* concentration in a 1.00 mol kg^{-1} NaCl solution somewhat less than 2.00 mol kg^{-1}. As a result, the freezing point depression of 1.00 mol kg^{-1} NaCl is not quite as large as that calculated on the basis of 100% dissociation.

As solutions of electrolytes are made more *dilute*, the observed and calculated freezing points come closer together. At ever greater dilutions, the association of ions is less of a complication because the ions are further apart, so the solutes behave more and more as if they were 100% separated into their ions.

Chemists compare the degrees of dissociation of electrolytes at different dilutions by a quantity called the **van't Hoff factor (*i*)**. This is the ratio of the observed freezing point depression to the value calculated on the assumption that the solute dissolves as a nonelectrolyte:

$$i = \frac{(\Delta T_f)_{\text{measured}}}{(\Delta T_f)\ \text{calculated as a nonelectrolyte}}$$

The theoretical van't Hoff factor, *i*, is 2 for NaCl, KCl and $MgSO_4$, which break up into two ions on 100% dissociation. For K_2SO_4, the theoretical value of *i* is 3 because each K_2SO_4 unit gives three ions. The actual van't Hoff factors for several electrolytes at different dilutions are given in table 10.5. Notice that with decreasing concentration (i.e. at higher dilutions) the experimental van't Hoff factors agree better with their corresponding theoretical van't Hoff factors.

TABLE 10.5 Effect of concentration on van't Hoff factor

	van't Hoff factor (*i*)

	Molal concentration (mol salt/kg water)			If 100% dissociation occurred
Salt	0.1	0.01	0.001	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

The increase in the percentage of complete dissociation that comes with greater dilution is not the same for all salts. In going from molalities of 0.1 to 0.001 mol kg^{-1}, the increase in % dissociation of KCla, as measured by the change in *i*, is only about 7%. For K_2SO_4, the increase for the same dilution is about 22%, a difference caused by the anion SO_4^{2-}. This anion has twice the charge of the anion in KCl, so the SO_4^{2-} ion attracts K^+ more strongly than can Cl. Hence, letting an ion of 2- charge and an ion of 1+ charge get farther apart by dilution has a greater effect on their acting independently than giving ions of 1- and 1+ charge more room. When *both*cation and anion are doubly charged, the improvement in % dissociation with dilution is even greater. We can see from table 10.5 that there is an almost 50% increase in the value of *i* for $MgSO_4$ as we go from a 0.1 to a 0.001 mol kg^{-1} solution.

There are many substances in which dissociation is far from complete. For example, in1.00 mol kg^{-1} aqueous acetic acid (a weak acid), the following equilibrium exists:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

The solution freezes at -1.90 °C. This is only a little lower than that expected (-1.86 °C) if no ionisation occurred, which is evidence for only a small amount of ionisation. We can estimate % ionisation by the following calculation.

We first use the data to calculate the *apparent molality* of the solution: i.e. the molality of all dissolved species, CH_3COOH, CH_3COO^- and H_3O^+. We again use $\Delta T_f = K_f b$, but now letting *b* stand for the apparent molality. K_f is 1.86 K mol^{-1} kg so:

$$b = \frac{\Delta T_f}{K_f} = \frac{1.90\,\text{K}}{1.86\,\text{K mol}^{-1}\text{kg}}$$

$$= 1.02\,\text{mol kg}^{-1}$$

If there is 1.02 mol of all solute species in 1 kg of solvent, we have 0.02 mol of solute species more than we started with, because we began with 1.00 mol of acetic acid. Since we get just one *extra* particle for each acetic acid molecule that ionises, the extra 0.02 mol of particles must have come from the ionisation of 0.02 mol of acetic acid. So:

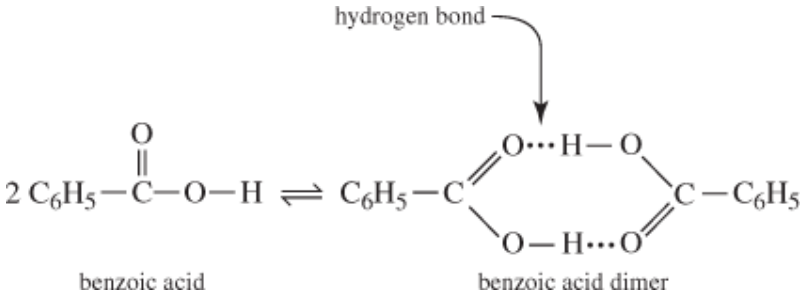
$$\%\,\text{ionisation} = \frac{\text{mol of acid ionised}}{\text{mol of acid available}} \times 100\%$$

$$= \frac{0.02}{1.00} \times 100\%$$

$$= 2\%$$

In other words, this procedure estimates the % ionisation in 1.00 mol kg^{-1} acetic acid to be 2%. (Other kinds of measurements offer better precision, and the % ionisation of acetic acid at this concentration is actually less than 1%.) We will discuss the ionisation of acids in greater detail in chapter 11.

Some molecular solutes produce smaller colligative effects than their molal concentrations would lead us to predict. This is often evidence that solute molecules are clustering or undergoing **association** in solution. For example, when dissolved in benzene, benzoic acid molecules associate as **dimers** held together by hydrogen bonds:



Because of association, the depression of the freezing point of a 1.00 mol kg^{-1} solution of benzoic acid in benzene is only about half of the calculated value. By forming a dimer, benzoic acid has an effective molecular mass twice that normally calculated. The larger effective molar mass reduces the molal concentration of particles by a factor of two, and the effect on the freezing point depression is halved.

It is appropriate that we have finished this chapter with two examples involving acids. In the next chapter, we will look at the solution properties of acids and bases in detail, and we will see that the behaviour of these compounds in solution is governed by the principles we have outlined in this and the previous two chapters.

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SUMMARY

Introduction to Solutions and Solubility

A solution is a homogeneous mixture of two or more pure substances that can be gases, liquids or solids. The liquid in a liquid solution is called the solvent, and the dissolved substance is the solute. A saturated solution contains the maximum possible amount of dissolved solute at the given temperature and pressure.

Gaseous Solutions

All gases mix spontaneously in all proportions. As the enthalpy change for mixing is usually small, owing to the very low inter atomic or intermolecular forces between the gas atoms or molecules, the mixing process is essentially entropy driven.

Liquid Solutions

In contrast to gaseous solutions, liquid solutions have significant intermolecular interactions involving solvent molecules so they generally have significant enthalpies of solution, $\Delta_{sol}H$. The two contributions to $\Delta_{sol}H$ when a gas dissolves in a liquid are the energy required to open 'pockets' in the solvent and the energy released when gas molecules occupy these pockets. $\Delta_{sol}H$ values are usually positive for gases in organic solvents and negative for gases in water. The solubilities of gases in water usually decrease with increasing temperature. Henry's law, $c_{gas} = k_H p_{gas}$, states that the concentration of a gas in a liquid at constant temperature is directly proportional to the partial pressure of the gas above the solution.

Two liquids that mix completely in all proportions are said to be miscible, while those that do not mix are immiscible. Liquids of similar polarities are often miscible; in other words, 'like dissolves like'. Dissolution of an ionic compound in water gives the hydrated free ions, a specific form of solvation. Polar molecules are generally soluble in polar solvents and vice versa.

The molar enthalpy of solution of a solid is the enthalpy change when 1 mole of a crystalline substance is dissolved in a solvent. The solubility of a solid in a liquid is temperature dependent and generally increases with increasing temperature.

Quantification of Solubility: the Solubility Product

The solubility product, K_{sp}, is the equilibrium constant for the dis-solution of a slightly soluble salt in a solvent (usually water). For the general equilibrium:

$$M_aX_b(s) \rightleftharpoons aM^{b+}(aq) + bX^{a-}(aq)$$

it is written as $K_{sp} = [Mb^{b+}]^a[X^{a-}]^b$. The molar solubility ($s$) of a salt at a specified temperature is the amount of the salt dissolved in 1 litre of a saturated solution at that temperature. The relationship between s and K_{sp} depends on the nature of the salt. For a 1: 1 salt, $K_{sp} = s^2$, for a 1: 2 salt, $K_{sp} = 4s^3$, for a 1: 3 salt, $K_{sp} = 27s^4$ and, for a 2: 3 salt, $K_{sp} = 108s^5$.

The effect of adding a common ion to a saturated solution of a slightly soluble salt can be calculated by comparing Q_{sp} (sometimes called the ionic product) with K_{sp}. We can use the same method to predict if a precipitate will form when two solutions are mixed. The common ion effect shows that salts are always less soluble in the presence of a common ion, providing no further chemical reaction is possible.

Colligative Properties of Solutions

A solution containing a nonvolatile solute boils at a higher temperature and freezes at a lower

temperature than the pure solvent. This can be explained in terms of the colligative properties of the solvent. In so doing, instead of expressing solution composition in terms of molar concentration or molarity, it is necessary to use molal concentration or molality (b), which is defined as:

$$b = \frac{\text{amount of solute (mol)}}{\text{mass of solvent (Kg)}}$$

We use mole fractions, x, when explaining the effect of a solute on boiling and freezing points. Raoult's law, $p_{\text{solution}} = x_{\text{solvent}} p^*_{\text{solvent}}$, shows that the pressure above a solution is proportional to the mole fraction of the solvent in a dilute solution. This is due to a reduction in the number of molecules of solvent at the surface of the solution, which leads to a lower vapour pressure for the solution than for the pure solvent. An ideal solution obeys Raoult's law. Each component of an ideal solution consisting of two volatile liquids A and B obeys Raoult's law, such that $p_{\text{total}} = x_A p^*_A + x_B p^*_B$. The boiling point elevation and freezing point depression of a solution containing a nonvolatile solute is due to the reduced vapour pressure of the solution relative to that of the pure solvent. The magnitudes of these effects can be determined using the equations $\Delta T_b = K_b b$ and $\Delta T_f = K_f b$, where K_b and K_f are the molal boiling point elevation constant and the molal freezing point depression constant of the solvent, respectively, and b is the molality of the solution (mol kg^{-1}).

Dialysis is the passage of water and small solute particles through a semipermeable membrane, while osmosis is the passage of solvent only. Osmosis occurs through an osmotic membrane and results in a net shift of solvent from the side less concentrated in solute to the side more concentrated. The osmotic pressure (Π) is that required to stop this net flow of solvent when one of the liquids is pure water. The van't Hoff equation for osmotic pressure is $\Pi V = nRT$ and is analogous to the ideal gas equation.

Freezing point depression can be used to estimate the degree of dissociation of ionic salts in solution. These results often show that such salts do not dissociate completely but exist to a certain extent as ion pairs in solution. The van't Hoff factor (i) measures the degree of dissociation of an electrolyte in solution. As a solution becomes more dilute, the degree of dissociation increases. Freezing point depression also gives evidence for the association of molecular solutes in solution.

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KEY CONCEPTS AND EQUATIONS

Henry's law *(section 10.3)*

This law:

$$c_{gas} = k_H p_{gas}$$

allows calculation of the solubility of a gas in a solvent at a given pressure from its solubility at another pressure.

Like-dissolves-like rule *(section 10.3)*

This rule uses chemical composition and structure to predict whether two substances can form a solution.

Solubility product constant, K_{sp} *(section 10.4)*

We use K_{sp} to calculate the molar solubility of a salt, either in pure water or in a solution that contains a common ion. Comparison of K_{sp} with Q_{sp} allows us to decide whether a precipitate will form on mixing ionic solutions.

Molar solubility *(section 10.4)*

We can use molar solubility to calculate the value of K_{sp} for a slightly soluble salt.

Common ion effect *(section 10.4)*

The presence of a common ion in a solution lowers the solubility of a salt containing that common ion in the solution.

Molal concentration (molality) *(section 10.5)*

The law:

$$\text{molality} = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

provides a temperature-independent concentration expression for use with colligative properties.

Raoult's law *(section 10.5)*

This expression:

$$p_{solution} = x_{solvent} p^*_{solvent}$$

is used to calculate the effect of a solute on the vapour pressure of a solution.

Freezing point depression (ΔT_f) and boiling point elevation (ΔT_b) *(section 10.5)*

The expressions:

$$\Delta T_f = K_f b$$

and:

$$\Delta T_b = K_b b$$

enable us to estimate freezing and boiling points, molar masses and % dissociation of a weak electrolyte.

Equation for osmotic pressure *(section 10.5)*

We use this equation:

$$\Pi V = nRT$$

to estimate the osmotic pressure of a solution or to calculate molar masses from osmotic pressure and concentration data.

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REVIEW QUESTIONS

Introduction to Solutions and Solubility

10.1 Define the following terms.

(a) solution

(b) solvent

(c) solute

(d) solubility

(e) saturated solution

(f) dissolution

Gaseous Solutions

10.2 Why do two gases mix spontaneously when they are brought into contact?

Liquid Solutions

10.3 When substances form liquid solutions, what two factors determine the solubility of the solute in the solvent?

10.4 Methanol, CH_3OH, and water are miscible in all proportions. What does this mean? Explain how the —OH unit in methanol contributes to this.

10.5 Petrol and water are immiscible. What does this mean? Explain why they are immiscible in terms of structural features of their molecules and forces of attraction between them.

10.6 Iodine, I_2, is only very slightly soluble in water but dissolves readily in tetrachloromethane, a nonpolar solvent. Why do you think this is?

10.7 Iodine dissolves far better in ethanol (to form 'tincture of iodine', an old antiseptic) than in water. What does this tell us about the alcohol molecules compared with water molecules?

10.8 The value of $\Delta_{sol}H$ for a particular soluble compound is +26 kJ mol^{-1}. If a nearly saturated solution is prepared in an insulated container (e.g. a coffee cup calorimeter), will the system's temperature increase or decrease as the solute dissolves?

10.9 Which would be expected to have the larger hydration enthalpy, Al^{3+} or Li^{+}? Why? (Both ions are about the same size.)

10.10 The value of $\Delta_{sol}H$ for the formation of an acetone–water solution is negative. Explain this in terms of intermolecular forces of attraction.

10.11 The value of $\Delta_{sol}H$ for the formation of an ethanol–hexane solution is positive. Explain this in terms of intermolecular forces of attraction.

10.12 If the value of $\Delta_{sol}H$ for the formation of a mixture of two liquids *A* and *B* is 0, what does this imply about the relative strengths of *A*—*A*, *B*—*B* and *A*—*B* intermolecular attractions?

10.13 If a saturated solution of NH_4NO_3 in 100 g of solvent at 70 °C is cooled to 10 °C, what mass of solute will precipitate? (Use data in figure 10.15.)

10.14 A hot concentrated solution in which equal masses of NaI and NaBr are dissolved is slowly cooled from 50 °C. Which salt precipitates first? (Use data in figure 10.15.)

10.15 Fishermen know that, on hot summer days, the largest fish are found in deep sinks in lake bottoms, where the water is coolest. Use the temperature dependence of oxygen solubility in water to explain why.

10.16 What is Henry's law?

10.17 Mountain streams often contain fewer living things than equivalent streams at sea level. In terms

of oxygen solubility at different pressures, give one reason why this might be true.

10.18 Why does a bottled carbonated beverage fizz when you take the cap off?

QuantifiCation of Solubility: the Solubility Product

10.19 What is the difference between Q_{sp} and K_{sp}?

10.20 Use the following equilibrium to demonstrate why the K_{sp} expression does not include the concentration of $Ba_3(PO_4)_2$ in the denominator.

$$Ba_3(PO_4)_2(s) \rightleftharpoons 3Ba^{2+}(aq) + 2PO_4{}^{3-}(aq)$$

10.21 What is the common ion effect? Use the solubility equilibrium for AgCl to illustrate the common ion effect.

10.22 With respect to K_{sp}, what conditions must be met before a precipitate forms in a solution?

10.23 What limits the accuracy and reliability of solubility calculations based on K_{sp} values?

Colligative Properties of Solutions

10.24 How does the molality of a solution vary with increasing temperature? How does the molarity of a solution vary with increasing temperature?

10.25 Suppose a 1.0 mol kg^{-1} solution of a solute is made using a solvent with a density of 1.15 g mL^{-1}. Is the molarity of this solution numerically larger or smaller than 1.0? Explain.

10.26 What specific fact about a physical property of a solution must be true to call it a colligative property?

10.27 Viewed at a molecular level, what causes a solution containing a nonvolatile solute to have a lower vapour pressure than the solvent at the same temperature?

10.28 What kinds of data are needed to find out if a solution of two miscible liquids is almost exactly an ideal solution?

10.29 When octane is mixed with ethanol, the vapour pressure of the octane over the solution is higher than what we would calculate using Raoult's law. Why? Explain the discrepancy in terms of intermolecular attractions.

10.30 When an aqueous solution of sodium chloride starts to freeze, why don't the ice crystals contain ions of the salt?

10.31 Explain why a nonvolatile solute dissolved in water gives the system:

(a) a higher boiling point than water

(b) a lower freezing point than water.

10.32 Why do we call dialysing and osmotic membranes ‘semipermeable’? What is the opposite of ‘permeable’?

10.33 What is the key difference between dialysing and osmotic membranes?

10.34 What is meant by ‘dialysis’?

10.35 At a molecular level, explain why in osmosis there is a net migration of solvent from the side of the membrane less concentrated in solute to the side more concentrated in solute.

10.36 Two glucose solutions of unequal molarity are separated by an osmotic membrane. Which solution *loses* water, the one with the higher or the lower molarity?

10.37 What is the difference between a hypertonic solution and a hypotonic solution?

10.38 Why are colligative properties of solutions of ionic compounds usually more pronounced than those of solutions of molecular compounds of the same molalities?

10.39 What is the van't Hoff factor? What is its expected value for all nondissociating molecular

solutes? If its measured value is slightly larger than 1.0, what does this suggest about the solute? What is suggested by a van't Hoff factor of approximately 0.5?

10.40 Which aqueous solution, if either, is likely to have the higher boiling point, 0.50 mol kg^{-1} NaI or 0.50 mol kg^{-1} Na_2CO_3?

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REVIEW PROBLEMS

10.41 Consider the formation of a solution of aqueous potassium chloride. Write the thermochemical equations for the:

(a) conversion of solid KCl into its gaseous ions

(b) subsequent formation of the solution by hydration of the ions.

The lattice enthalpy of KCl is 690 kJ mol^{-1}, and the hydration enthalpy of the ions is -686 kJ mol^{-1}.

(c) Calculate the enthalpy of solution of KCl in kJ mol^{-1}.

10.42 Suppose the lattice enthalpy of KCl was just 2% greater than the value given in table 10.2. What then would be the calculated $\Delta_{sol}H$ (in kJ mol^{-1})? How would this new value of $\Delta_{sol}H$ compare with that given in the table? By what percentage is the new value different from the value in the table? (The aim of this calculation is to show that small percentage errors in two large numbers, such as lattice enthalpy and hydration enthalpy, can cause large percentage changes in the absolute difference between them.)

10.43 If the enthalpy of solution of an ionic compound in water is +14 kJ mol^{-1}, and the lattice enthalpy is 630 kJ mol^{-1}, estimate the hydration enthalpy of the ions in the compound.

10.44 If the enthalpy of solution of an ionic compound in water is -50 kJ mol^{-1}, and the hydration enthalpy is -890 kJ mol^{-1}, estimate the lattice enthalpy of the ionic compound.

10.45 The solubility of methane, the chief component of natural gas, in water at 20 °C and 1×10^5 Pa pressure is 0.025 g L^{-1}. What is its solubility in water at 1.5×10^5 Pa and 20 °C?

10.46 At 9.74×10^4 Pa and 20 °C, nitrogen has a solubility in water of 0.018 g L^{-1}. At 8.16×10^4 Pa and 20 °C, its solubility is0.015 g L^{-1}. Show that nitrogen obeys Henry's law.

10.47 If the solubility of a gas in water is 0.010 g L^{-1} at 25 °C, and the partial pressure of the gas over the solution is 1.0×10^5 Pa, predict the solubility of the gas at the same temperature but at double the pressure.

10.48 If 100.0 mL of water is shaken with oxygen gas at 1.0×10^5 Pa, 0.0039 g of O_2 will dissolve. Estimate the Henry's law constant for oxygen gas in water.

10.49 Write the K_{sp} expressions for each of the following compounds: (a) CaF_2, (b) Ag_2CO_3, (c) $PbSO_4$, (d) $Fe(OH)_3$,(e) PbI_2, (f) $Cu(OH)_2$, (g) AgI, (h) Ag_3PO_4, (i) $PbCrO_4$,(j) $Al(OH)_3$, (k) $ZnCO_3$, (l) $Zn(OH)_2$.

10.50 Barium sulfate, $BaSO_4$, is so insoluble that it can be swallowed without significant danger, even though Ba^{2+} is toxic. At 25 °C, 1.00 L of water dissolves only 0.002 45 g of $BaSO_4$. Calculate K_{sp} for $BaSO_4$.

10.51 A student found that a maximum of 0.800 g $AgOOCCH_3$ can dissolve in 100 mL of water. What are the molar solubility and the K_{sp} for this salt?

10.52 It was found that the molar solubility of $BaSO_3$ in0.10 m $BaCl_2$ is 8.0×10^{-6} M. What is the value of K_{sp} for $BaSO_3$?

10.53 A student prepared a saturated solution of $CaCrO_4$ and found that, when 156 mL of the solution evaporated, 0.649 g of $CaCrO_4$ was left behind. What is the value of K_{sp} for this salt?

10.54 At 25 °C, the molar solubility of Ag_3PO_4 is1.8×10^{-5} mol L^{-1}. Calculate K_{sp} for this salt.

10.55 The molar solubility of $Ba_3(PO_4)_2$ in water at 25 °C is 1.4×10^{-8} mol L^{-1}. What is the value of K_{sp} for this salt?

10.56 Use the data in table 10.3 to determine the molar solubilities of the following compounds in water: (a) $PbBr_2$, (b) Ag_2CrO_4,(c) PbI_2.

10.57 At 25 °C, the value of K_{sp} for LiF is 1.7×10^{-3} and that for BaF_2 is 1.7×10^{-6}. Which salt, LiF or BaF_2, has the larger molar solubility in water? Calculate the solubility of each in units of mol L^{-1}.

10.58 At 25 °C, the value of K_{sp} for AgCN is 2.2×10^{-16} and that for $Zn(CN)_2$ is 3×10^{-16}. In terms of grams per 100 mL of solution, which salt is the more soluble in water?

10.59 A salt with a formula in the form MX has a value of K_{sp} equal to 3.2×10^{-10}. Another slightly soluble salt, MX_3, must have what value of K_{sp} if the molar solubilities of the two salts are to be identical?

10.60 Calcium sulfate is found in plaster. At 25 °C, the value of K_{sp} for $CaSO_4$ is 2.4×10^{-5}. What is the calculated molar solubility of $CaSO_4$ in water?

10.61 Copper(I) chloride, CuCl, has $K_{sp} = 1.9 \times 10^{-7}$ at 25 °C. Calculate the molar solubility of CuCl in (a) pure water,(b) 0.0200 M HCl solution, (c) 0.200 M HCl solution and(d) 0.150 M $CaCl_2$ solution at 25 °C.

10.62 Gold(III) chloride, $AuCl_3$, has $K_{sp} = 3.2 \times 10^{-25}$ at 25 °C. Calculate the molar solubility of $AuCl_3$ in (a) pure water, (b) 0.010 M HCl solution, (c) 0.010 M $MgCl_2$ solution and (d) 0.010 M $Au(NO_3)_3$ solution at 25 °C. Assume that $AuCl_3$ does not react with any of the compounds in (b), (c) or (d).

10.63 Calculate the molar solubility of Ag_2CrO_4 at 25 °C in (a) 0.200 M $AgNO_3$ and (b) 0.200 M Na_2CrO_4. (For Ag_2CrO_4 at 25 °C, $K_{sp} = 1.2 \times 10^{-1}2$.)

10.64 What is the molar solubility of $Mg(OH)_2$ in 0.20 M NaOH at 25 °C? (For $Mg(OH)_2$, $K_{sp} = 7.1 \times 10^{-12}$ at 25 °C.)

10.65 Calculate the molar solubility of $CaSO_4$ in 0.015 M $CaCl_2$ at 25 °C.

10.66 Calculate the molar solubility of AgCl in 0.050 M $AlCl_3$ at 25 °C.

10.67 In an experiment, 2.20 g of NaOH(s) is added to 250 mL of 0.10 M $FeCl_2$ solution at 25 °C. What mass of $Fe(OH)_2$ is formed? What is the molar concentration of Fe^{2+} in the final solution?

10.68 Suppose that 1.75 g of NaOH(s) is added to 250 mL of 0.10 M $NiCl_2$ solution at 25 °C. What mass, in grams, of $Ni(OH)_2$ is formed?

10.69 What is the molar solubility of $Ca(OH)_2$ in (a) 0.10 M $CaCl_2$ and (b) 0.10 M NaOH at 25 °C?

10.70 Does a precipitate of $PbCl_2$ form when 0.0150 mol of $Pb(NO_3)_2$ and 0.0120 mol of NaCl is dissolved in 1.00 L of solution at 25 °C?

10.71 Silver acetate, $AgOOCCH_3$, has $K_{sp} = 2.3 \times 10^{-3}$ at 25 °C. Does a precipitate form when 0.015 mol of $AgNO_3$ and 0.25 mol of $Ca(OOCCH_3)_2$ is dissolved in a total volume of 1.00 L of solution at 25 °C?

10.72 Does a precipitate of $PbBr_2$ form if 50.0 mL of 0.0100 M $Pb(NO_3)_2$ is mixed with (a) 50.0 mL of 0.0100 M KBr and (b) 50.0 mL of 0.100 M NaBr at 25 °C?

10.73 Does a precipitate of silver acetate, $AgOOCCH_3$, form if 22.0 mL of 0.100 M $AgNO_3$ is added to

45.0 mL of 0.0260 M $NaOOCCH_3$ at 25 °C? (For $AgOOCCH_3$, $K_{sp} = 2.3 \times 10^{-3}$ at 25 °C.)

10.74 Both AgCl and AgI are very slightly soluble salts, but the solubility of AgI is much less than that of AgCl, as can be seen by their K_{sp} values. Suppose that a solution contains both Cl^- and I^- with $[Cl^-] = 0.050$ M and $[I^-] = 0.050$ M at 25 °C. If solid $AgNO_3$ is added to 1.00 L of this mixture (so that no appreciable change in volume occurs), what is the value of $[I^-]$ when AgCl first begins to precipitate?

10.75 Suppose that Na_2SO_4 is added gradually to 100 mL of a solution that contains both Ca^{2+} ions (0.15 M) and Sr^{2+} ions (0.15 M) at 25 °C. (a) What is the Sr^{2+} concentration (in mol L^{-1}) when $CaSO_4$ just begins to precipitate? (b) What percentage of the strontium ion has precipitated when $CaSO_4$ just begins to precipitate?

10.76 What is the molality of NaCl in a solution that is 3.000 M NaCl with a density of 1.07 g mL^{-1}?

10.77 A solution of acetic acid, CH_3COOH, has a concentration of 0.143 M and a density of 1.00 g mL^{-1}. What is the molality of this solution?

10.78 What is the molal concentration of glucose, $C_6H_{12}O_6$, (a sugar found in many fruits) in a solution made by dissolving 24.0 g of glucose in 1.00 kg of water? What is the mole fraction of glucose in the solution?

10.79 An aqueous solution of propan-2-ol, $CH_3CH(OH)CH_3$, (rubbing alcohol) has a mole fraction of alcohol equal to 0.250. What is the molality of the alcohol?

10.80 An aqueous solution of $NaNO_3$ has a concentration of 0.363 mol kg^{-1} and a density of 1.0185 g mL^{-1}. Calculate the molar concentration of $NaNO_3$ and mole fraction of $NaNO_3$ in the solution.

10.81 The vapour pressure of water is 3.13×10^3 Pa at 25 °C. What is the vapour pressure of a solution prepared by dissolving 65.0 g of $C_6H_{12}O_6$ (a nonvolatile solute) in 150 g of water? (Assume the solution is ideal.)

10.82 At 25 °C, the vapour pressures of benzene, C_6H_6, and toluene, C_7H_8, are 1.23×10^4 and 3.54×10^3 Pa, respectively. A solution is prepared by mixing 60.0 g of benzene and 40.0 g of toluene. At what pressure will this solution boil?

10.83 Pentane, C_5H_{12}, and heptane, C_7H_{16}, are two hydrocarbon liquids present in petrol. At 20 °C, the vapour pressure of pentane is 5.53×10^4 Pa and the vapour pressure of heptane is4.74×10^3 Pa. What is the total vapour pressure of a solution prepared by mixing equal masses of the two liquids?

10.84 The vapour pressure of pure methanol, CH_3OH, at 30 °C is 2.11×10^4 Pa. What mass of the nonvolatile solute glycerol, $HOCH_2CH(OH)CH_2OH$, must be added to 100 g of methanol to obtain a solution with a vapour pressure of 1.84×10^4 Pa?

10.85 A solution containing 8.3 g of a nonvolatile, nondissociating substance dissolved in 1 mole of chloroform, $CHCl_3$, has a vapour pressure of 6.72×10^4 Pa. The vapour pressure of pure $CHCl_3$ at the same temperature is 6.92×10^4 Pa. Calculate (a) the mole fraction of the solute, (b) the amount of solute in the solution and (c) the molar mass of the solute.

10.86 At 21.0 °C, a solution of 18.26 g of a nonvolatile, nonpolar compound in 33.25 g of bromoethane, CH_3CH_2Br, has a vapour pressure of 4.42×10^4 Pa. The vapour pressure of pure bromoethane at this temperature is 5.26×10^4 Pa. What is the molar mass of the compound?

10.87 Estimate the boiling and freezing points of a 2.00 mol kg^{-1} solution of sugar in water. (It is

largely the sugar in ice-cream that makes it difficult to keep ice-cream frozen hard.)

10.88 Glycerol, $HOCH_2CH(OH)CH_2OH$ (M = 92 g mol^{-1}), is essentially a nonvolatile liquid that is very soluble in water. A solution is made by dissolving 46.0 g of glycerol in 250 g of water. Calculate the approximate freezing point of the solution and the boiling point of the solution.

10.89 What mass of sucrose, $C_{12}H_{22}O_{11}$, is needed to lower the freezing point of 100 g of water by 3.00 °C?

10.90 What is the boiling point of the solution described in question 10.89?

10.91 A solution of 12.00 g of an unknown nondissociating compound dissolved in 200.0 g of benzene freezes at 3.45 °C. Calculate the molar mass of the unknown.

10.92 A solution of 14 g of a nonvolatile, nondissociating compound in 1.0 kg of benzene boils at 81.7 °C. Calculate the molar mass of the unknown.

10.93 A nondissociating molecular compound has the empirical formula C_4H_2N. If 3.84 g of the compound in 500 g of benzene gives a freezing point depression of 0.307 °C, what are its molar mass and molecular formula?

10.94 Benzene reacts with hot concentrated nitric acid dissolved in sulfuric acid to give chiefly nitrobenzene, $C_6H_5NO_2$. A by-product is often obtained, which comprises 42.86% C, 2.40% H and 16.67% N (by mass). The boiling point of a solution of 5.5 g of the by-product in 45 g of benzene was 1.84 °C higher than that of benzene.

(a) Calculate the empirical formula of the by-product.

(b) Calculate a molar mass of the by-product and determine its molecular formula.

10.95 An aqueous solution of a compound with a very high molar mass was prepared at a concentration of 2.0 g L^{-1} at 25 °C. Its osmotic pressure was 2.76 Pa. Calculate the molar mass of the compound.

10.96 A saturated solution of 0.400 g of a polypeptide in 1.00 L of an aqueous solution has an osmotic pressure of4.92×10^2 Pa at 27 °C. What is the approximate molar mass of the polypeptide?

10.97 The vapour pressure of water at 20 °C is 2.30×10^3 Pa. Calculate the vapour pressure at 20 °C of a solution made by dissolving 10.0 g of NaCl in 100 g of water. (Assume complete dissociation of the solute and an ideal solution.)

10.98 What mass of $AlCl_3$ would have to be dissolved in 150 mL of water to give a solution that has a vapour pressure of 5.09×10^3 Pa at 35 °C? (Assume complete dissociation of the solute and ideal solution behaviour. At 35 °C, the vapour pressure of pure water is 5.55×10^3 Pa.)

10.99 Below are the concentrations of the most abundant ions in sea water.

Ion	**Molality (mol kg^{-1})**
chloride	0.566
sodium	0.486
magnesium	0.055
sulfate	0.029
calcium	0.011
potassium	0.011
hydrogen carbonate	0.002

Use these data to estimate the osmotic pressure of sea water at 25 °C. What is the minimum

pressure needed to desalinate sea water by reverse osmosis?

10.100 What is the expected freezing point of a 0.20 mol kg^{-1} solution of $CaCl_2$? (Assume complete dissociation.)

10.101 The freezing point of a 0.10 mol kg^{-1} solution of mercury(I) nitrate is approximately -0.27 °C. Show how this suggests that the formula of the mercury(I) ion is Hg_2^{2+}.

10.102 A 1.00 mol kg^{-1} aqueous solution of HF freezes at -1.91 °C. What is the percentage ionisation of HF in the solution?

10.103 An aqueous solution of a weak electrolyte, HX, with a concentration of 0.125 mol kg^{-1} has a freezing point of -0.261 °C. What is the percentage ionisation of the compound (to two significant figures)?

10.104 The van't Hoff factor for the solute in 0.100 mol kg^{-1} $NiSO_4(aq)$ is 1.19. What would this factor be if the solution behaved as if it were 100% dissociated?

10.105 What is the expected van't Hoff factor for K_2SO_4 in an aqueous solution, assuming 100% dissociation?

10.106 A 0.118 mol kg^{-1} solution of LiCl has a freezing point of -0.415 °C. What is the van't Hoff factor for this solute at this concentration?

10.107 What is the approximate osmotic pressure of a 0.118 mol kg^{-1} solution of LiCl at 10 °C? (Use the data in question 10.106.)

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10.108 The 'bends' is a medical emergency caused when a scuba diver rises too quickly to the surface from a deep dive. The origin of the problem is seen in the calculations in this question. At 37 °C (normal body temperature), the solubility of N_2 in water is0.015 g L^{-1} when its pressure over the solution is 1.0×10^5 Pa. Air is approximately 78 mol % N_2. What amount of N_2 is dissolved per litre of blood (essentially an aqueous solution) when a diver inhales air at a pressure of 1.0×10^5 Pa? What amount of N_2 dissolves per litre of blood when the diver is submerged to a depth of approximately 30 m, where the total pressure of the air being breathed is 4.0×10^5 Pa? If the diver surfaces quickly, how many millilitres of N_2 gas, in the form of tiny bubbles, are released into the bloodstream from each litre of blood (at 37 °C and 1.0×10^5 Pa)?

10.109 Deep-sea divers sometimes substitute helium for nitrogen in the air that they carry in their tanks to prevent the 'bends', because helium is much less soluble in blood than nitrogen. Use the simple molecular model of gas solubility discussed on pp. 391–2 to explain why helium is relatively insoluble in water.

10.110 Use the simple molecular model of gas solubility discussed on pp. 391–2 to explain why N_2 gas solubility in water decreases as the temperature of the solution rises from room temperature to about 70 °C, and then begins to increase.

10.111 The vapour pressure of a mixture of 400 g of tetrachloromethane and 43.3 g of an unknown compound is 1.80×10^4 Pa at 30 °C. The vapour pressure of pure tetrachloromethane at 30 °C is 1.88×10^4 Pa, while that of the pure unknown is 1.12×10^4 Pa. What is the approximate molar mass of the unknown?

10.112 Magnesium hydroxide, $Mg(OH)_2$, found in some antacids, has a solubility of 7.05×10^{-3} g L^{-1} at 25 °C. Calculate K_{sp} for $Mg(OH)_2$.

10.113 Solid $Mn(OH)_2$ is added to a solution of 0.100 M $FeCl_2$. After reaction, what are the molar concentrations of Mn^{2+} and Fe^{2+} in the solution? (For $Mn(OH)_2$, $K_{sp} = 1.6 \times 10^{-13}$.)

10.114 Suppose that 50.0 mL of 0.12 M $AgNO_3$ is added to 50.0 mL of 0.048 M NaCl solution.

(a) What mass of AgCl forms?

(b) Calculate the final concentrations of all of the ions in the solution that is in contact with the precipitate.

(c) What percentage of the Ag^+ ions precipitates?

10.115 A sample of hard water was found to have 278 ppm (parts per million) Ca^{2+} ions. A 1.00 g sample of Na_2CO_3 was dissolved in 1.00 L of this water. What is the new concentration of Ca^{2+} in ppm? (Assume that the addition of Na_2CO_3 does not change the volume, and assume that the densities of the aqueous solutions involved are all 1.00 g mL^{-1}.)

10.116 What is the osmotic pressure of a 0.010 M aqueous solution of a molecular compound at 25 °C?

10.117 The osmotic pressure of a dilute solution of a slightly soluble polymer in water was measured using the osmometer in figure 10.31. The difference in the heights of the liquid levels was 1.26 cm at 25 °C. Assume the solution has a density of1.00 g mL^{-1}.

(a) What is the osmotic pressure of the solution?

(b) What is the molarity of the solution?

(c) At what temperature would the solution freeze?

(d) Use your answers to (a)–(c) to explain why freezing point depression cannot be used to determine the molecular masses of compounds composed of very large molecules.

10.118 Consider an aqueous 1.00 mol kg^{-1} solution of Na_3PO_4, a compound with useful detergent properties. Calculate the boiling point of the solution assuming that:

(a) it does not ionise at all in solution

(b) the van't Hoff factor for Na_3PO_4 reflects 100% dissociation into its ions.

The 1.00 mol kg^{-1} solution boils at 100.83 °C at 1.0×10^5 Pa.

(c) Calculate the van't Hoff factor for the solute in this solution.

10.119 In an aqueous solution of KNO_3, the concentration is 0.9159 mol % of the salt. The solution's density is1.0489 g mL^{-1}. Calculate the (a) molal concentration of KNO_3, (b) percentage (w/w) of KNO_3 and (c) molarity of the KNO_3 in the solution.

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KEY TERMS

association
boiling point elevation (ΔTb)
colligative property
common ion
common ion effect
dialysis
dimers
dissociation
dissolution
enthalpy of solution ($\Delta_{sol}H$)
freezing point depression (ΔTf)
Henry's law
hydration
hydration enthalpy
hypertonic
hypotonic
ideal solution
immiscible
insoluble
ion pair
ionic product
isotonic
lattice enthalpy
like-dissolves-like rule
miscible
molal boiling point elevation constant (Kb)
molal concentration (b)
molal freezing point depression constant (Kf)
molality (b)
molar concentration (c)
molar solubility (*s*)
molarity (c)
mole fraction (*x*)
nonvolatile
osmosis
osmotic membrane
osmotic pressure (II)
Raoult's law
saturated solution
solubility
solubility product (Ksp)
soluble
solute
solution
solvation
solvation enthalpy
solvent
van't Hoff factor (*i*)

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CHAPTER

11 Acids and Bases

Of all the planets and moons in our solar system, the Earth is the only one which has been found to support life as we know it. This is due to a combination of factors, including the distance from the Sun, an atmosphere containing oxygen, and the presence of plentiful amounts of water that is neither too acidic nor too basic. For many years, it was wondered if life existed on Venus, our closest planetary neighbour, as it is about the same size as Earth and has an atmosphere. However, a number of probes have shown that, in addition to the enormous surface pressure (about 100 times that on Earth) and high surface temperature (˜460 °C), the upper atmosphere contains significant amounts of sulfuric acid, a strong, corrosive acid, inhalation of which would be fatal to any pioneering astronauts. Attention has therefore turned to Mars as a target for human exploration.

However, there are some forms of life on Earth, called acidophiles, which can exist, and indeed thrive, in highly acidic environments with pH values approaching 0. These are often found in geothermal areas in which the concentration of sulfur-containing compounds is high. One such acidophile is the alga *Cyanidium caldarium*, whose green colour is often seen around New Zealand's thermal areas. The photograph shows the crater lake on New Zealand's White Island, with the green colour arising, in part, from the presence of this alga. *Cyanidium caldarium* has managed to adapt to the highly acidic conditions by being able to pump acid out of its cells and using acid-resistant polysaccharide molecules to protect the cells from the acidic environment.

In this chapter, we will discuss a number of aspects of acids and bases. We will investigate the various definitions of acids and bases, show that there is an enormous range of acid and base strengths and that these can be rationalised on the basis of molecular structure, quantify Brønsted–Lowry acid and base behaviour using the concepts of pH, K_a and K_b, and study titrations of acids and bases.





KEY TOPICS

11.1 The Brønsted–Lowry definition of acids and bases
11.2 Acid–base reactions in water
11.3 Strong acids and bases
11.4 Weak acids and bases
11.5 The molecular basis of acid strength
11.6 Buffer solutions
11.7 Acid–base titrations
11.8 Lewis acids and bases

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11.1 The Brønsted–lowry Definition of Acids and Bases

In chapter 10, we looked at the nature of solutes and showed how freezing point depression measurements give us information about the degree of dissociation of a particular solute. Similar information can also be obtained by measurement of the conductivity of a solution, and this technique is both simpler to carry out and more sensitive than freezing point depression. It is effective because only solutions that contain ions will conduct an electric current. The magnitude of the electric current depends on the concentration and nature of the ions in the solution. A high concentration of ions allows the passage of a larger current, and therefore gives a larger conductivity than a low concentration, while a pure solvent that contains no ions will have a conductivity of zero.

We tend to think of water as consisting solely of H_2O molecules. Each molecule comprises a central oxygen atom that is covalently bound to two hydrogen atoms, and we might therefore expect that liquid water would have no ionic character. However, measurements show that pure water does exhibit a small conductivity, consistent with the presence of ions. (This is the reason that, unlike the unfortunate French singer Claude François, writer of the song 'My Way', you should never try to change a light bulb while standing in the bath.) These ions arise from the reaction of water with itself, according to the following equation.

$$H_2O(1) + H_2O(1) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The net result of this reaction is the transfer of a proton (H^+, a hydrogen atom minus an electron) from one molecule of water to another, and formation of the ionic species H_3O^+ (the **hydronium ion (H_3O^+)**) and OH^- (the **hydroxide ion (OH^-)**). Reactions such as this, which involve the transfer of a single proton from one species to another are called **acid–base reaction**. The reaction of water with itself represents arguably the simplest example of such a reaction. In this case, water acts as both an acid and a base.

The concept of acids and bases has been known for hundreds of years, but it is only relatively recently that definitions of the words 'acid' and 'base' have been agreed upon. The word acid derives from the Latin *acidus*, meaning sour; acids do indeed taste sour, but it is not a good idea to taste them in the laboratory. The word alkali, which is synonymous with base, comes from the Arabic *al-qaliy*, literally 'the ashes', referring to the ashes of the saltwort plant that grows in alkaline soils. The first comprehensive theory concerning acids and bases appeared in 1884 in the PhD thesis of the Swedish chemist, Svante Arrhenius (1859–1927, Nobel Prize in chemistry, 1903), who was nearly failed for proposing that ions could exist in solution. He defined an acid as a substance that released H^+ ions when dissolved in water, and a base as a substance that gave rise to OH^- ions on dissolution in water. This definition is similar to the more general **Brønsted–Lowry** definition of acids and bases, which we will use from this point. This was proposed by Johannes Brønsted, a Danish chemist, and Thomas Lowry, an English chemist, independently of each other in 1923. They considered that acid–base reactions involved proton (H^+) transfer between an acid and a base, which they defined as follows:

- An **acid** is a proton donor.
- A **base** is a proton acceptor.

In other words, a Brønsted–Lowry acid will donate a proton to a Brønsted–Lowry base, which will accept it. From now on, we will refer to Brønsted–Lowry acids and bases simply as acids and bases. To illustrate the Brønsted–Lowry concept, let's return to the example involving water that we introduced previously. We stated that water acted as both an acid and a base, and we can now explain this with reference to the Brønsted–Lowry definition.

One water molecule acts as a proton donor, and is therefore an acid. This water molecule becomes OH^-

on the right-hand side of the equation. The other water molecule accepts the donated proton, and therefore acts as a base. This water molecule is converted to H_3O^+ on the right-hand side of the equation. It is instructive to consider this reaction in terms of the structures shown in figure 11.1.

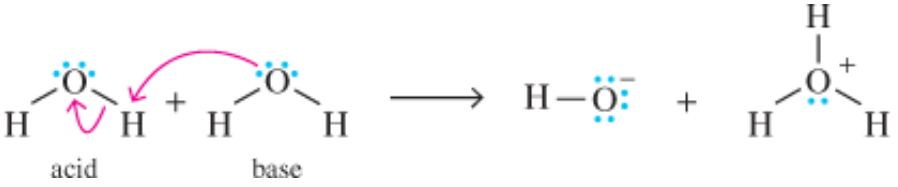
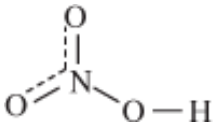
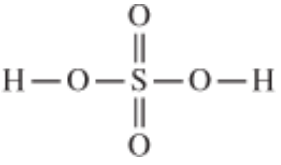
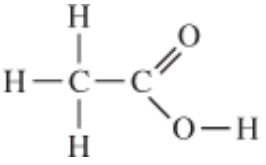
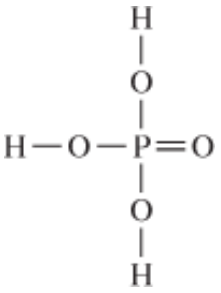


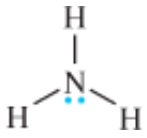
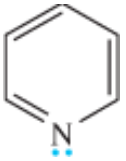
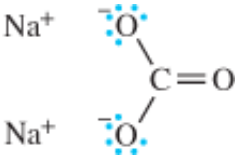
FIGURE 11.1 A mechanistic view of the acid–base reaction of one water molecule with another.

Obviously, in order for H_2O to act as an acid, it must, according to the Brønsted–Lowry definition, have a proton to donate. However, the mere presence of hydrogen atoms, which are potential protons, is not sufficient for a chemical species to act as an acid. For example, methane, CH_4, contains four hydrogen atoms but shows essentially no acidic properties. For a hydrogen atom to be measurably acidic, it must be bound to another atom via an appreciably polar bond, and therefore acids tend to contain hydrogen atoms bound to group 16 or 17 elements. Figure 11.1 also shows that, for H_2O to act as a base and accept the donated proton, it must have a lone pair of electrons to which the donated proton can covalently bond. The presence of one or more lone pairs is a prerequisite for a species to act as a base, but not all species containing lone pairs act as bases; for example, the chloride ion, Cl^-, contains four lone pairs, but displays negligible basic properties. Bases usually contain group 15 or 16 elements, the atoms of which (especially group 16) are often deprotonated and hence negatively charged. Table 11.1 lists a number of common acids and bases that would be found in any chemistry laboratory. You can see that the acids contain a very polar H—*X* bond, while the bases contain N and deprotonated O atoms with one and three lone pairs respectively.

TABLE 11.1 Some common acids and bases

Formula	Name	Structure
Acids		
HCl	hydrochloric acid[(a)]	
HNO_3	nitric acid	
H_2SO_4	sulfuric acid	
CH_3COOH	acetic acid	
H_3PO_4	phosphoric acid	



Bases		
NaOH	sodium hydroxide	
NH_3	ammonia[(b)]	
C_5H_5N	pyridine	
Na_2CO_3	sodium carbonate	

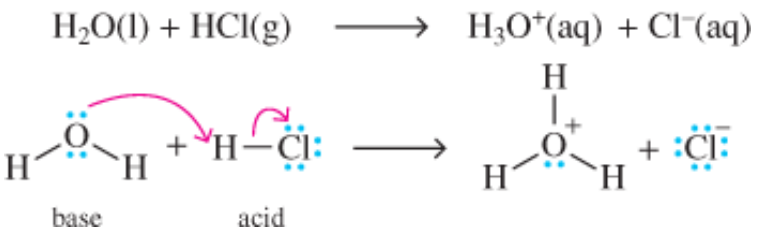
(a) Pure HCl is a gas at room temperature, and is called hydrogen chloride. Hydrochloric acid refers to a solution of HCl in water.

(b) Pure NH_3 is a gas at room temperature. In the laboratory, it is often used as an aqueous solution.

It can be seen from the structures of the acids in table 11.1 that, in some cases, there is more than one very polar H—X bond, and these acids can donate more than one proton. Such acids are collectively called **polyprotic acid**. Hydrochloric acid, nitric acid and acetic acid, each of which can donate only one proton, are examples of **monoprotic acids**. Sulfuric acid can donate two protons and is called a **diprotic acid** whereas phosphoric acid, which can donate three protons, is a **triprotic acid**.

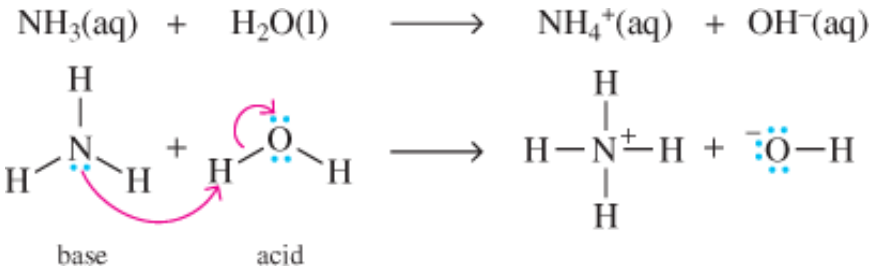
Similarly, some bases can accept more than one proton and are collectively called **polyprotic base**. Sodium hydroxide, ammonia and pyridine are examples of **monoprotic bases**, whereas carbonate ion is a **diprotic base**.

We now consider the reactions that occur when we place an acid or a base in water. We begin by using a chemical equation and a mechanistic diagram to see what happens when we dissolve gaseous hydrogen chloride in water.



Here, HCl is the acid and H_2O is the base. HCl donates a proton to H_2O, thereby becoming Cl^-, while H_2O, on accepting the proton, becomes H_3O^+, the hydronium ion. This reaction goes essentially to completion and we say that HCl dissociates completely in aqueous solution.

Similarly, if we dissolve gaseous ammonia, NH_3, in water, we obtain aqueous ammonia, $NH_3(aq)$, in which the following reaction occurs.



In this reaction, H_2O acts as an acid, donating a proton to NH_3 and thus becoming OH^-, while NH_3 acts as a base by accepting the proton from H_2O to give NH_4^+. However, this reaction differs from that for HCl in that it proceeds almost negligibly in the forward direction, and the reaction of ammonia with water is therefore far from complete. Note that water, the solvent in both reactions, acts as a base in the former reaction and an acid in the latter; compounds such as this that can act as either an acid or a base are called **amphiprotic**.

Conjugate Acid–base Pairs

It is informative to write the reverse equations for the reactions of HCl and NH_3 with water.

$$Cl^-(aq) + H_3O^+(aq) \rightarrow HCl(aq) + H_2O(1)$$
$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(1)$$

We can see that the reverse reactions also involve transfer of a proton, and are therefore themselves acid–base reactions. In the reaction:

$$Cl^-(aq) + H_3O^+(aq) \rightarrow HCl(aq) + H_2O(1)$$

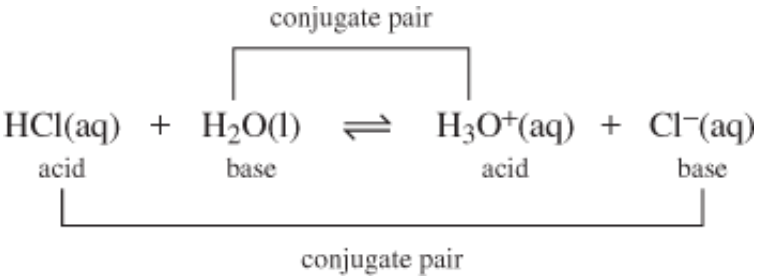
H_3O^+ acts as an acid, donating a proton to Cl–, which acts as a base by accepting it. Similarly, in the reaction:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(1)$$

NH_4^+ acts as an acid, donating a proton to the base OH^-. This illustrates a general feature of all Brønsted–Lowry acid–base reactions: *both the forward and reverse reactions are acid–base reactions*. Furthermore, there are always two sets of species on either side of the equation that differ only by a proton, and we call these **conjugate acid–base pair**. In the reaction:

$$HCl(aq) + H_2O(1) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

both HCl and Cl^-, and H_2O and H_3O^+ differ only by a proton. We showed that HCl acts as an acid in the forward reaction and Cl^- acts as a base in the reverse reaction. Therefore, Cl^- is the **conjugate base** of HCl, and HCl is the **conjugate acid** of Cl^-. Using the same reasoning, we can see that H_2O is the conjugate base of H_3O^+, and H_3O^+ is the conjugate acid of H_2O.



As both the forward and reverse reactions are acid–base reactions, and occur to some extent, it is usual to write acid–base reactions as equilibria. We will look at how we quantify these equilibria later in this chapter.

WORKED EXAMPLE 11.1

Determining the Conjugate Bases of Brønsted–Lowry Acids

What are the conjugate bases of nitric acid, HNO_3, and the hydrogen sulfate ion, HSO_4^-?

Analysis

The members of a conjugate acid–base pair differ by one proton, with the acid having the greater number of protons. To find the formula of the base, we remove one proton from the acid.

Solution

Removing one proton from HNO_3 leaves NO_3^-. The nitrate ion, NO_3^-, is thus the conjugate base of HNO_3. Removing a proton from HSO_4^- leaves its conjugate base, SO_4^{2-}.

Is our answer reasonable?

As a check, we can compare the two formulae in each pair.

$$HNO_3 \quad NO_3^-$$
$$HSO_4^- \quad SO_4^{2-}$$

In each case, the formula on the right has one fewer proton than the formula on the left, so it is the conjugate base. We have answered the question correctly.

PRACTICE EXERCISE 11.1

Write the formula of the conjugate base of each of the following Brønsted–Lowry acids.

(a) H_2O

(b) HI

(c) HNO_2

(d) H_3PO_4

(e) $H_2PO_4^-$

(f) HPO_4^{2-}

(g) H_2SO_4

(h) NH_4^+

(i) CH_3COOH

(j) C_6H_5OH

(k) $(CH_3)_3NH^+$

WORKED EXAMPLE 11.2

Identifying Conjugate Acid–base Pairs in a Brønsted–lowry Acid–base Reaction

The anion of sodium hydrogen sulfate, HSO_4^-, reacts as follows with the phosphate ion, PO_4^{3-}.

$$HSO_4^-(aq) + PO_4^{3-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HPO_4^{2-}(aq)$$

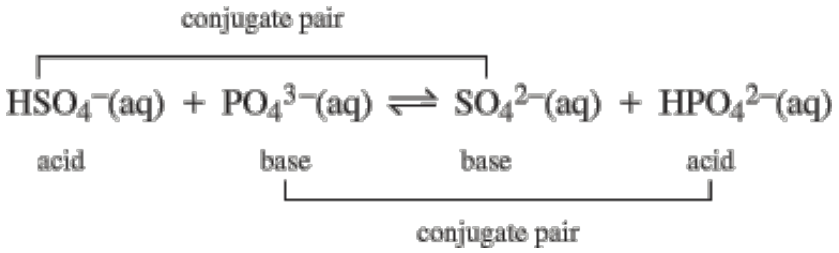
Identify the two conjugate acid–base pairs.

Analysis

There are two things that help us to identify the conjugate acid–base pairs in an equation. One is that the members of a conjugate pair differ by a proton. The second is that the members of each pair must be on opposite sides of the reaction arrow. In each pair, the acid has the larger number of protons.

Solution

Two of the formulae in the equation contain PO_4, so they must belong to the same conjugate pair. The one with the most protons, HPO_4^{2-}, is the acid, and the other, PO_4^{3-}, is the base. Therefore, one conjugate acid–base pair is HPO_4^{2-} and PO_4^-. The other two ions, HSO_4^- and SO_4^{2-}, belong to the second conjugate acid–base pair; HSO_4^- is the conjugate acid and SO_4^{2-} is the conjugate base.



Is our answer reasonable?

A check satisfies us that we have fulfilled the requirements that each conjugate pair has one member on each side of the arrow and that the members of each pair differ from each other by one (and only one) proton.

PRACTICE EXERCISE 11.2

One kind of baking powder contains sodium bicarbonate and calcium dihydrogen phosphate. When water is added, the following reaction occurs.

$$HCO_3^-(aq) + H_2PO_4^-(aq) \rightleftharpoons H_2CO_3(aq) + HPO_4^{2-}(aq)$$

Identify the two acids and the two bases in this reaction. (The H_2CO_3 decomposes to release CO_2, which causes the cake to rise.)

PRACTICE EXERCISE 11.3

When some of the strong cleaning agent 'trisodium phosphate' is mixed with household vinegar, which contains acetic acid, the following reaction occurs. Identify the pairs of conjugate acids and bases.

$$PO_4^{3-}(aq) + CH_3COOH(aq) \rightleftharpoons HPO_4^{2-}(aq) + CH_3OO^-(aq)$$

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11.2 Acid–base Reactions in Water

In many of the examples we have considered so far, water has acted as both the solvent, and either the acid or the base. However, acid–base reactions can occur in any solvent, and can even occur in the absence of solvent, as shown in figure 11.2.

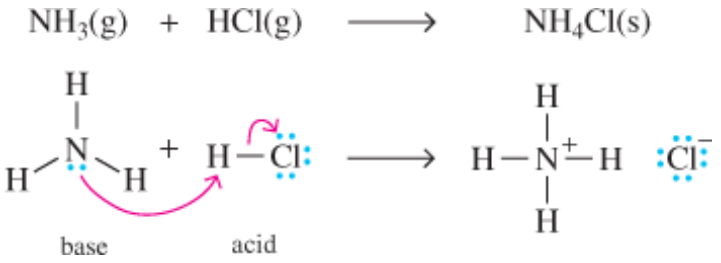




FIGURE 11.2 The reaction of gaseous HCl with gaseous NH_3. As each gas escapes from its concentrated aqueous solution and mingles with the other, a cloud of tiny crystals of $NH_4Cl(s)$ forms above the bottles. Andy Washnik

This is also a proton transfer reaction, in which gaseous HCl donates a proton to gaseous NH_3, as shown in the mechanistic diagram. Given that most acid–base reactions of interest occur in aqueous solution, we will concentrate on water as the solvent for the majority of our discussions.

The Autoprotolysis of Water

We have shown that water can react with itself to generate hydronium and hydroxide ions according to the equation:

$$H_2O(1) + H_2O(1) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

This reaction, in which a proton is transferred between identical molecules, is called **autoprotolysis** (sometimes called autoionisation). The extent of the autoprotolysis of water can be determined using the equilibrium constant for this process. Using the methods developed in chapter 9, and remembering that pure

liquids do not appear in an equilibrium constant expression, we write the equilibrium constant for the reaction as:

$$K_W = [H_3O^+][OH^-] = 1.0 \times 10^{-14} (T = 25.5\,^\circ C)$$

The extraordinary importance of this equilibrium means that the equilibrium constant is given the special symbol K_w and is called the **autoprotolysis constant of water**. Its very small value shows that the autoprotolysis of water proceeds only to a very small extent and that the equilibrium concentrations of H_3O^+ and OH^- in pure water are small. We can calculate just how small by using the value of K_w and realising from the stoichiometry of the reaction that the equilibrium concentrations of H_3O^+ and OH^- in pure water must be the same.

$$K_W = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$$

If $[H_3O^+] = [OH^-]$, then:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ \text{mol L}^{-1}$$

Therefore, the $[H_3O^+]$ and $[OH^-]$ in pure water at 25.0 °C are both 1.0×10^{-7} mol L^{-1}. Like most equilibrium constants, the value of K_w is temperature dependent and increases as the temperature increases. For example, at 40.0 °C, $K_w = 3.0 \times 10^{-14}$ and pure water at this temperature has $[H_3O^+] = [OH^-] = 1.7 \times 10^{-7}$ mol L^{-1}. Table 11.2 lists values of K_w at a number of temperatures.

TABLE 11.2 K_w at various temperatures

Temperature (°C)	K_w
0	1.5×10^{-15}
10	3.0×10^{-15}
20	6.8×10^{-15}
25	1.0×10^{-14}
30	1.5×10^{-14}
40	3.0×10^{-14}
50	5.5×10^{-14}
60	9.5×10^{-14}

We say that pure water is **neutral**, because it contains equal concentrations of H_3O^+ and OH^-. Aqueous solutions in which $[H_3O^+] > [OH^-]$ are termed **acidic**, while **basic** (or **alkaline**) solutions have $[H_3O^+] < [OH^-]$. There is an inverse relationship between $[H_3O^+]$ and $[OH^-]$ in aqueous solution at constant temperature; as one increases, the other must decrease in order to keep K_w constant. If we know the value of only one of $[H_3O^+]$ or $[OH^-]$ in a solution, we can use K_w to calculate the other, as illustrated in worked example 11.3.

WORKED EXAMPLE 11.3

Finding $[H_3O^+]$ from $[OH^-]$ or $[OH^-]$ from $[H_3O^+]$

In a sample of blood at 25 °C, $[H_3O^+] = 4.6 \times 10^{-8}$ M. Find $[OH^-]$ and decide if the sample is acidic, basic or neutral.

Analysis

We know that the values of $[H_3O^+]$ and $[OH^-]$ are related to each other through K_w at 25 °C as follows.

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-14}$$

If we know one concentration, we can always find the other.

Solution

We substitute the given value of $[H_3O^+]$ into this equation and solve for $[OH^-]$.

$$1.0 \times 10^{-14} = (4.6 \times 10^{-8})[OH^-]$$

Solve for $[OH^-]$, remembering that its units are mol L^{-1} or M.

$$[OH^-] = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-8}} \text{ M}$$

$$= 2.2 \times 10^{-7} \text{ M}$$

When we compare a $[H_3O^+]$ of 4.6×10^{-8} M with a $[OH^-]$ of 2.2×10^{-7} M, we see that $[OH^-] > [H_3O^+]$. Our answer, then, is that the blood is slightly basic.

Is our answer reasonable?

We know $K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$. So one check is to note that, if $[H_3O^+]$ is slightly *less* than 1×10^{-7}, $[OH^-]$ will be slightly *more* than 1×10^{-7}, as it is.

PRACTICE EXERCISE 11.4

An aqueous solution of sodium bicarbonate, $NaHCO_3$, has $[OH^-] = 7.8 \times 10^{-6}$ M. What is $[H_3O^+]$? Is the solution acidic, basic or neutral?

The Concept of pH

As we have seen previously, the concentrations of H_3O^+ and OH^- in pure water are very small, and the same is often true of $[H_3O^+]$ and $[OH^-]$ in aqueous solutions of acids and bases. To avoid working with such inconveniently small numbers, we commonly express $[H_3O^+]$ in terms of the **pH** of the solution. This approach was developed by the Danish chemist Søren Sørensen (1868–1939) in 1909. pH is defined as the negative logarithm of the concentration of H_3O^+ in a solution, or, in equation form:

$$\text{pH} = -\log\left[H_3O^+\right]$$

We can also define the **pOH** of a solution as:

$$\mathrm{pOH} = -\log[\mathrm{OH}^-]$$

In both cases, p is simply an abbreviation for '-log' (p is derived from the German word *Potenz* meaning 'power'). It is important to realise that log means $\log_{10}$, rather than natural logarithm (ln or $\log_e$). It is vital that you appreciate the difference between the two types of logarithms — for example, $\log(1 \times 10^2) = 2$, whereas $\ln(1 \times 10^2) \approx 4.605$. You should also ensure that you know under which circumstances the different types of logarithms are used; you generally use log only in calculations involving pH or (as we will see) pK_a.

Having shown that $[H_3O^+] = 1.0 \times 10^{-7}$ mol L^{-1} in pure water at 25.0 °C, we can now calculate the pH of pure water under these conditions.

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00$$

There are two things to note here. Firstly, you cannot take the logarithm of a quantity that has units, and therefore we must either implicitly drop the concentration units of $[H_3O^+]$ before taking the logarithm or treat the term $[H_3O^+]$ as being the dimensionless quantity $\frac{[H_3O^+]}{c^\ominus}$, as we did in similar situations in chapter 9. Secondly, the number of decimal places in a logarithm of any number is equal to the number of significant figures in that number. Thus our pH is given to two decimal places, 7.00.

The fact that pure water has a pH of 7 at 25.0 °C is probably a familiar result to many of you. Not so familiar perhaps is the pOH of pure water at 25.0 °C. Again, we have shown that $[OH^-] = 1.0 \times 10^{-7}$ under these conditions and therefore:

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00$$

In both cases, you can see that it is much more convenient to write 7.00 than 1.0×10^{-7} (or indeed 0.000 000 10).

We showed previously that solutions with $[H_3O^+] > [OH^-]$ are acidic, while those with $[H_3O^+] < [OH^-]$ are basic. This means that (at 25.0 °C) solutions with pH < 7 are acidic, and those with pH > 7 are basic (or alkaline).

It is important that you are proficient in dealing with logarithms on your calculator and are able to convert from $[H_3O^+]$ to pH and from pH to $[H_3O^+]$ without any trouble. The latter involves taking the antilogarithm of the *negative* of the pH, i.e. $[H_3O^+] = 10^{-\mathrm{pH}}$.

A simple relationship between pH and pOH can be derived, starting from the K_w expression. To do this, we make use of the property of logarithms which says that the logarithm of the product of two numbers is equal to the sum of the logarithms of those numbers, i.e. $\log(ab) = \log(a) + \log(b)$.

We know that $[H_3O^+][OH^-] = K_w$. If we now take the negative logarithm of both sides, we obtain:

$$-\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] = -\log K_\mathrm{W}$$

But $-\log[H_3O^+] = \mathrm{pH}$, $-\log[OH^-] = \mathrm{pOH}$ and $-\log K_w = \mathrm{p}K_w$.

Therefore:

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_\mathrm{w}$$

where **pK_w** is the negative logarithm of K_w. At 25.0 °C, $K_w = 1.0 \times 10^{-14}$ and therefore this becomes:

$$\mathrm{pH} + \mathrm{pOH} = 14$$

Note that this equation applies only at 25.0 °C and we will assume this temperature in calculations throughout this chapter. Because pH and pOH are related by such a simple expression, it is usual to talk almost exclusively in terms of the pH of a solution, and pOH is rarely used.

It should be noted that our definition of pH:

$$pH = -\log[H_3O^+]$$

is an approximation. The exact definition involves the use of activity (*a*), a concept we have met briefly in chapter 9 (p. 353), rather than concentration, and is written as:

$$pH = -\log a_{H_3O^+}$$

However, provided that we work under dilute conditions, concentration is an acceptable approximation to activity, and we will use the equation pH = -log[H_3O^+] throughout the rest of the book.

Worked examples 11.4, 11.5 and 11.6 illustrate the types of problems you may encounter concerning the manipulations of pH, pOH, [H_3O^+] and [OH^-].

WORKED EXAMPLE 11.4

Calculating pH and pOH from [H_3O^+]

The dune lakes on Fraser Island, off the Queensland coast, are appreciably acidic due to the presence of natural organic acids from plant material. The water in Lake Barga (figure 11.3), the most acidic lake, was found to have an H_3O^+ concentration of 7.1×10^{-5} M at 25 °C. What are the pH and pOH values of the lake's water?



FIGURE 11.3 Lake Barga, the most acidic lake on Fraser Island, Queensland.

Analysis

If we know the value of $[H_3O^+]$, we can use $pH = -\log[H_3O^+]$ to find the pH.

Solution

$$pH = -\log[H_3O^+]$$

We substitute $[H_3O^+] = 7.1 \times 10^{-5}$ M into this expression to give:

$$pH = -\log(7.1 \times 10^{-5})$$

We first take the logarithm of this number and then take the negative of the logarithm. Using a calculator to find the logarithm of 7.1×10^{-5} gives the value - 4.15 (note the negative sign). To find the pH, we change its algebraic sign.

$$pH = -(-4.5) = 4.15$$

Once we know the pH, the pOH is easily found by using the equation pH + pOH = 14.00 at 25 °C. Therefore, the pOH of the lake water is:

$$\begin{aligned} pOH &= 14.00 - 4.15 \\ &= 9.85 \end{aligned}$$

Is our answer reasonable?

The value of $[H_3O^+]$ is between 1×10^{-5} and 1×10^{-4}, so the pH has to be between 5 and 4 (the antilogarithms of 1×10^{-5} and 1×10^{-4}, respectively), which it is. Therefore, the pOH must be between 9 and 10, as it is.

PRACTICE EXERCISE 11.5

A soft drink has a H_3O^+ concentration of 3.67×10^{-4} mol L^{-1}. What are the pH and pOH values of this drink? Is it acidic, basic or neutral?

WORKED EXAMPLE 11.5

Calculating pH from $[OH^-]$

What is the pH of a sodium hydroxide solution at 25 °C in which the hydroxide ion concentration is 0.0026 M?

Analysis

There are two ways to solve this problem. We could use the K_w expression:

$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$$

and the given value of the hydroxide ion concentration to find $[H_3O^+]$ and then calculate the pH using $pH = -\log[H_3O^+]$.

The second way is to calculate the pOH from the hydroxide ion concentration ($pOH = -\log[OH^-]$) and then subtract the pOH from 14.00 to find the pH. While both methods are valid and give the same answer, the second path requires less effort, so let's proceed that way.

Solution

We use the equation:

$$pOH = -\log[OH^-]$$

and substitute $[OH^-] = 0.0026$ M into this to give:

$$pOH = -\log(0.0026)$$

Taking the logarithm gives -2.59. Therefore:

$$pOH = -(-2.59) = (2.59)$$

Then we subtract this pOH value from 14.00 to find the pH.

$$\begin{aligned} pH &= 14.00 - 2.59 \\ &= 11.41 \end{aligned}$$

Notice that the pH in this basic solution is well above 7.

Is our answer reasonable?

The molar concentration of the hydroxide ion is between 1×10^{-3} and 1×10^{-2}, so the pOH must be between 3 and 2 (the antilogarithms of 1×10^{-3} and 1×10^{-2}, respectively) which it is. Thus, the pH should be between 11 and 12.

PRACTICE EXERCISE 11.6

The concentration of OH^- in the water in which a soil sample has soaked overnight is 1.47×10^{-9} mol L^{-1}. What is the pH of the solution?

WORKED EXAMPLE 11.6

Calculating $[H_3O^+]$ from pH

'Calcareous soil' is soil rich in calcium carbonate and is particularly abundant along the south coast of Australia. The pH of the moisture in such soil generally ranges from just over 7 to as high as 8.3. After one particular soil sample was soaked in water, the pH of the water was measured to be 8.14. What value of $[H_3O^+]$ corresponds to a pH of 8.14? Is the soil acidic or basic?

Analysis

The equation we use to calculate $[H_3O^+]$ from pH is $[H_3O^+] = 10^{-pH}$.

Solution

We substitute the pH value, 8.14, into the equation above, which gives:

$$[H_3O^+] = 10^{-8.14}$$

We therefore need to calculate 10 to the power of -8.14. The easiest way to do this on a calculator is to press the '10^x' key and then enter -8.14. (Note that, on some calculators, you may have to do these in the opposite order.) Because the pH has two digits following the decimal point, we obtain two significant figures in the H_3O^+ concentration. Therefore, the answer, correctly rounded, is:

$$[H_3O^+] = 7.2 \times 10^{-9}\ \text{M}$$

Because pH > 7 and $[H_3O^+] < 1 \times 10^{-7}$ M, the soil is basic.

Is our answer reasonable?

The given pH value of 8.14 is between 8 and 9, so the H_3O^+ concentration must lie between 10^{-8} and 10^{-9} mol L^{-1}, as we found.

PRACTICE EXERCISE 11.7

Find the values of $[H_3O^+]$ and $[OH^-]$ that correspond to each of the following pH values. State whether each solution is acidic or basic.

(a) 2.30 (the approximate pH of lemon juice)

(b) 3.85 (the approximate pH of sauerkraut)

(c) 10.81 (the pH of milk of magnesia, a laxative and an antacid)

(d) 3.50 (the pH of orange juice, on average)

(e) 11.61 (the pH of dilute, household ammonia)

The pH scale ranges from 0 to 14 for most practical applications, although negative values of pH can be obtained in very acidic solutions and pH values greater than 14 occur in concentrated aqueous bases. A 0.10 mol L^{-1} solution of HCl(aq) has a pH of 1.00, while a 0.10 mol L^{-1} solution of NaOH(aq) has a pH of 13.00. Figure 11.4 shows the pH values of some common aqueous solutions. Accurate pH values (±0.01 pH units) can be easily determined with a pH meter, which uses a glass electrode that is sensitive to H_3O^+ ions (see figure 11.5). Less accurate values can be obtained using pH paper (figure 11.6), while blue and red litmus paper is used only in a qualitative manner to determine whether a solution is acidic or basic.

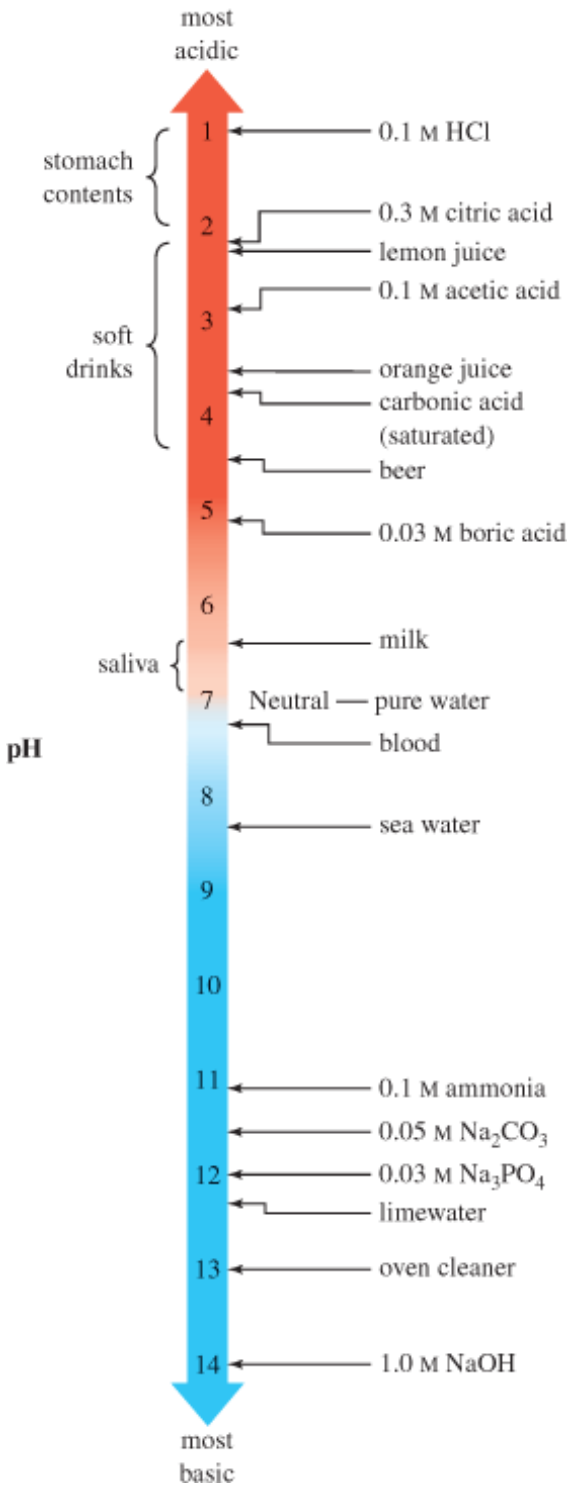

most acidic
1
2
3
4
5
6
7
8
9
10
11
12
13
14
most basic
pH
stomach contents
soft drinks
saliva
0.1 M HCl
0.3 M citric acid
lemon juice
0.1 M acetic acid
orange juice
carbonic acid (saturated)
beer
0.03 M boric acid
milk
Neutral — pure water
blood
sea water
0.1 M ammonia
0.05 M Na_2CO_3
0.03 M Na_3PO_4
limewater
oven cleaner
1.0 M NaOH

FIGURE 11.4 The pH scale.
Airphoto Australia/Peter Harrison



FIGURE 11.5 A pH meter has a special combination electrode that is sensitive to hydrogen ion concentration. After the instrument has been calibrated using solutions of known pH, the electrode is dipped into the solution to be tested and the pH is read from the meter. The pH meter detects the difference between the H_3O^+ concentrations in the tested solution and the solution inside the electrode as a voltage, which is then converted to a pH value.
Charles D Winters



FIGURE 11.6 A pH test paper. The colour of this Hydrion® test strip changed to green when a drop of the orange juice was placed on it. According to the colour code, the pH of the juice is approximately 3.

The Strength of Acids and Bases

We stated previously that the pH of a 0.10 M solution of HCl(aq) is 1.00. This means that $[H_3O^+]$ in this solution is 0.10 M and, therefore, implies that the reaction:

$$HCl(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

proceeds to completion; in other words, HCl is completely dissociated in water. However, if we measure the pH of a 0.10 M aqueous solution of the seemingly similar acid HF, we find that it is not 1.00 but 2.10. You can show therefore that $[H_3O^+]$ in the HF solution is not 0.10 M, but 7.9×10^{-3} M, and this means that the reaction:

$$HF(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

does not proceed to completion. In fact, at any particular time, only about 1 in 13 molecules of HF have reacted with water to form H_3O^+ and F^-, with the majority remaining undissociated. We find a similar situation with a 0.10 M aqueous solution of acetic acid, CH_3COOH. The measured pH of this solution is again not 1.00 but 2.88, which corresponds to $[H_3O^+] = 1.3 \times 10^{-3}$ M and again means that the equilibrium:

$$CH_3COOH(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

lies very much towards the reactants. Obviously there is a fundamental difference between HCl and both HF and CH_3COOH. HCl is able to transfer its proton completely to water, while HF and CH_3COOH are very poor proton donors towards water. This means they exist predominantly as molecules in aqueous solution, with the result being a low concentration of ions in solution. This can be illustrated using conductivity, the concept we used to open this chapter (p. 427). Figure 11.7 shows the different conductivities of aqueous solutions containing HCl and CH_3COOH. This behaviour shows the different strengths of the acids. We say that HCl is a **strong acid**, whereas both HF and CH_3COOH are **weak acids**. A general definition of these terms is as follows:

- A strong acid reacts completely with water to give quantitative formation of H_3O^+.
- A weak acid reacts incompletely with water to form less than stoichiometric amounts of H_3O^+.

There are analogous definitions for bases:

- A **strong base** reacts completely with water to give quantitative formation of OH^-.
- A **weak base** reacts incompletely with water to form less than stoichiometric amounts of OH^-.

Note that these definitions strictly apply only to Brønsted-Lowry acids in aqueous solution.

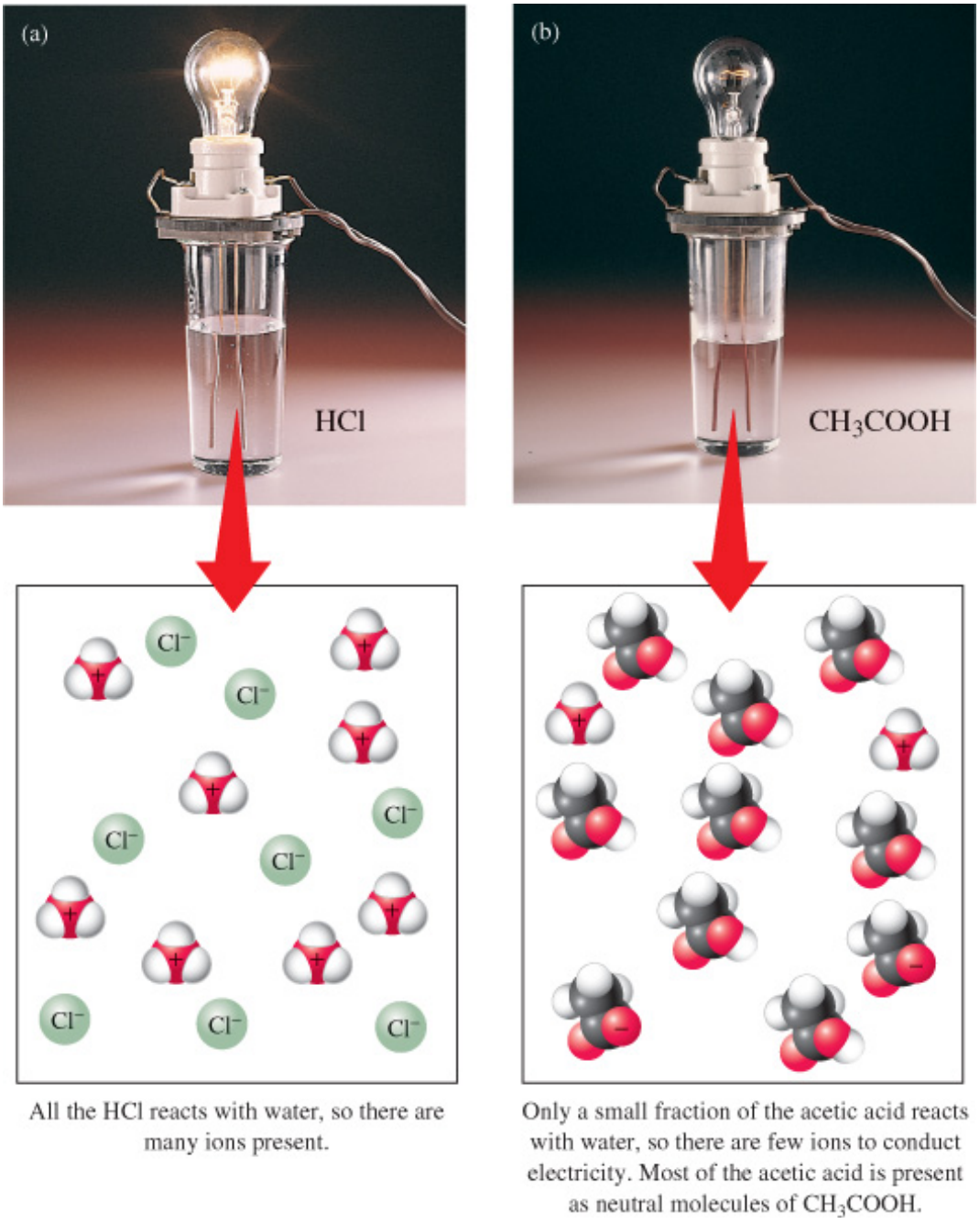


FIGURE 11.7 Electrical conductivity of solutions of strong and weak acids at equal concentrations. The wires lead to a battery (not shown), which provides electrical power to light the bulb:

(a) HCl reacts completely with water to give H_3O^+ and Cl^-, resulting in high conductivity, thus enabling the light to glow brightly.

(b) CH_3COOH reacts with water to give only very small amounts of H_3O^+ and CH_3COO^-, so the light is dimmer.

Michael Watson

The use of the words ‘strong’ and ‘weak’ is somewhat unfortunate, as it implies that there is a distinct cut-off point between strong and weak acids. This is not the case. Our definition of strong acids and bases implies that they are completely dissociated in water and should therefore have comparable strengths — this is true only if we restrict ourselves to relatively dilute aqueous solutions. However, weak acids and bases show an enormous range of strengths in aqueous solution; rather than relying on the qualitative concept ‘weak’ to describe their behaviour, it is more informative to quantify their ability to either donate or accept a proton by looking at the value of the equilibrium constant for their reaction with water, and we do this in section 11.4 (p. 443). We will

first look at the nature of strong acids and bases in aqueous solution.

Chemical Connections

Swimming Pools and Soil

Swimming pools and soil are just two examples of many situations where pH is important. The water in swimming pools is more than just water; it is a dilute solution of compounds that prevent the growth of bacteria and stabilise the pool lining while allowing us to swim safely in the pool. The pH of a swimming pool should be between 7.2 and 7.6.

The pH can also affect the availability of substances that plants need for growth (figure 11.8). A pH of 6 to 7 is best for most plants; most nutrients are more soluble when the soil is slightly acidic than when it is neutral or slightly basic. If the soil pH is too high, metal ions that plants need, such as iron and manganese, will precipitate and not be available in the ground water. A very low pH is not good either; if the pH drops to 4–5, metal ions such as aluminium, that are toxic to many plants, are released as their compounds become more soluble. A low pH also in hibits the growth of beneficial bacteria that decompose organic matter in the soil to release nutrients, especially nitrogen.



FIGURE 11.8 Hydrangeas grown in acidic soil have blue flowers (left), while those grown in alkaline soils have pink/red flowers (right).

It is important to be able to measure the pH of these systems. Commercial pH test kits use acid–base indicators. Kits for testing the pH of pool water (figure 11.9) use phenol red indicator, which changes colour over the pH range of 6.4–8.2.



FIGURE 11.9 Swimming pool test kit. This apparatus is used to test both pH and chlorine concentration. The colour of the indicator tells us that the pH of the pool water is approximately 7.6, which is slightly basic.

This places the intermediate colour of the indicator within the desired range of 7.2–7.6. To use the kit, we pour some pool water into the plastic cylinder and add five drops of the indicator solution. We then shake the mixture until it is homogeneous and compare the colour with the standards to estimate the pH. The colour that most closely matches that of the solution gives the approximate pH. We can then decide whether the pH should be adjusted by addition of particular compounds. Similar test kits are available for water in an aquarium, except that the indicator used is bromothymol blue, which changes colour over a pH range of 6.0–7.6. This matches the desired pH range for such water.

Soil test kits (figure 11.10) use a ‘universal indicator’, which is a mixture of indicators that enable estimation of pH over a wide range.



FIGURE 11.10 Testing soil pH. The indicator reveals that the soil sample being tested has a pH of approximately 6.5, which is slightly acidic.
Geoff Kidd

To use the kit, we put a sample of the soil in the plastic apparatus provided and then add water, along with a tablet of the indicator. We shake the mixture and compare the colour of the water with the colour chart.

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11.3 Strong Acids and Bases

We have defined a strong acid as an acid that donates a proton completely to water. Using this definition, for any strong acid HA, the reaction:

$$HA(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

proceeds to completion. Similarly, our definition of a strong base says that OH^- is formed quantitatively on reaction with water, and therefore the reaction of any strong base B with water:

$$B(aq) + H_2O(1) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

should also proceed to completion.

A list of some strong acids and bases is given in table 11.3.

TABLE 11.3 Examples of strong acids and bases

Strong acids[(a)]	Strong bases
$HClO_4$ ($HOClO_3$), perchloric acid	LiOH, lithium hydroxide
HCl, hydrochloric acid	NaOH, sodium hydroxide
HBr, hydrobromic acid	KOH, potassium hydroxide
HI, hydroiodic acid	$Ca(OH)_2$, calcium hydroxide
HNO_3 ($HONO_2$), nitric acid	RbOH, rubidium hydroxide
H_2SO_4 ($(HO)_2SO_2$), sulfuric acid	$NaOCH_3$, sodium methoxide
HCF_3SO_3 ($HOSO_2CF_3$), trifluoromethanesulfonic acid	CsOH, caesium hydroxide

(a) The molecular formulae of the acids in parentheses emphasise the actual structure of each acid; note that the acidic proton is attached to an O atom in all cases.

The fact that strong acids undergo complete dissociation tells us something about the basicity of their conjugate bases. For example, the equilibrium:

$$HCl(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

lies almost completely to the right-hand side, and therefore the reverse reaction occurs to only a negligible extent. This means that Cl^-, the conjugate base of HCl, does not readily accept a proton from H_3O^+, and consequently Cl^- must be a very weak base. Such behaviour is common to all strong acids and we can make the generalisation that *the conjugate base of a strong acid is very weak*. We will investigate this concept further when we discuss weak acids and bases (section 11.4). We should also note that H_3O^+ is the strongest acid and OH^- is the strongest base that can exist in aqueous solution. We have already seen that the strong acid HCl donates its proton almost completely to water to form H_3O^+, and the same is true of all acids stronger than H_3O^+; they react completely when dissolved in water to form H_3O^+ and none of the undissociated acid is present. Likewise, any base stronger than OH^- will, when dissolved in water, quantitatively deprotonate water to give OH^-. Hence, there are limits to the range of acidities and basicities that can be accessed in water and, if we want to go beyond these limits, we must use a different solvent.

pH Calculations in Solutions of Strong Acids and Bases

As strong acids and bases react with water almost completely, the calculation of pH in solutions containing strong acids or bases is a relatively straightforward exercise in stoichiometry.

When the solute in an aqueous solution is a strong monoprotic acid, such as HCl or HNO_3, we expect to obtain 1 mole of H_3O^+ for every mole of the acid in the solution. Thus, a 1.0×10^{-2} M solution of HCl contains 1.0×10^{-2} mol L^{-1} of H_3O^+, and a 2.0×10^{-3} M solution of HNO_3 contains 2.0×10^{-3} mol L^{-1} of H_3O^+.

To calculate the pH of a solution of a strong monoprotic acid, we use $[H_3O^+]$ obtained from the stated molar concentration of the acid. Thus, the 1.0×10^{-2} M HCl solution mentioned above has $[H_3O^+] = 1.0 \times 10^{-2}$ M, and therefore the pH = $-\log[H_3O^+] = -\log(1.0 \times 10^{-2}) = 2.00$.

For strong bases, calculating the pH from the OH^- concentration is similarly straight forward. A 5.0×10^{-2} M solution of NaOH contains 5.0×10^{-2} mol L^{-1} of OH^- because the base is fully dissociated and each mole of NaOH releases 1 mole of OH^- when it dissociates. Therefore, pOH = $-\log(5.0 \times 10^{-2}) = 1.30$, and pH = 14.00 - 1.30 = 12.70 at 25 °C.

For bases such as $Ba(OH)_2$, we have to recognise that 2 moles of OH^- are released by each mole of the base.

$$Ba(OH)_2(s) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

Therefore, if a solution contained 1.0×10^{-2} mol $Ba(OH)_2$ per litre, the concentration of OH^-would be 2.0×10^{-2} M. Of course, once we know the OH^- concentration we can calculate pOH, from which we can calculate the pH. Worked example 11.7 illustrates the kinds of calculations we have just described.

WORKED EXAMPLE 11.7

Calculating pH, pOH, $[H_3O^+]$ and $[OH^-]$ for aqueous solutions of strong acids or bases

Calculate the pH, pOH, $[H_3O^+]$ and $[OH^-]$ of the following solutions at 25 °C: (a) 2.0×10^{-2} M HCl and (b) 3.5×10^{-4} M $Ba(OH)_2$. HCl is a strong acid and $Ba(OH)_2$ is a strong base.

Analysis

The solute in (a) is HCl, a strong acid. It gives quantitative formation of H_3O^+ and therefore the reaction:

$$HCl(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

proceeds to completion. From each mole of HCl, we expect 1 mole of H_3O^+, so we can use

the molar concentration of HCl to obtain $[H_3O^+]$, from which we can calculate the pH, pOH and $[OH^-]$.

The solute in (b) is $Ba(OH)_2$, a strong base. From each mole of $Ba(OH)_2$, 2 moles of OH^- are liberated, according to the equation:

$$Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2OH^-(aq)$$

and this proceeds to completion. We use the molarity of $Ba(OH)_2$ to calculate the hydroxide ion concentration. From $[OH^-]$ we can calculate $[H_3O^+]$, pOH and pH.

Solution

(a) Because HCl is completely dissociated, in 2.0×10^{-2} M HCl, $[H_3O^+] = 2.0 \times 10^{-2}$ M. Therefore:

$$pH = -\log[H_3O^-] = -\log(2.0 \times 10^{-2}) = 1.70$$

Thus, in 2.0×10^{-2} M HCl, the pH is 1.70. The pOH is (14.00 - 1.70) = 12.30. To find $[OH^-]$, we can use this value of pOH.

$$[OH^-] = 10^{-pOH} = 10^{-12.30} = 5.0 \times 10^{-13}\ M$$

Notice how much smaller $[OH^-]$ is in this acidic solution than it is in pure water. This makes sense because the solution is quite acidic.

(b) As noted, $Ba(OH)_2$ is a strong base, and so for each mole of $Ba(OH)_2$ we obtain 2 moles of OH^-. Therefore:

$$[OH^-] = 2 \times (3.5 \times 10.4^{-4})\ M = 7.0 \times 10^{-4}\ M$$
$$pOH = -\log[OH^-] = -\log(7.0 \times 10^{-4}) = 3.15$$

Thus the pOH of this solution is 3.15, and the pH = (14.00 - 3.15) = 10.85. We can then obtain $[H_3O^+]$ from the equation:

$$[H_3O^+] = 10^{-pH}$$
$$= 10^{-10.85} = 1.4 \times 10^{-11}\ M$$

We would expect the concentration of H_3O^+ to be very low because the solution is quite basic.

Is our answer reasonable?

In (a), the concentration of H_3O^+ is between 10^{-2} M and 10^{-1} M and so the pH must be between 1 and 2, as we found. In (b), the molarity of OH^- is between 10^{-4} M and 10^{-3} M. Hence, the pOH must be between 3 and 4, which it is.

PRACTICE EXERCISE 11.8

Calculate $[H_3O^+]$ and the pH of an aqueous

5.0×10^{-3} M NaOH solution.

PRACTICE EXERCISE 11.9

Rhododendrons are shrubs that produce beautiful flowers in spring. They grow well only in soil with a pH of 5.5 or slightly lower. What is the H_3O^+ concentration in the soil moisture if the pH is 5.5?

Suppression of the Autoprotolysis of Water

In the preceding calculations, we have assumed that all of the H_3O^+ or OH^- in the solutions of strong acid or base comes from the acid or the base respectively. However, there is another potential source of both H_3O^+ and OH^- in an aqueous solution, namely water. We have seen that the autoprotolysis of water gives rise to low concentrations of H_3O^+ and OH^-, and we will now show the conditions under which we are justified in neglecting these contributions. We will consider only a solution of strong acid, but realise that analogous arguments apply for a solution of a strong base.

In an aqueous solution of any acid, there are two sources of H_3O^+; the acid itself, and water. Thus,

$$[H_3O^+]_{\text{total}} = [H_3O^+]_{\text{from acid}} + [H_3O^+]_{\text{from } H_2O}$$

Except in *very* dilute solutions of strong acids, the amount of H_3O^+ contributed by water ($[H_3O^+]_{\text{from } H_2O}$) is negligible compared with the amount of H_3O^+ from the acid ($[H_3O^+]_{\text{from acid}}$). For instance, in worked example 11.7 we saw that in 2.0×10^{-2} M HCl the $[OH^-]$ was 5.0×10^{-13} M. The only source of OH^- in this acidic solution is from the autoprotolysis of water, and the amounts of OH^- and H_3O^+ formed by the autoprotolysis of water must be equal. Therefore, $[H_3O^+]$ from H_2O also equals 5.0×10^{-13} M. If we now look at the total $[H_3O^+]$ for this solution, we have:

$$\begin{aligned}[H_3O^+]_{\text{total}} &= \underset{\text{(from HCl)}}{2.0 \times 10^{-2}\ \text{M}} + \underset{\text{(from } H_2O\text{)}}{5.0 \times 10^{-13}\ \text{M}} \\ &= 2.0 \times 10^{-2}\ \text{M (rounded correctly)}\end{aligned}$$

In any solution of an acid, the autoprotolysis of water is suppressed by the H_3O^+ produced by the acid. This is a demonstration of the common ion effect we first discussed in chapter 10 (p. 404); in this case, H_3O^+ is the common ion, and the large excess of H_3O^+ from the acid suppresses the autoprotolysis of water.

We can rationalise this by considering the autoprotolysis equilibrium of water.

$$H_2O(1) + H_2O(1) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

If we add another source of H_3O^+ to water, we instantaneously increase the reaction quotient Q_w (where

$Q_w = [H_3O^+][OH^-]$), so that $Q_w > K_w$. Therefore, the equilibrium shifts towards the reactants to decrease Q_w, resulting in lower amounts of both H_3O^+ and OH^- *from the autoprotolysis of water*. Similar reasoning also applies to the addition of another source of OH^- to water. Therefore, addition of either H_3O^+ or OH^- to water suppresses the autoprotolysis of water. The maximum possible contribution of $[H_3O^+]$ or $[OH^-]$ from the autoprotolysis of water is 1.0×10^{-7} M at 25.0 °C, and, in most cases, especially when strong acids or bases are involved, this can be safely ignored. However, as shown in worked example 11.8, there are exceptions.

WORKED EXAMPLE 11.8

Calculating the pH of *Very* Dilute Strong Acid Solutions

Calculate the pH of a 1.0×10^{-10} M solution of HCl(aq).

Analysis

At first glance, this appears a simple matter of equating $[H_3O^+]$ to the concentration of the acid, as we have done in previous examples concerning strong acid solutions. However, if we do this, we obtain a pH of 10, which is obviously incorrect as it would mean that the solution of HCl is basic! In this case, we need to take *both* possible sources of H_3O^+ into account — HCl and H_2O — and see which one, if any, dominates.

Solution

We start by calculating the contribution of H_3O^+ from both water and HCl. We know that the HCl solution is 1.0×10^{-10} M, and therefore:

$$[H_3O^+]_{\text{from HCl}} = 1.0 \times 10^{-10}\ \text{M}$$

Ordinarily, the addition of acid to water would suppress the autoprotolysis of water through the common ion effect (H_3O^+ is the common ion), meaning that the contribution of H_3O^+ from this would be less than 1.0×10^{-7} M. However, in this case, the concentration of acid is very small compared with that resulting from the autoprotolysis of water, and we can therefore say, to a very good approximation:

$$[H_3O^+]_{\text{from } H_2O} = 1.0 \times 10^{-7}\ \text{M}$$

Hence:

$$\begin{aligned} \left[H_3O^+\right]_{\text{total}} &= 1.0 \times 10^{-7}\ \text{M} + 1.0 \times 10^{-10}\ \text{M} \\ &= 1.0 \times 10^{-7}\ \text{M (rounded correctly)} \end{aligned}$$

and the calculated pH becomes:

$$\begin{aligned} \text{pH} &= -\log\left[H_3O^+\right] \\ &= -\log(1.0 \times 10^{-7}) = 7.00 \end{aligned}$$

Is our answer reasonable?

A pH of 7 is certainly much more reasonable than a pH of 10. The strong acid is so dilute that, in this case, water is the major contributor of H_3O^+ to the solution.

PRACTICE EXERCISE 11.10

Calculate the pH of a 1.0×10^{-11} M solution of NaOH.

From now on, we assume that, except for *very* dilute solutions (10^{-6} M or less), the autoprotolysis of water can be neglected when calculating the pH of strong acids or bases.

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11.4 Weak Acids and Bases

Earlier in this chapter (p. 438), we stated that weak acids and weak bases react incompletely with water to give less than stoichiometric amounts of H_3O^+ and OH^- respectively. We can quantify the extent to which these reactions occur by looking at the values of their equilibrium constants. If we consider a weak monoprotic acid HA, we can write its reaction with water as:

$$HA(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

The equilibrium constant expression for this is therefore:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The equilibrium constant for the dissociation of an acid in aqueous solution is called the **acidity constant** and is given the symbol K_a. We can see that the value of K_a tells us how far the reaction has proceeded towards completion when equilibrium is established.

Similarly, we can write the equation for the reaction of a weak monoprotic base B with water as:

$$B(aq) + H_2O(1) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

and the corresponding equilibrium constant expression is:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

This is called the **basicity constant** and is given the symbol K_b.

When polyprotic acids or bases are considered, a separate equilibrium constant must be written for each proton loss or proton gain. For example, the diprotic acid H_2A will undergo two separate proton loss reactions in water, one involving H_2A and the other involving its conjugate base, HA^-. This gives rise to two separate K_a expressions.

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+ \quad K_{a1}\frac{[H_3O^+][HA^-]}{[H_2A]}$$

$$HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+ \quad K_{a2}\frac{[H_3O^+][A^{2-}]}{[HA^-]}$$

Analogous K_b expressions can be written for a polyprotic base.

Because weak acids and weak bases react with water only to a very small extent, both K_a and K_b values are generally significantly less than 1. For example, K_a for acetic acid is 1.8×10^{-5}, while K_b for pyridine is 1.7×10^{-9}. To put these values in perspective, it is again instructive (as we did in chapter 9) to write these numbers in an alternative form — for example, knowing that $10^{-5} = \frac{1}{10^5}$, we can write K_a for acetic acid as:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} = \frac{1.8}{10^5}$$

When written in this fashion, it is evident that the concentrations on the top line are *much* smaller than the concentration on the bottom. In other words, the concentration of undissociated acid at equilibrium is enormous compared with $[H_3O^+]$ and $[CH_3COO^-]$. This means that acetic acid is indeed a weak acid.

A similar approach can be used to emphasise the weakly basic nature of pyridine.

Because K_a and K_b values are usually significantly less than 1, it is often more convenient to use **pK_a** and **pK_b** values, where:

$$pK_a = -\log K_a$$
$$pK_b = -\log K_b$$

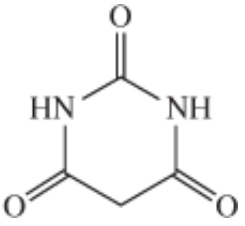
Both pK_a and pK_b are analogous to pH, and the defining equations are therefore similar. We can also write each equation in terms of K_a and K_b respectively, and these then become:

$$K_a = 10^{-pK_a}$$
$$K_b = 10^{-pK_b}$$

Note that polyprotic acids and bases have more than one pK_a or pK_b value.

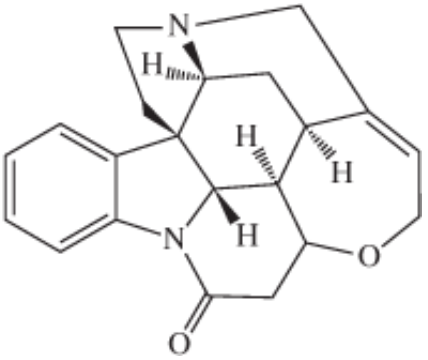
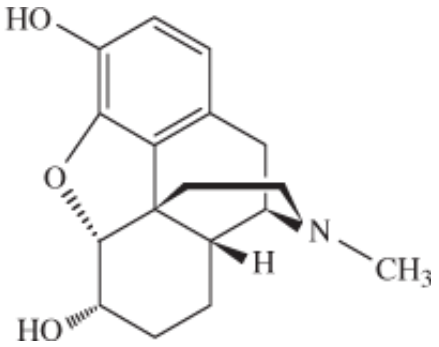
The strength of a weak acid is determined by its K_a value: the larger the K_a, the stronger the acid and the greater the degree of dissociation at equilibrium. Because of the negative sign in the defining equation for pK_a, the stronger the acid, the *smaller* is its pK_a value. The values of K_a and pK_a for some typical weak acids are given in table 11.4. A more complete list is located in appendix E. Similar arguments apply to K_b and pK_b values, some of which are given in table 11.5.

TABLE 11.4 K_a and pK_a values for weak monoprotic acids at 25 °C

Name of acid	Formula	K_a	pK_a
chloroacetic acid	$ClCH_2COOH$	1.4×10^{-3}	2.85
nitrous acid	HNO_2	7.1×10^{-4}	3.15
hydrofluoric acid	HF	6.8×10^{-4}	3.17
cyanic acid	HOCN	3.5×10^{-4}	3.46
formic acid	HCOOH	1.8×10^{-4}	3.74
barbituric acid	$C_4H_4N_2O_3$ 	9.8×10^{-5}	4.01
acetic acid	CH_3COOH	1.8×10^{-5}	4.74
hydrazoic acid	HN_3	1.8×10^{-5}	4.74
butanoic acid	$CH_3CH_2CH_2COOH$	1.5×10^{-5}	4.82
propanoic acid	CH_3CH_2COOH	1.4×10^{-5}	4.89
hypochlorous acid	HOCl	3.0×10^{-8}	7.52
hydrogen cyanide (aq)	HCN	6.2×10^{-10}	9.21
phenol	C_6H_5OH	1.3×10^{-10}	9.89
hydrogen peroxide			11.74

	H_2O_2	1.8×10^{-12}

TABLE 11.5 K_b and pK_b values for weak molecular bases at 25 °C

Name of base	Formula	K_b	pK_b
butylamine	$C_4H_9NH_2$	5.9×10^{-4}	3.23
methylamine	CH_3NH_2	4.4×10^{-4}	3.36
ammonia	NH_3	1.8×10^{-5}	4.74
hydrazine	N_2H_4	1.7×10^{-6}	5.77
strychnine	$C_{21}H_{22}N_2O_2$ 	1.0×10^{-6}	6.00
morphine	$C_{17}H_{19}NO_3$ 	7.5×10^{-7}	6.13
hydroxylamine	$HONH_2$	6.6×10^{-9}	8.18
pyridine	C_5H_5N	1.7×10^{-9}	8.77
aniline	$C_6H_5NH_2$	4.1×10^{-10}	9.36

WORKED EXAMPLE 11.9

Interpreting pK_a and Finding K_a

A certain acid was found to have a pK_a of 4.88. Is this acid stronger or weaker than acetic acid? What is the K_a for the acid?

Analysis

We can compare the acid strengths by comparing the pK_a values. The larger the pK_a, the

weaker is the acid. Finding K_a from pK_a involves the same kind of calculation as finding $[H_3O^+]$ from pH, which you learned to do earlier in this chapter.

Solution

From table 11.4, the pK_a of acetic acid is 4.74. The acid referred to in the problem has a pK_a of 4.88. Because the acid has a larger pK_a than acetic acid, it is a weaker acid.

To find K_a from pK_a, we use the equation:

$$K_a = 10^{-pK_a}$$

Substituting pK_a = 4.88:

$$K_a = 10^{-4.88} = 1.3 \times 10^{-5}$$

Is our answer reasonable?

As a quick check, we can compare the K_a values. For acetic acid, $K_a = 1.8 \times 10^{-5}$. This is larger than 1.3×10^{-5}, which tells us that acetic acid is the stronger acid. This agrees with our con clusion based on the pK_a values.

PRACTICE EXERCISE 11.11

Two acids, HX and HY, have pK_a values of 3.16 and 4.14, respectively. Which is the stronger acid? What are the K_a values for these acids?

Some molecules contain both an acidic site and a basic site, and this leads to interesting structural consequences. Consider, for example, the amino acid glycine. We would usually write the condensed structural formula of this molecule as NH_2CH_2COOH. However, it actually exists in the solid state as a **zwitterion**, a structure which contains both a positive and negative charge but which is overall neutral.



We will discuss such compounds in more detail in chapter 24.

We learned in chapter 9 how to manipulate equilibrium constant expressions and found that, when two chemical equations were added together, the equilibrium constant for the resulting equation was equal to the product of the equilibrium constants for the two reactions. This approach leads to an important result when applied to an acid and its conjugate base. Consider, for example, formic acid, HCOOH, a weak acid partly responsible for the sting of some ants (the word *formica* is Latin for 'ant'). The acid reacts with water according to the equation:

$$HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$

for which:

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

The conjugate base of formic acid, the formate ion, $HCOO^-$, reacts with water as follows:

$$HCOO^-(aq) + H_2O(1) \rightleftharpoons HCOOH(aq) + OH^-(aq)$$

and hence:

$$K_b = \frac{[HCOOH][OH^-]}{[HCOO^-]}$$

If we add these equations, we obtain the equation for the autoprotolysis of water.

$$\begin{array}{l} HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq) \\ HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq) \\ \hline H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \end{array}$$

If we multiply the expressions for K_a and K_b together, we obtain:

$$\frac{[H_3O^+][HCOO^-]}{[HCOOH]} \times \frac{[HCOOH][OH^-]}{[HCOO^-]} = [H_3O^+][OH^-] = K_w$$

or

$$K_aK_b = K_w$$

This relationship holds for *any* acid–base conjugate pair, regardless of the strength of the acid or base.

Another useful relationship can be derived by taking the negative logarithm of each side of $K_aK_b = K_w$ and remembering that the logarithm of the product of two numbers is the sum of their logarithms.

$$pK_a + pK_b = pK_w = 14.00 (\text{at } 25\ ^\circ C)$$

There are some important consequences of the relationship $K_aK_b = K_w$. One is that it is not necessary to tabulate both K_a and K_b for the members of an acid—base pair; if one K is known, the other can be calculated. For example, K_a for HCOOH and K_b for NH_3 are found in most tables of acid—base equilibrium constants, but these tables usually do not contain K_b for $HCOO^-$ or K_a for NH_4^+. If we need them, we can calculate them using $K_aK_b = K_w$.

PRACTICE EXERCISE 11.12

The value of K_a for HCOOH is 1.8×10^{-4}.

What is the K_b for the $HCOO^-$ ion?

Another interesting and useful observation is that *there is an inverse relationship between the strengths of the acid and base members of a conjugate pair*. This is illustrated graphically in figure 11.11. Because the product of K_a and K_b is a constant, the larger the value of K_a, the smaller the value of K_b. In other words, *the stronger the conjugate acid, the weaker its conjugate base*. Do not make the mistake of assuming that the conjugate base of a weak acid is strong. Inspection of figure 11.11 and use of the

relationship $pK_a + pK_b = 14.00$ show that, in fact, the conjugate base of a weak acid is weak. For example, the pK_a of acetic acid, a weak acid, is 4.74. Its conjugate base, the acetate ion, must therefore have a pK_b of (14.00 - 4.74) = 9.26, a value indicative of a weak base. Similar arguments apply for the conjugate acid of a weak base.

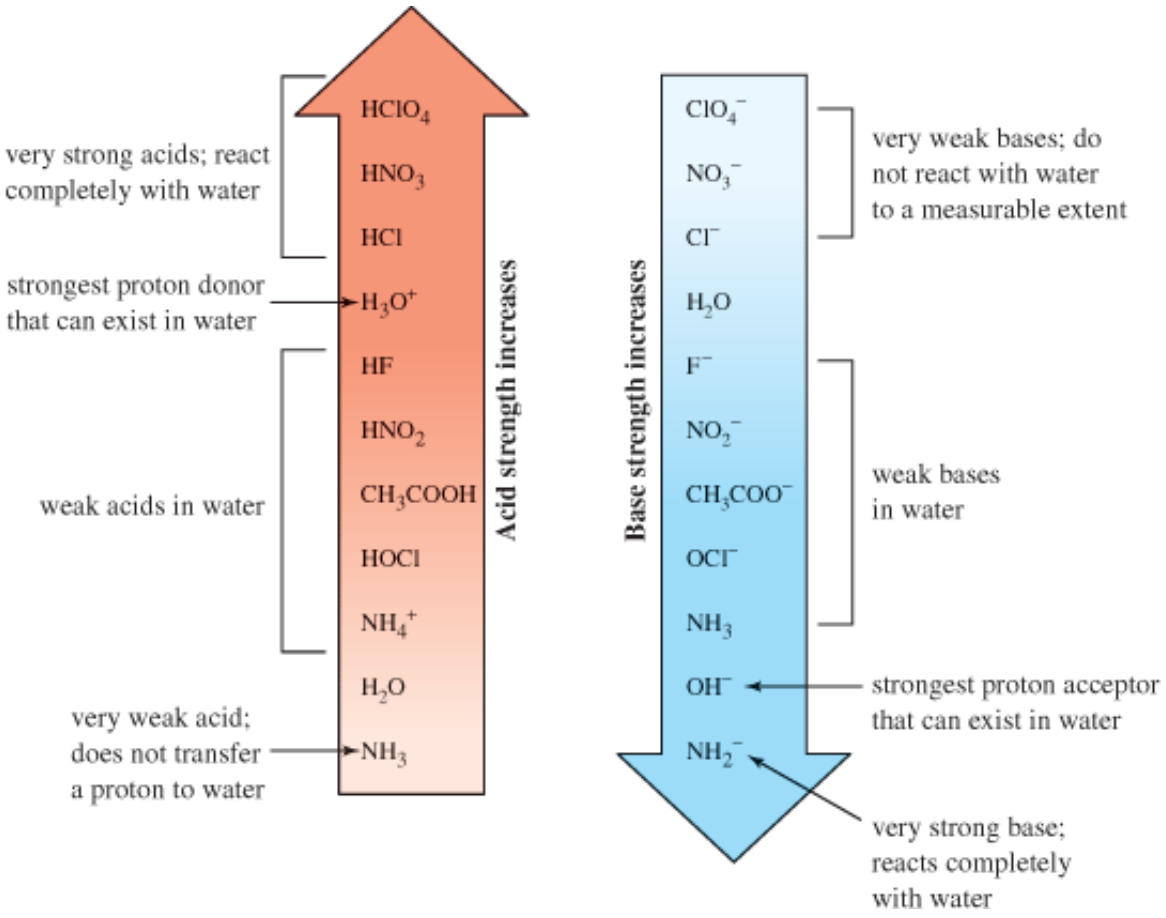


FIGURE 11.11 The relative strengths of conjugate acid–base pairs. The stronger the acid, the weaker its conjugate base. The weaker the acid, the stronger its conjugate base.

pH Calculations in Solutions of Weak Acids and Bases

In section 11.3, we learned how to calculate the pH of solutions of strong acids and bases. The calculations relied on the fact that, because strong acids and bases dissociate completely in water, the concentration of H_3O^+ or OH^- was equal to the initial concentration of the acid or base.

However, because weak acids and bases react incompletely with water, this is no longer the case. For weak acids and bases, we must use the value of K_a or K_b to determine $[H_3O^+]$ or $[OH^-]$ and hence pH. We will illustrate this by calculating the pH of a 1.0 M solution of acetic acid, CH_3COOH.

We begin by writing the balanced chemical equation for the reaction of the acid with water, and obtain the expression for K_a from this.

$$CH_3COOH(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \text{(from table 11.4)}$$

We cannot solve this equation for $[H_3O^+]$ directly in this form as there are two unknowns: $[CH_3COO^-]$

and [CH_3COOH]. The fact that these unknowns are related (the sum of [CH_3COO^-] and [CH_3COOH] must be 1.0 M, the initial concentration of the acid) allows the equation to be solved using arithmetic manipulations, but this involves solving a quadratic equation. However, it is usual to use a concentration table for calculations of this sort. We set this up in the same way as we did in chapter 9. We assume that the initial concentration of CH_3COOH is 1.0 M and the initial concentrations of both H_3O^+ and CH_3COO^- are 0. (Recall that there is a small nonzero concentration of H_3O^+ arising from the autoprotolysis of water, but we can safely neglect this as it is a maximum of 1.0. 10^{-7} M.) As the reaction proceeds to equilibrium, the concentration of CH_3COOH decreases by -*x*, and the concentrations of both H_3O^+ and CH_3COO^- increase by +*x*, owing to the stoichiometry of the reaction. At equilibrium, the concentrations of CH_3COOH, CH_3COO^- and H_3O^+ are (1.0 - *x*), *x* and *x*, respectively. Hence, we obtain the following concentration table (as in chapter 9, concentrations given in the question are highlighted).

	$H_2O + CH_3COOH \rightleftharpoons$	$H_3O^+ +$	CH_3COO^-
Initial concentration (mol L^{-1})	1.0	0	0
Change in concentration (mol L^{-1})	-*x*	+*x*	+*x*
Equilibrium concentration (mol L^{-1})	1.0 - *x*	*x*	*x*

When the values in the last row of the table are substituted into the expression for K_a we obtain:

$$K_a = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{1.0 - x} = 1.8 \times 10^{-5}$$

This equation involves a term in x^2, and it could be solved exactly using the quadratic formula. However, this and many other similar calculations involving weak acids and bases can be simplified. Recall from chapter 9 (p. 379) that, if the concentration from which *x* is subtracted is at least 400 times as large as *K*, we can make simplifying assumptions. In this case, the initial concentration of 1.0 M is indeed at least 400 times as large as K_a, 1.8×10^{-5}. Therefore, we can make the approximation (1.0 - *x*) ≈ 1.0. If we now replace 1.0 - *x* with 1.0 in the equation above, we obtain:

$$\frac{x^2}{1.0} = 1.8 \times 10^{-5}$$

We can now solve this directly:

$$x^2 = (1.0)(1.8 \times 10^{-15}) = 1.8 \times 10^{-5}$$
$$x = \sqrt{1.8 \times 10^{-15}} = 4.2 \times 10^{-3}\ \text{M}$$

We see that the value of *x* is indeed negligible compared with 1.0 M (i.e. if we subtract 4.2×10^{-3} M from 1.0 M and round correctly, we obtain 1.0 M). We also note that the same answer (to two significant figures) is obtained by solving the quadratic equation exactly, further justifying our assumption. This value corresponds to approximately 1 molecule in 240 of CH_3COOH being dissociated at equilibrium; CH_3COOH is indeed a weak acid. Having calculated *x*, and knowing that *x* = [H_3O^+] at equilibrium, we can find the pH of the solution by taking the negative logarithm of this number.

$$\text{pH} = -\log(4.2 \times 10^{-3}) = 2.38$$

Notice that when we make the approximation above, the initial concentration of the acid is used as if it were the equilibrium concentration. This approximation is valid when the equilibrium constant is small and the concentrations of the solutes are reasonably high — conditions that apply to most situations you will encounter. On pp. 454-6, we will discuss the conditions under which the approximation is not valid.

Recall also that we neglected any contribution of H_3O^+ from the autoprotolysis of water to the total $[H_3O^+]$ in the solution. We can show that this assumption is justified by looking at the magnitude of $[H_3O^+]$ due to the acid compared with $[H_3O^+]$ from water. The maximum possible $[H_3O^+]$ contributed by water is 1.0×10^{-7} M, and this will be smaller in reality owing to the common ion effect from the presence of the acid. Even if we compare the maximum possible $[H_3O^+]$ from water (1.0×10^{-7} M) with $[H_3O^+]$ from the acid (4.2×10^{-3} M), we see that it is negligibly small (4.2×10^{-3} M + 1.0×10^{-7} M = 4.2×10^{-3} M) and so our assumption is justified.

We will now look at some examples that illustrate typical weak acid and weak base equilibrium problems.

WORKED EXAMPLE 11.10

Calculating $[H_3O^+]$ and pH Values for a Solution of a Weak Acid from its K_a Value

Calcium propanoate, a compound used as a preservative in baked goods (figure 11.12), is a salt of the weak acid propanoic acid, CH_3CH_2COOH. A student planned an experiment that would use propanoic acid at a concentration of 0.10 M. Calculate the values of $[H_3O^+]$ and pH for this solution at 25 °C. For propanoic acid, $K_a = 1.4 \times 10^{-5}$ at 25 °C.

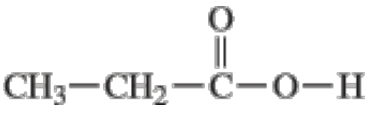




FIGURE 11.12 The calcium salt of propanoic acid, calcium propanoate, is used as a preservative in baked products.

Analysis

First, we write the balanced equation for the reaction of the acid with water and obtain the expression for K_a from this.

$$CH_3CH_2COOH(aq) + H_2O(1) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

The initial concentration of the acid is 0.10 M, and the initial concentrations of both ions are 0 M. The concentration of CH_3CH_2COOH will change by $-x$ and those of $CH_3CH_2COO^-$ and H_3O^+ will increase by $+x$ as the reaction proceeds to equilibrium. We can now construct the concentration table.

Solution

	H_2O + CH_3CH_2COOH $\rightleftharpoons$	H_3O^+ +	$CH_3CH_2COO^-$
Initial concentration (mol L^{-1})	0.10	0	0
Change in concentration (mol L^{-1})	$-x$	$+x$	$+x$
Equilibrium concentration (mol L^{-1})	0.10 - x	x	x

As propanoic acid is a weak acid, it dissociates only to a small extent and therefore x is very small. We can then make the simplifying approximation that $(0.10 - x) \approx 0.10$, so we take the equilibrium concentration of CH_3CH_2COOH to be 0.10 M. Substituting these quantities into the K_a expression gives:

$$K_a = \frac{[H_3O^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]} = \frac{(x)(x)}{0.10 - x} \approx \frac{(x)(x)}{0.10} = 1.4 \times 10^{-5}$$

We can now solve this for x:

$$x^2 = (0.10)(1.4 \times 10^{-15}) = 1.4 \times 10^{-6}$$

$$x = \sqrt{1.4 \times 10^{-6}} = 1.2 \times 10^{-3}$$

We know that $x = [H_3O^+]$ and therefore:

$$[H_3O^+] = 1.2 \times 10^{-3}\,M$$

Finally, we calculate the pH:

$$pH = -\log[H_3O^+] = -\log(1.2 \times 10^{-3})$$

$$= 2.92$$

Is our answer reasonable?

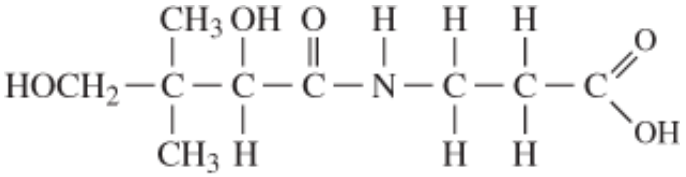
First, we see that the calculated pH is less than 7. This tells us that the solution is acidic, which it should be for a solution of an acid. Also, the pH is higher than it would be if the acid were strong. (A 0.10 M solution of a strong acid would have $[H_3O^+] = 0.10$ M and pH = 1.0.) If we wish to further check the accuracy of the calculation, we can substitute the calculated equilibrium concentrations into the expression for K_a. If the calculated quantities are correct, we should obtain the numerical value of K_a.

$$\frac{[H_3O^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]} = \frac{(x)(x)}{0.10} = \frac{(1.2 \times 10^{-3})^2}{0.10} = 1.4 \times 10^{-5} = K_a$$

The check works, so we have done the calculation correctly.

PRACTICE EXERCISE 11.13

Pantothenic acid is also called vitamin B_5. It is also a weak acid with $K_a = 3.9 \times 10^{-5}$. Calculate $[H_3O^+]$ and the pH of a 0.050 M solution of pantothenic acid.



pantothenic acid

WORKED EXAMPLE 11.11

Calculating the pH of a solution of a weak base

A solution of hydrazine, N_2H_4, a weak base, has a concentration of 0.25 M. What is the pH of the solution? Hydrazine has $K_b = 1.7 \times 10^{-6}$.

Analysis

This example is analogous to worked example 11.10, except that we are now dealing with a weak base and using K_b rather than K_a.

Solution

We begin with the balanced chemical equation and obtain the K_b expression.

$$N_2H_4(aq) + H_2O(l) \rightleftharpoons N_2H_5^+(aq) + OH^-(aq)$$

$$K_b = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]}$$

Again, the concentration of N_2H_4 will change by $-x$ and those of $N_2H_5^+$ and OH^- will increase by $+x$ as the reaction proceeds to equilibrium. We construct the concentration table as follows.

	H_2O +	N_2H_4	$\rightleftharpoons$	$N_2H_5^+$	+	OH^-
Initial concentration (mol L^{-1})		0.25		0		0
Change in concentration (mol L^{-1})		$-x$		$+x$		$+x$
Equilibrium concentration (mol L^{-1})		0.25 - x		x		x

Because hydrazine is a weak base, it reacts with water only to a small extent. We can therefore make the same approximation that we made for a weak acid; that is $(0.25 - x) \approx 0.25$. We substitute the values from the concentration table into the K_b expression.

$$K_b = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]} = \frac{(x)(x)}{0.25 - x} \approx \frac{(x)(x)}{0.25} = 1.7 \times 10^{-6}$$

We solve this for x as follows.

$$\begin{aligned} x^2 &= (0.25)(1.7 \times 10^{-6}) = 4.3 \times 10^{-7} \\ x &= \sqrt{4.3 \times 10^{-7}} = 6.5 \times 10^{-4} \end{aligned}$$

This value represents the hydroxide ion concentration, from which we can calculate the pOH.

$$\begin{aligned} \text{pOH} &= -\log[OH^-] \\ &= -\log(6.5 \times 10^{-4}) \\ &= 3.19 \end{aligned}$$

The pH of the solution can then be obtained from the relationship:

$$\begin{aligned} \text{pH} + \text{pOH} &= 14.00 \\ \text{pH} &= 14.00 - 3.19 \\ &= 10.81 \end{aligned}$$

Is our answer reasonable?

As stated in the question, hydrazine is a weak base, so we would expect a pH > 7. We can quickly check to see whether the value of x and our assumed equilibrium concentration of N_2H_4 (0.25 M) are correct by substituting them into the expression for K_b and comparing the result with the numerical value of K_b. Doing this gives 1.7×10^{-6}, which is the same as K_b, so the value of x is correct.

PRACTICE EXERCISE 11.14

Pyridine, C_5H_5N, is a toxic, foul-smelling liquid for which $K_b = 1.7 \times 10^{-9}$. What is the pH of a 0.010 M aqueous solution of pyridine?

PRACTICE EXERCISE 11.15

Phenol, C_6H_5OH, is a weakly acidic organic compound, commonly used as a disinfectant, for which $K_a = 1.3 \times 10^{-10}$. What is the pH of a 0.15 M solution of phenol in water?

In worked examples 11.10 and 11.11, we have calculated the pH given the value of K_a or K_b. We can also use measured values of pH to calculate K_a or K_b values, as shown in worked example 11.12.

WORKED EXAMPLE 11.12

Calculating K_a and pK_a from pH

Lactic acid, $CH_3CH(OH)COOH$, is a monoprotic acid that is present in sour milk and yoghurt. The pH of a 0.100 M solution of lactic acid is 2.44 at 25 °C. Calculate K_a and pK_a for lactic acid at this temperature.

Analysis

In this case we are given the pH of the solution, from which we can calculate $[H_3O^+]$. In essence, this is the reverse of the previous examples. We use the balanced chemical equation to construct a concentration table and then substitute the calculated equilibrium concentrations into the expression for K_a.

Solution

We begin by writing the balanced chemical equation and obtaining the expression for K_a.

$$CH_3CH(OH)COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CH(OH)COO^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3CH(OH)COO^-]}{[CH_3CH(OH)COOH]}$$

In this problem, the only source of the ions H_3O^+ and $CH_3CH(OH)COO^-$ is the acid. As a result, the equilibrium concentration of H_3O^+ must be identical to that of $CH_3CH(OH)COO^-$ because the reaction gives these ions in a 1 : 1 ratio. However, we do not have the values of either $[H_3O^+]$ or $[CH_3CH(OH)COO^-]$; all we have is the pH of the 0.100 M solution. We start

by finding $[H_3O^+]$ from the pH. This gives us the *equilibrium* value of $[H_3O^+]$.

$$\begin{aligned}[H_3O^+] &= 10^{-pH} = 10^{-2.44} \\ &= 3.6 \times 10^{-3}\ M\end{aligned}$$

Because $[CH_3CH(OH)COO^-] = [H_3O^+]$, we know that $[CH_3CH(OH)COO^-] = 3.6 \times 10^{-3}$ M at equilibrium. We now set up the concentration table, given that the initial concentration of lactic acid is 0.100 M.

	$H_2O + CH_3CH(OH)COOH \rightleftharpoons$	$H_3O^+ +$	$CH_3CH(OH)COO^-$
Initial concentration (mol L^{-1})	0.100	0	0
Change in concentration (mol L^{-1})	-3.6×10^{-3}	$+3.6 \times 10^{-3}$	$+3.6 \times 10^{-3}$
Equilibrium concentration (mol L^{-1})	$0.100 - 3.6 \times 10^{-3} = 0.096$	3.6×10^{-3}	3.6×10^{-3}

This problem differs from the previous worked examples in that we know the value of x (3.6×10^{-3} M) but we do not know K_a. We proceed by substituting the equilibrium values into the K_a expression. We know that both $[H_3O^+]$ and $[CH_3CH(OH)COO^-] = 3.6 \times 10^{-3}$ M, and, from the concentration table, that $[CH_3CH(OH)COOH] = (0.100 - x) = (0.100 - 3.6\times10^{-3}) = 0.096$ M. (Note that, because we know the value of x in this case, we do not have to make the assumption that $(0.100 - x) \approx 0.100$.) Therefore:

$$\begin{aligned}K_a &= \frac{[H_3O^+]\,[CH_3CH(OH)COO^-]}{[CH_3CH(OH)COO]} = \frac{(3.6\times10^{-3})(3.6\times10^{-3})}{0.096} \\ &= 1.4\times10^{-4}\end{aligned}$$

Thus the K_a for lactic acid is 1.4×10^{-4}. To find pK_a, we take the negative logarithm of K_a.

$$\begin{aligned}pK_a &= -\log K_a \\ &= -\log(1.4\times10^{-4}) \\ &= 3.85\end{aligned}$$

Is our answer reasonable?

Weak acids have small acidity constants, so the value we obtained for K_a seems to be reasonable. We should also check the entries in the concentration table to be sure they are reasonable. For example, the 'changes' for the ions are both positive, meaning both of their concentrations are increasing. This is the way it should be. Also, we have the concentration of lactic acid decreasing, as it must do.

PRACTICE EXERCISE 11.16

Few substances are more effective in relieving intense pain than morphine. Morphine is an alkaloid — a weakly basic compound obtained from plants. The pH of a 0.010 M aqueous solution of morphine is 10.10. Calculate the K_b and pK_b for morphine. Use the symbol B, rather than the chemical formula of morphine given in table 11.5, when you write the equation.

pH Calculations in Solutions of Salts of Weak Acids and Bases

We have seen that Cl^-, the conjugate base of the strong acid HCl, is a very weak base and shows essentially no tendency to react with H_3O^+ to form HCl. This means that Cl^- is even less likely to act as a base towards H_2O, and we can say that Cl^- has essentially no basic properties. Therefore, an aqueous solution of NaCl has a pH of 7.00 at 25 °C. This is true of the conjugate bases of all strong monoprotic acids. Thus, dilute aqueous solutions of salts such as NaBr, NaI, $NaNO_3$, and, indeed, any sodium salt of a strong monoprotic acid, have pH values of 7.00 at 25 °C. However, this is not the case for the salt of a weak acid, such as $NaOOCCH_3$, which has a pH > 7, or the salt of a weak base, such as NH_4Cl, which has a pH < 7 at this temperature. If we dissolve each of these in water, we get complete dissociation into the respective ions as follows.

$$NaOOCCH_3(s) \xrightarrow{H_2O} Na^+(aq) + CH_3COO^-(aq)$$

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$$

The CH_3COO^- and NH_4^+ ions are then involved in the following equilibria:

$$CH_3COO^-(aq) + H_2O(1) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

$$NH_4^+(aq) + H_2O(1) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

and the two solutions are therefore slightly basic and slightly acidic, respectively.

As illustrated in figure 11.11 (p. 446), conjugate base strength increases as acid strength decreases, and therefore the salts of weak acids can be appreciably basic. Similarly, the salts of weak bases are generally slightly acidic. We can see that this is the case by looking at pK_a and pK_b values for conjugate pairs. For example, as we have seen, acetic acid, CH_3COOH, has a pK_a of 4.74, and this means that the acetate ion, CH_3COO^-, has a pK_b of 14.00 - 4.74 = 9.26. If we consider HCN, an even weaker acid (pK_a = 9.21), we can see that the cyanide ion, CN^-, has a pK_b of 14.00 - 9.21 = 4.79, making it almost as strong a base as ammonia, NH_3. We can use the pK_a and pK_b values to calculate the pH of aqueous solutions containing the salts of weak acids and bases, as shown in worked examples 11.13 and 11.14.

WORKED EXAMPLE 11.13

Calculating the pH of a salt solution

What is the pH of a 0.10 M solution of NaOCl at 25 °C? For HOCl, $K_a = 3.0 \times 10^{-8}$.

Analysis

OCl^- is the conjugate base of the weak acid HOCl, and we therefore expect the solution to be slightly basic. As we are given only K_a for HOCl and we are asked to find the pH, we use K_b, which we can obtain from K_a, to solve this problem. As usual, we start with a balanced chemical equation and obtain the expression for the appropriate equilibrium constant from this.

Solution

First, we write the chemical equation for the reaction of OCl^- with water and the corresponding K_b expression.

$$OCl^-(aq) + H_2O(1) \rightleftharpoons HOCl(aq) + OH^-(aq)$$

$$K_b = \frac{[HOCl]\,[OH^-]}{[OCl^-]}$$

The data provided in the problem give the K_a for HOCl, but we can calculate K_b because $K_aK_b = K_w$ for a conjugate pair.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.3 \times 10^{-7}$$

Now let us set up the concentration table. The only source of HOCl and OH^- is the reaction of OCl^-, so their concentrations each increase by x and the concentration of OCl^- decreases by x as the reaction proceeds to equilibrium.

	$H_2O + OCl^-$ $\rightleftharpoons$	HOCl	+ OH^-
Initial concentration (mol L^{-1})	0.10	0	0
Change in concentration (mol L^{-1})	$-x$	$+x$	$+x$
Equilibrium concentration (mol L^{-1})	(0.10 - x)	x	x

At equilibrium, the concentrations of HOCl and OH^- are the same, x.

$$[HOCl] = [OH^-] = x$$

As OCl^- is a weak base, it reacts with water only to a small extent, and therefore x is small. We can then make the approximation that (0.10 - x) ≈ 0.10 and so $[OCl^-]$ = 0.10 M at equilibrium. We substitute the values into the K_b expression to give:

$$K_b = \frac{[HOCl]\,[OH^-]}{[OCl^-]} = \frac{(x)(x)}{0.10 - x} \approx \frac{(x)(x)}{0.10} = 3.3 \times 10^{-7}$$

We solve this for x as follows:

$$x^2 = (0.10)(3.3 \times 10^{-7}) = 3.3 \times 10^{-8}$$
$$x = \sqrt{3.3 \times 10^{-8}} = 1.8 \times 10^{-4}\ \text{M}$$

This value of x represents the OH^- concentration, from which we can calculate the pOH and then the pH.

$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-] \\ &= -\log(1.8 \times 10^{-4}) \\ &= 3.74 \\ \text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 3.74 \\ &= 10.26 \end{aligned}$$

The pH of this solution is 10.26.

Is our answer reasonable?

From the nature of the salt, we expect the solution to be basic. The calculated pH corresponds to a basic solution, so the answer seems reasonable. We can also check the accuracy of the answer by substituting the calculated equilibrium concentrations into the expression for K_b.

$$\frac{[\text{HOCl}]\,[\text{OH}^-]}{[\text{OCl}^-]} = \frac{(x)(x)}{0.10} = \frac{\left(1.8 \times 10^{-4}\right)^2}{0.10} = 3.2 \times 10^{-7}$$

The result is acceptably close to the value of K_b, so our answers are correct.

WORKED EXAMPLE 11.14

Calculating the pH of a salt solution

What is the pH of a 0.20 M solution of hydrazinium chloride, N_2H_5Cl at 25 °C? Hydrazine, N_2H_4, is a weak base with $K_b = 1.7 \times 10^{-6}$.

Analysis

The hydrazinium ion, $N_2H_5^+$, is the conjugate acid of the weak base hydrazine, N_2H_4, and therefore we expect a solution containing this ion to be slightly acidic. We proceed in a similar fashion to worked example 11.13, starting, as ever, with the balanced chemical equation and the appropriate equilibrium constant expression. As we have seen, Cl^- is an extremely weak base; it reacts with water to a negligible extent and does not affect the pH of the solution. It can therefore be neglected in our calculations.

Solution

We will begin with the balanced chemical equation for the reaction of $N_2H_5^+$ with water and write the K_a expression.

$$N_2H_5^+(aq) + H_2O(1) \rightleftharpoons H_3O + (aq) + N_2H_3(aq)$$

$$K_a = \frac{\left[H_3O^+\right][N_2H_4]}{\left[N_2H_5^+\right]}$$

The problem has given us K_b for N_2H_4, but we need K_a for $N_2H_5^+$. We obtain this by solving the equation $K_aK_b = K_w$ for K_a.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-6}} = 5.9 \times 10^{-9}$$

Now we set up the concentration table. The initial concentrations of H_3O^+ and N_2H_4 are both set to zero. Next, we indicate that the concentration of $N_2H_5^+$ decreases by x and the concentrations of H_3O^+ and N_2H_4 both increase by x as the reaction proceeds to equilibrium.

	$H_2O + N_2H_5^+$ ⇋	$H_3O^+ + N_2H_4$	
Initial concentration (mol L^{-1})	0.20	0	0
Change in concentration (mol L^{-1})	$-x$	$+x$	$+x$
Equilibrium concentration (mol L^{-1})	0.20 - x	x	x

At equilibrium, equal amounts of H_3O^+ and N_2H_4 are present, and their equilibrium concentrations are each equal to x.

$$\left[H_3O^+\right] = [N_2H_4] = x$$

As $N_2H_5^+$ is a weak acid, it reacts with water to a small extent. We can assume that $(0.20 - x) \approx 0.20$ because $0.2 > 400 \times K_a$, and therefore $[N_2H_5^+] = 0.20$ M at equilibrium. We then substitute quantities into the equilibrium constant expression.

$$K_a = \frac{\left[H_3O^+\right][N_2H_4]}{\left[N_2H_5^+\right]} = \frac{(x)(x)}{0.20 - x} \approx \frac{(x)(x)}{0.20} = 5.9 \times 10^{-9}$$

We solve this for x as follows:

$$x^2 = (0.20)\left(5.9 \times 10^{-9}\right) = 1.2 \times 10^{-9}$$

$$x = \sqrt{1.2 \times 10^{-9}} = 3.4 \times 10^{-5}\,\text{M}$$

Since $x = [H_3O^+]$, the pH of the solution is:

$$\text{pH} = -\log\left[H_3O^+\right] = -\log\left(3.4 \times 10^{-5}\right)$$

$$= 4.47$$

Is our answer reasonable?

The active solute species in the solution is a weak acid and the calculated pH is less than 7, so the answer seems reasonable. Check the accuracy yourself by substituting equilibrium concentrations into the expression for K_a.

PRACTICE EXERCISE 11.17

What is the pH of a 0.10 M solution of $NaNO_2$? Use the pK_a of HNO_2 from table 11.4.

PRACTICE EXERCISE 11.18

What is the pH of a 0.10 M solution of NH_4Br? Use the pK_b of NH_3 from table 11.5.

Solutions that Contain the Salt of a Weak Acid and a Weak Base

We saw previously that both the NH_4^+ cation and CH_3COO^- anion affect the pH of an aqueous solution. We now address what happens when both the cation and anion in a single salt are able to affect the pH. Whether or not the salt has a net effect on the pH now depends on the relative strengths of its ions, one functioning as an acid and the other as a base. If they are matched in their respective strengths, the salt has no net effect on pH. Consider, for example, a solution of ammonium acetate, NH_4OOCCH_3, in which the ammonium ion is an acidic cation and the acetate ion is a basic anion. However, K_a of NH_4^+ is 5.6×10^{-10} and K_b of CH_3COO^- just happens to be the same, 5.6×10^{-10}. The cation tends to produce H_3O^+ ions to the same extent that the anion tends to produce OH^-. So, in aqueous ammonium acetate, $[H_3O^+] = [OH^-]$, and the solution has a pH of 7.

Consider, now, ammonium formate, NH_4OOCH. The formate ion, $HCOO^-$, is the conjugate base of the weak acid formic acid and has $K_b = 5.6 \times 10^{-11}$. Comparing this value with the (slightly larger) K_a of the ammonium ion, 5.6×10^{-10}, we see that NH_4^+ is slightly stronger as an acid than the formate ion is as a base. As a result, a solution of ammonium formate is slightly acidic. The exact calculation of pH in such solutions is difficult, and we are concerned here only in predicting if the solution is acidic, basic or neutral.

WORKED EXAMPLE 11.15

Predicting how a salt affects the pH of its solution

Is a 0.20 M aqueous solution of NH_4F acidic, basic or neutral?

Analysis

This is a salt in which the cation is a weak acid (it is the conjugate acid of a weak base, NH_3) and the anion is a weak base (it is the conjugate base of a weak acid, HF). The question is: 'How do the two ions compare in their abilities to affect the pH of the solution?' We have to compare their respective K_a and K_b values to compare their strengths.

Solution

K_a of NH_4^+ (calculated from the K_b of NH_3) is $5.6 \times 10^{-1}0$. Similarly, K_b of F^- is 1.5×10^{-11} (calculated from the K_a of HF, 6.8×10^{-4}). Comparing the two equilibrium constants, we see that K_a for the acid, NH_4^+, is greater than K_b for the base, F^-. Therefore, the reaction of NH_4^+ with water to give H_3O^+ proceeds to a greater extent than the reaction of F^- with water to give OH^-. This means that, at equilibrium, $[H_3O^+] > [OH^-]$, and we expect the solution to be slightly acidic.

Is our answer reasonable?

There is not much to check here except to be sure that we have done the arithmetic correctly.

PRACTICE EXERCISE 11.19

Is an aqueous solution of ammonium cyanide, NH_4CN, acidic, basic or neutral?

Situations where Simplifying Assumptions do not Work

On pp. 447-53, we used initial concentrations of acids and bases as though they were equilibrium concentrations when we performed calculations. This is only an approximation, as we discussed on p. 447, but it works most of the time. Unfortunately, it does not work in all cases, so we will now examine those conditions under which simplifying approximations do not work. We will also study how to solve problems when the approximations cannot be used.

When a weak acid HA reacts with water, its concentration is reduced as the ions form. If we let x represent the amount of acid that reacts per litre, the equilibrium concentration becomes:

$$[HA]_{equilibrium} = [HA]_{initial} - x$$

In previous problems, we have assumed that [HA]equilibrium ≈ $[HA]_{equilibrium}$ ≈ $[HA]_{initial}$ because *x* is small compared with [HA]initial. However, this is the case only if $[HA]_i$nitial is greater than, or equal to, 400 times the value of K_a. As the value of K_a of the weak acid increases, our assumption becomes less valid because the extent of dissociation of the acid increases, and $[HA]_{equilibrium}$ is no longer approximately equal to $[HA]_{initial}$.

When our assumption is not valid, we must solve a quadratic equation as we did in chapter 9. We also assumed that we could safely neglect any contribution to $[H_3O^+]$ or $[OH^-]$ from the autoprotolysis of water. This is the case only if the value of $[H_3O^+]$ or $[OH^-]$ from the acid or base is greater than 1×10^{-5} (i.e. at least 100 times 1×10^{-7}, the maximum possible contribution from water). This will generally be the case, and we assume we can continue to neglect the autoprotolysis of water from here on. We illustrate a situation that requires use of the quadratic formula in worked example 11.16.

WORKED EXAMPLE 11.16

Using the Quadratic Formula in Equilibrium Products

Chloroacetic acid, $ClCH_2COOH$, is used as a herbicide and in the manufacture of dyes and other organic chemicals. It is a weak acid with $K_a = 1.4 \times 10^{-3}$. What is the pH of a 0.010 M solution of $ClCH_2COOH$ at 25 °C?

Analysis

Before we begin the solution, we check to see whether we can use our usual simplifying approximation. We do this by calculating $400 \times K_a$ and then comparing the result with the initial concentration of the acid.

$$400 \times K_a = 400\left(1.4 \times 10^{-3}\right) = 0.56$$

The initial concentration of $ClCH_2COOH$ is *less than* 0.56 M, so we know the simplification does not work. We therefore have to set up a concentration table and then use a quadratic equation to obtain the solution.

Solution

We begin by writing the balanced chemical equation and the K_a expression.

$$ClH_2COOH(aq) + H_2O(1) \rightleftharpoons H_3O^+(aq) + ClCH_2COO^-(aq)$$

$$K_a = \frac{[H_3O^+][ClCH_2COO^-]}{[ClCH_2COOH^-]} = 1.4 \times 10^{-3}$$

The initial concentration of the acid will be reduced by an amount, -*x*, as it reacts with water to form the ions. From this, we build the concentration table, assuming, as always, that the

initial concentrations of the ions are zero.

	$H_2O + ClCH_2COOH \rightleftharpoons H_3O^+ + ClCH_2COO^-$		
Initial concentration (mol L^{-1})	0.010	0	0
Change in concentration (mol L^{-1})	$-x$	$+x$	$+x$
Equilibrium concentration (mol L^{-1})	$0.010 - x$	x	x

Substituting equilibrium concentrations into the equilibrium expression gives:

$$K_a = \frac{[H_3O^+][ClCH_2COO^-]}{[ClCH_2COOH^-]} = \frac{(x)(x)}{0.010 - x} = 1.4 \times 10^{-3}$$

This time we cannot assume (0.010 - x) = 0.010. To solve the problem, we first rearrange the expression to obtain the familiar form of a quadratic equation. We do this by multiplying both sides by (0.010 - x). This gives:

$$\begin{aligned} x^2 &= (0.010 - x)\left(1.4 \times 10^{-3}\right) \\ x^2 &= \left(1.4 \times 10^{-5}\right) - \left(1.4 \times 10^{-3}\right)x \\ x^2 &+ \left(1.4 \times 10^{-3}\right)x - \left(1.4 \times 10^{-5}\right) = 0 \end{aligned}$$

This is a general quadratic equation of the form:

$$ax^2 + bx + c = 0$$

$$ax^2 + bx + c = 0$$

We now use the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

and make the substitutions a = 1, b = 1.4×10^{-3} and c = -1.4×10^{-5}. Entering these into the quadratic formula gives:

$$
\begin{aligned}
x &= \frac{-1.4\times10^{-3} \pm \sqrt{\left(1.4\times10^{-3}\right)^2 - 4(1)\left(-1.4\times10^{-5}\right)}}{2(1)} \\
&= \frac{-1.4\times10^{-3} \pm \sqrt{2.0\times -10^{-5} + 5.6\times10^{-5}}}{2} \\
&= \frac{-1.4\times10^{-3} \pm \sqrt{5.8\times10^{-5}}}{2} \\
&= \frac{-1.4\times10^{-3} \pm 7.6\times10^{-3}}{2} \\
x &= 3.1\times10^{-3}\,\text{M and } x = -4.5\times10^{-3}\,\text{M}
\end{aligned}
$$

We know that *x* cannot be negative because that would give negative concentrations for the ions, which is impossible, so we choose the first value as the correct one. This yields the following equilibrium concentrations.

$$
\begin{aligned}
\left[H_3O^+\right] &= 3.1\times10^{-3}\,\text{M} \\
[ClCH_2COO^-] &= 3.1\times10^{-3}\,\text{M} \\
[ClCH_2COOH] &= 0.010 - x = 0.010 - 0.0031 \\
&= 0.007\,\text{M}
\end{aligned}
$$

Finally, we calculate the pH of the solution.

$$
\begin{aligned}
\text{pH} &= -\log\left(3.1\times10^{-3}\right) \\
&= 2.51
\end{aligned}
$$

Notice that *x* is not negligible compared with the initial concentration, so the simplifying approximation would not have been valid. We can calculate the error that would be produced if we made the simplifying approximation in this case. We would obtain the same equation.

$$
K_a = \frac{\left[H_3O^+\right][ClCH_2COO^-]}{[ClCH_2COOH]} = \frac{(x)(x)}{0.010 - x} = 1.4\times10^{-3}
$$

and, making the assumption that (0.010 - *x*) ≈ 0.010, we would then obtain:

$$
K_a = \frac{\left[H_3O^+\right][ClCH_2COO^-]}{[ClCH_2COOH]} = \frac{(x)(x)}{0.010} = 1.4\times10^{-3}
$$

Solving this for *x* would give:

$$
\begin{aligned}
x^2 &= (0.010)\left(1.4\times10^{-3}\right) = 1.4\times10^{-5} \\
x &= \sqrt{1.4\times10^{-5}} = 3.7\times10^{-3}
\end{aligned}
$$

Therefore, making the assumption gives $[H_3O^+] = 3.7 \times 10^{-3}$ M, compared with the correct value of 3.1×10^{-3} M from solution of the quadratic equation, approximately a 20% error.

Is our answer reasonable?

As before, a quick check can be performed by substituting the calculated equilibrium concentrations into the equilibrium expression.

$$K_a = \frac{[H_3O^+][ClCH_2COO^-]}{[ClCH_2COOH]} = \frac{(x)(x)}{0.010 - x} = \frac{(3.1 \times 10^{-3})^2}{0.007} = 1.4 \times 10^{-3}$$

The value we obtain equals K_a, so the equilibrium concentrations are correct.

PRACTICE EXERCISE 11.20

Calculate the pH of a 0.0010 M solution of dimethylamine, $(CH_3)_2NH$. Dimethylamine is a weak base with $K_b = 9.6 \times 10^{-4}$.

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11.5 The Molecular Basis of Acid Strength

Up until this point, we have labelled acids as either strong or weak, but have not explained what determines the strength of a particular acid. In this section, we will show that a variety of factors contribute to the overall strength of an acid.

Binary acids

A binary acid is defined as an acid containing H and only one other element, generally a nonmetal. The simplest binary acids are the monoprotic species HF, HCl, HBr and HI containing group 17 elements. Diprotic binary acids include H_2O and H_2S, whereas NH_3 and CH_4 are examples of, albeit extremely weak, triprotic and tetraprotic binary acids, respectively. The observed order of acid strengths of these acids is (from weakest to strongest):

$$CH_4 < NH_3 < H_2O < H_2S < HF < \ < HCl < HBr < HI$$

In order for each of these compounds to act as an acid, a single H—X bond must be broken, so it might be expected there would be some correlation between the H—X bond enthalpy (which can be thought of as the ease with which the bond can be broken) and the acid strength. As can be seen from table 11.6, this is not the case.

TABLE 11.6 Bond enthalpies for cleavage of some H—X bonds

Bond	Bond enthalpy for homolytic cleavage (kJ mol^{-1})	Bond enthalpy forheterolytic cleavage (kJ mol^{-1})
C—H	412	1744
N—H	388	1688
O—H	463	1633
S—H	338	1468
F—H	565	1554
Cl—H	431	1395
Br—H	366	1353
I—H	299	1314

This is perhaps not surprising when you consider the definition of bond enthalpy. Recall (p. 313) that a bond enthalpy refers to the process:

$$H—X(g) \rightarrow H(g) + X(g)$$

in which the bond in the gas phase molecule undergoes **homolytic cleavage** (the bond breaks evenly so that one electron is given to each of the atoms involved in the bond) to give electrically neutral species; such a process is in fact very different from that involved in proton donation from H—X to water, which occurs via **heterolytic cleavage** (the bond breaks unevenly so that both electrons are given to one of the atoms involved in the bond) to form solvated ions, according to the equation:

$$H—X(aq) + H_2O(1) \rightarrow H_3O^+(aq) + X^-(aq)$$

A good correlation between the acidity and the heterolytic H—X bond energies in the gas phase does exist, as can be seen in table 11.6; these gas phase data, however, neglect solvent effects and do not therefore constitute an acceptable approximation of reality.

A more realistic approach that does include solvent effects uses the Hess's law cycle shown in figure 11.13.

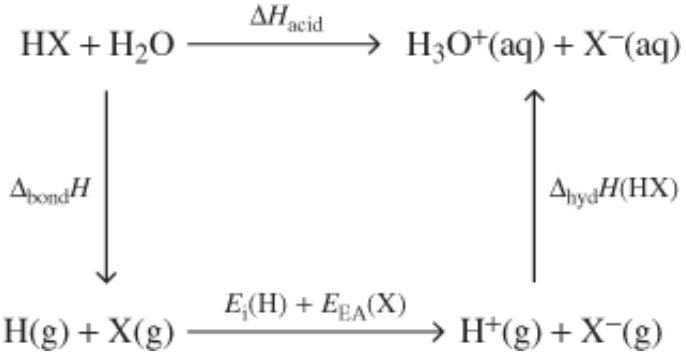


FIGURE 11.13 A Hess's law cycle for the dissociation of an acid in aqueous solution.

The value of ΔH_{acid}, the enthalpy change for the dissociation of the acid in its standard state (gas for all acids except H_2O) in water, can be calculated for the binary acids listed in table 11.7 using available thermochemical data; $\Delta_{bond}H$ is the H—X bond energy (homolytic cleavage), E_i(H) is the ionisation energy of the gaseous hydrogen atom (1312 kJ mol^{-1}), E_{EA} is the electron affinity of X(g), and $\Delta_{hyd}H$ (HX) is the hydration enthalpy (p. 397) of gaseous HX.

TABLE 11.7 Enthalpy and energy changes involved in the dissociation of a variety of acids in aqueous solution at 25 °C

Acid (HX)	$\Delta_{bond}H$ (kJ mol^{-1})	E_i(H) + E_{EA}(X)(kJ mol^{-1})	$\Delta_{hyd}H$(HX)(kJ mol^{-1})	ΔH_{acid}(kJ mol^{-1})
CH_4 (X = CH_3)	412	1303	–1583	132
NH_3 (X = NH_2)	388	1241	–1603	26
H_2O (X = OH)	463	1134	-1623	15[(a)]
H_2S (X = SH)	338	1090	-1443	-15
HF (X = F)	565	990	–1613	–58
HCl (X = Cl)	431	963	–1470	–76
HBr (X = Br)	366	987	–1439	–86
HI (X = I)	299	1017	–1394	–78

(a) To provide a meaningful comparison with the other acids, H_2O must be vaporised, a process which requires 41 kJ mol^{-1}. The final value of 15 kJ mol^{-1} includes this contribution.

It can be seen, from the data in table 11.7, that the trends in the ΔH_{acid} values correlate well with the

acid strengths; as ΔH_{acid} becomes less positive (more negative), the acid strength increases. It can also be seen that no single contributing factor to ΔH_{acid} is primarily responsible for the observed trend in acid strengths. While it may be tempting to attribute the increasing acidity in the monoprotic acids from HF to HI to the significant decrease in $\Delta_{bond}H$, this is almost exactly opposed by the decrease in $\Delta_{hyd}H$ values. Similarly, an increase in electron affinity of X does appear to correlate well with an increase in acidity, but this breaks down for HBr and HI. It should also be noted that the above approach neglects entropic effects, which will undoubtedly contribute to the overall energetics of the acid dissociation process.

Having said this, two general observations concerning the acid strength of binary acids can be made:

1. The acid strength of binary acids increases going across a period (for example, $CH_4 < NH_3 < H_2O < HF$).
2. The acid strength of binary acids increases going down a group (for example, $HF < HCl < HBr < HI$).

The first observation has been attributed to the increasing electronegativity of X, rendering the H—X bond more polar, while the second has been explained by the increasing size of X, making the H—X bond longer and, therefore, weaker. As the data in table 11.7 show, however, such simple interpretations should be treated with caution, and are generally best avoided.

PRACTICE EXERCISE 11.21

Using only the periodic table, choose the stronger acid of each of the following pairs.

(a) H_2Se or HBr,

(b) H_2Se or H_2Te,

(c) CH_3OH or CH_3SH

Oxoacids

Acids composed of hydrogen, oxygen and some other element are called oxoacids (see table 11.8). Those that are strong acids in water are marked in the table by asterisks.

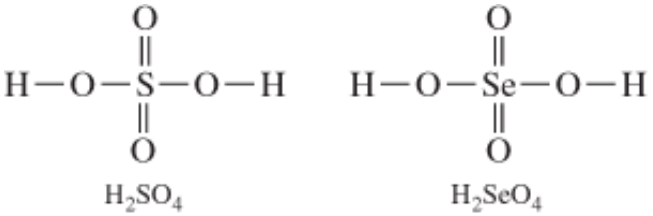
TABLE 11.8 Some oxoacids of nonmetals and metalloids[a]

Group 14	
H_2CO_3	carbonic acid[b]
Group 15	
*HNO_3	nitric acid[a]
HNO_2	nitrous acid
H_3PO_4	phosphoric acid
H_3PO_3	phosphorous acid[c]
H_3AsO_4	arsenic acid

H_3AsO_3	arsenous acid
Group 16	
*H_2SO_4	sulfuric acid
H_2SO_3	sulfurous acid[(d)]
*H_2SeO_4	selenic acid
H_2SeO_3	selenous acid
Group 17	
HOF	hypofluorous acid[(e)]
*$HClO_4$	perchloric acid
*$HClO_3$	chloric acid
$HClO_2$	chlorous acid
HOCl	hypochlorous acid
*$HBrO_4$	perbromic acid[(f)]
*$HBrO_3$	bromic acid
HOBr	hypobromous acid
HIO_4 (H_5IO_6)[(g)]	periodic acid
HOI	hypoiodous acid
HIO_3	iodic acid

(a) Strong acids are marked with asterisks.
(b) Predominantly $CO_2(aq)$.
(c) Phosphorous acid, despite its formula, is only a diprotic acid. It should more correctly be written as $HPO(OH)_2$.
(d) Hypothetical. An aqueous solution actually contains just dissolved sulfur dioxide, $SO_2(aq)$.
(e) Unstable at room temperature
(f) Pure perbromic acid is unstable; a dihydrate is known.
(g) H_5IO_6 is formed from $HIO_4 + 2H_2O$.

A feature common to the structures of all oxoacids is the presence of O—H groups bonded to some central atom. For example, the structures of two oxoacids of the group 16 elements are:



H_2SO_4
sulfuric acid

H_2SeO_4
selenic acid

As with the binary acids, several general observations about the acid strengths of oxoacids can be made:

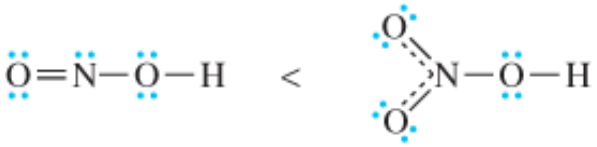
1. Within groups of oxoacids with the same number of oxygen atoms, the acid strength increases going up a group. This is best illustrated by oxoacids containing group 17 elements. The

hypohalous acids, all of which are weak, increase in strength in the order HOI < HOBr < HOCl, with pK_a values of 10.64, 8.68 and 7.52, respectively (note that HOF is unstable, decomposing rapidly at room temperature). For the strong group 17 oxoacids with the general formula HXO_4, the order of acid strength is $HIO_4 < HBrO_4 < HClO_4$ (note that HFO_4 is unknown, as F cannot accommodate more than an octet of electrons). Similarly, in the group 16 acids, we find that H_2SeO_4 is weaker than H_2SO_4 (the third member of this series, 'H_2TeO_4' actually exists as $Te(OH)_6$ and does not therefore provide a valid comparison); in group 15, H_3AsO_4(pK_a = 2.25) is slightly weaker than H_3PO_4 (pK_a = 2.15).

PRACTICE EXERCISE 11.22

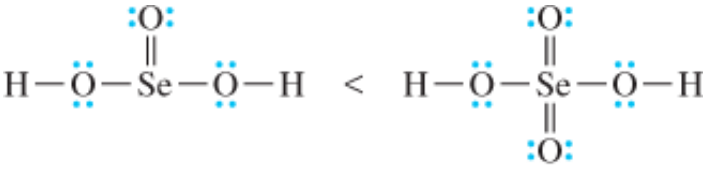
Which is the stronger acid, $HClO_3$ or $HBrO_3$?

2. Within groups of oxoacids with the same number of oxygen atoms, the acid strength increases across a period. This can be seen in oxoacids containing period 3 elements, where acid strength increases in the order $H_3PO_4 < H_2SO_4 < HClO_4$.
3. Acid strength increases as the number of lone oxygen atoms increases. (A lone oxygen atom is one that is bonded only to the central atom and not a hydrogen atom.) There are numerous examples that demonstrate this observation. For example, nitrous acid, HNO_2, which contains one lone oxygen atom, is a weak acid (pK_a = 3.15) while nitric acid, HNO_3, is a strong acid.



nitrous acid nitric acid

A similar situation is seen with selenous acid, H_2SeO_3, and selenic acid, H_2SeO_4, where the latter, having two lone oxygen atoms, is a much stronger acid.

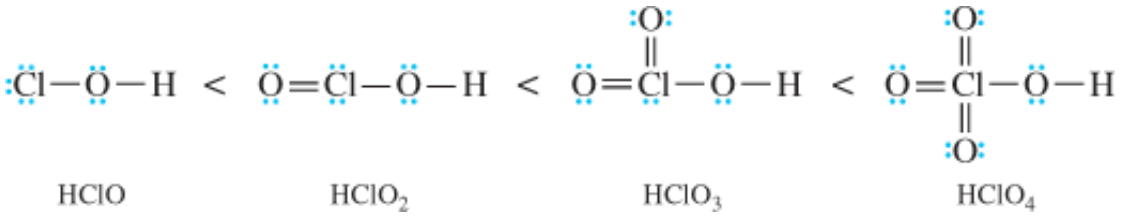


H_2SeO_3 selenous acid H_2SeO_4 selenic acid

Among oxoacids of the halogens, we find the same trend in acid strengths. For the oxoacids of chlorine, for instance, we find the trend:

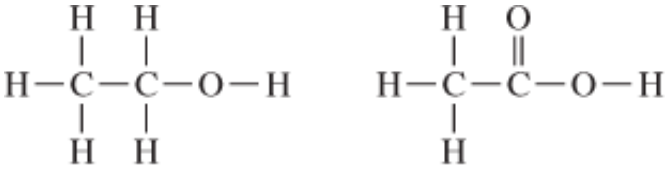
$$HClO < HClO_2 < HClO_3 < HClO_4$$

Comparing their structures we have:



HClO $<$ $HClO_2$ $<$ $HClO_3$ $<$ $HClO_4$

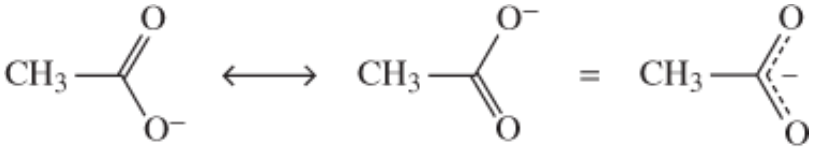
The acid-strengthening effect of lone oxygen atoms is not limited to inorganic oxoacids. Consider, for example, ethanol and acetic acid.



ethanol acetic acid

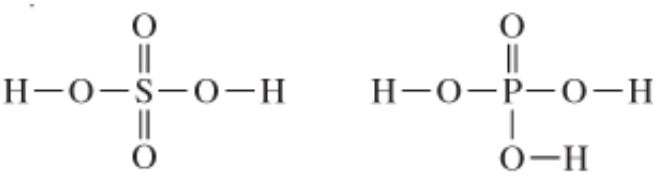
Ethanol displays negligible acid properties in water (pK_a = 15.9). However, incorporation of a lone oxygen atom as a replacement for two protons yields acetic acid, which is eleven orders of magnitude more acidic (pK_a = 4.74). This enormous increase in acidity has been ascribed in part to the differing stabilities of the respective conjugate bases, which is governed by their ability to delocalise the negative charge arising from the loss of a proton.

The acetate ion can be drawn as two equivalent resonance structures (chapter 5), with the negative charge on either of the carboxylate O atoms. The actual structure of the acetate ion lies somewhere between these two forms, with the negative charge delocalised over the two O atoms and the carboxylate carbon atom.



acetate ion

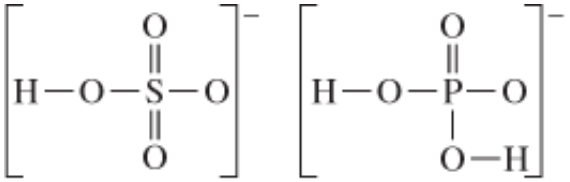
This 'spreading out' or **resonance stabilisation** of the negative charge results in a lowering in energy relative to the situation where the charge is localised on a single atom. The ethoxide ion cannot undergo such resonance stabilisation, and we therefore expect ethanol to be a weaker acid than acetic acid. An analogous situation occurs in the oxoacids of main-group elements. Consider the acids H_2SO_4 and H_3PO_4:



H_2SO_4 H_3PO_4

sulfuric acid phosphoric acid

As you can see in their structures, H_2SO_4 has two lone oxygen atoms and H_3PO_4 has only one. Loss of a proton from each gives the following species:



HSO_4^- $H_2PO_4^-$

In oxoanions such as these, the lone oxygen atoms carry most of the negative charge, rather than the oxygen atoms bonded to hydrogen atoms. This charge actually spreads over the lone oxygen atoms. In HSO_4^-, therefore, each lone oxygen atom carries a charge of about $\frac{1}{3}-$. By the same reasoning, in $H_2PO_4^-$ each lone oxygen atom carries a charge of about $\frac{1}{2}-$. The smaller negative charge on the lone oxygen atoms in HSO_4^- makes this ion less able to attract H_3O^+ ions, so HSO_4^- is a weaker base than $H_2PO_4^-$. In other words, HSO_4^- cannot become H_2SO_4 again as readily as $H_2PO_4^-$ can become H_3PO_4. There are thus two factors that make H_2SO_4 a stronger acid than H_3PO_4in water. One is the greater tendency of H_2SO_4 to donate a proton and the other is the lesser tendency of HSO_4^- to accept a proton.

PRACTICE EXERCISE 11.23

In each pair, select the stronger acid.

(a) HIO_3 or HIO_4,

(b) H_3AsO_3 or H_3AsO_4

Chemistry Research

The Strongest Acid

In this chapter, we have discussed the concept of acid and base strength, and we have related this to the extent of dissociation of the acid or base at equilibrium — for example, strong acids are completely dissociated and weak acids are incompletely dissociated. But are some strong acids more completely dissociated than others? Or, to put it another way, is there such a thing as ‘the strongest acid’ that can be isolated? The answer to this question is yes, and the person who made this acid is a New Zealander.

Professor Christopher Reed is Professor of Chemistry at the University of California at Riverside, in the USA. He was born in Auckland and, after completing his PhD at the University of Auckland, he moved to the USA to carry out postdoctoral research and stayed there following his appointment to the faculty. In 2004, he published a paper in the international chemistry journal *Angewandte Chemie* titled ‘The strongest isolable acid’, where he reported the synthesis and characterisation of a carborane acid with the chemical formula $H(CHB_{11}Cl_{11})$. (A carborane is a molecule or ion that has a framework composed of carbon and boron atoms.)

The structure of this acid is shown in figure 11.14. It consists of a proton and an anionic $(CHB_{11}Cl_{11})^-$ carborane unit and is a solid at room temperature. The extraordinary acid strength of $H(CHB_{11}Cl_{11})$ is evidenced by the fact that it can protonate molecules that are extremely weak bases. For example, reaction with benzene, C_6H_6, gives the protonated benzenium ion as the salt $(C_6H_7)^+(CHB_{11}Cl_{11})^-$. The acid strength of $H(CHB_{11}Cl_{11})$ was quantified using NMR (nuclear magnetic resonance) and IR (infrared) spectroscopies (see chapter 20) and these

techniques showed it to be the strongest known acid. Professor Reed and his co-workers have also prepared a number of similarly strong acids that differ in the substituents around the carborane core; these include $H(CHB_{11}H_5Cl_6)$, $H(CHB_{11}H_5Br_6)$ and $H(CHB_{11}H_5I_6)$, all of which are slightly weaker acids than $H(CHB_{11}Cl_{11})$. However, $H(CHB_{11}H_5Cl_6)$ is still a sufficiently strong acid to be able to protonate the weakly basic C_{60} molecule. These carborane acids appear to be at least one million times stronger than sulfuric acid.

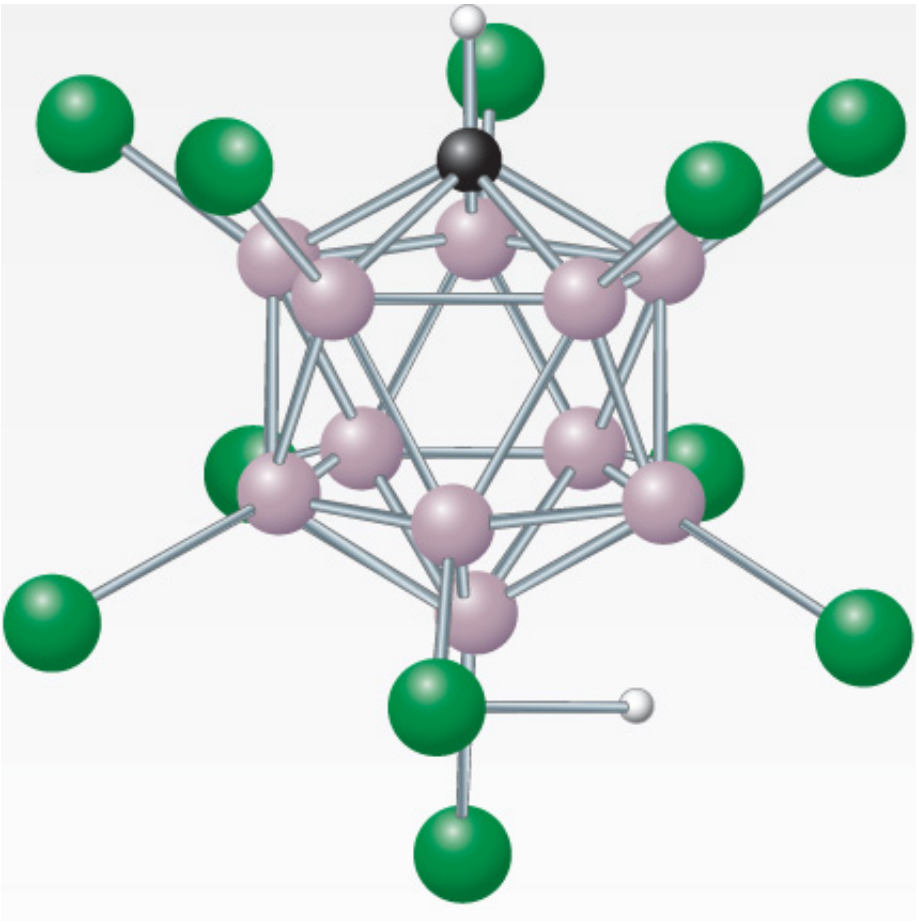


FIGURE 11.14 Representation of the structure of a carborane acid with the chemical formula $H(CHB_{11}Cl_{11})$.

Of course, if $H(CHB_{11}Cl_{11})$ is the strongest isolable acid, this must mean that its conjugate base, $CHB_{11}CL_{11}^-$, must be incredibly weak and therefore unreactive towards protonation. This low basicity has allowed the isolation and characterisation of the hydronium ion, H_3O^+, in the compound $[H_3O][CHB_{11}Cl_{11}]\cdot 4C_6H_6$, and the $H_5O_2^+$ ion in the compound $[H_5O_2][CHB_{11}Cl_{11}]\cdot C_6H_6$, both of which were isolated from benzene solution. Similar carborane anions have been used to isolate unusual cations such as the *tert*-butyl carbocation $(CH_3)_3C^+$, and the first example of a 3-coordinate silicon cation. It is certain that carborane anions will find use in the isolation of further exotic cations in future.

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11.6 Buffer Solutions

The control and maintenance of pH is crucial in many chemical and biological systems. For example, if the pH of your blood, which is typically 7.35 to 7.42, were to change to either 7.00 or 8.00, you would die. Fortunately, nature has developed a sophisticated chemical system which maintains blood pH within the vital limits. Figure 11.15 shows another application of a buffer solution.



FIGURE 11.15 A practical application of a buffer. Baking soda, which is sodium bicarbonate, is sometimes added to swimming pools to control the pH of the water.
Kari-Ann Tapp

A **buffer solution** is one that contains appreciable amounts of both a weak acid and its conjugate base, or a weak base and its conjugate acid. As a result of this, a buffer solution resists change in pH after the addition of small amounts of either acid or base, and also on moderate dilution. The pH values over which a buffer is effective at maintaining the pH are determined by either pK_a or pK_b of the weak acid or weak base, respectively, and the ratio of the concentrations of conjugate pairs present in the solution.

pH Calculations in Buffer Solutions

We will first consider a buffer solution containing equal amounts of a weak acid HA and its conjugate base A^-. A buffer solution works by being able to react to neutralise added H_3O^+ or OH^-. If we add a source of H_3O^+ to the above solution, it will react with A^- to form HA.

$$H_3O^+(aq) + A^-(aq) \rightarrow HA(aq) + H_2O(l)$$

If we add OH^- to the buffer solution, it will react with HA to form A^-.

$$OH^+(aq) + HA^-(aq) \rightarrow A^-(aq) + H_2O(l)$$

Both reactions serve to 'mop up' any added acid or base, which means that the pH of the solution remains relatively constant. We can calculate the pH of buffer solutions, both before and after the addition of either acid or base, by application of the methods we have learned so far. Consider, for example, a buffer solution containing acetic acid, CH_3COOH, and sodium acetate, $NaOOCCH_3$. Addition of acid to this solution will cause the following reaction to occur:

$$H_3O^+(aq) + CH_3COO^-(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$$

while added base will be neutralised as follows:

$$OH^-(aq) + CH_3COOH(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

Worked example 11.17 shows how we carry out calculations involving the pH of buffer solutions.

WORKED EXAMPLE 11.17

Calculating the pH of a Buffer

To study the effects of a weakly acidic medium on the rate of corrosion of a metal alloy, a student prepared a buffer solution in which [$NaOOCCH_3$] = 0.11 M and [CH_3COOH] = 0.090 M. What is the pH of this solution at 25 °C?

Analysis

The buffer solution contains both the weak acid CH_3COOH and its conjugate base CH_3COO^-, and we are given the concentrations of both. We can solve the problem by using either K_a for CH_3COOH or K_b for CH_3COO^-. We will show in detail how to use the former, and will look at the latter in practice exercise 11.24. We begin by looking up the value of K_a for CH_3COOH, then set up a concentration table and solve for [H_3O^+] using the simplifying approximations developed earlier.

Solution

We begin with the balanced chemical equation and the expression for K_a.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

We set up the concentration table and take the initial concentrations of CH_3COOH and CH_3COO^- to be the values given in the problem. We assume the initial [H_3O^+] = 0 and therefore this must increase by $+x$ as the reaction proceeds to equilibrium. The other changes follow from that. The completed table is shown below.

	H_2O + CH_3COOH $\rightleftharpoons$	H_3O^+	+ CH_3COO^-
Initial concentration (mol L^{-1})	0.090	0	0.11
Change in concentration (mol L^{-1})	$-x$	$+x$	$+x$

Equilibrium concentration (mol L^{-1})	0.090 - *x*	*x*	0.11 + *x*

For buffer solutions, the quantity *x* will be very small. This is because the conjugate base of the weak acid is already present in solution, so this suppresses the dissociation of the weak acid as a result of the common ion effect. We can therefore safely assume that (0.090 - *x*) ≈ 0.090 and (0.11 + *x*) ≈ 0.11. Substituting these quantities into the K_a expression gives:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(0.11+x)}{0.090-x} \approx \frac{(x)(0.11)}{0.090} = 1.8 \times 10^{-5}$$

We solve for *x* as follows:

$$\begin{aligned} 0.11x &= (0.090)(1.8 \times 10^{-5}) \\ x &= \frac{(0.090)(1.8 \times 10^{-5})}{0.11} \\ &= 1.5 \times 10^{-5} \end{aligned}$$

Because *x* equals $[H_3O^+]$, we now have $[H_3O^+] = 1.5 \times 10^{-5}$ M. Then we calculate pH:

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] = -\log(1.5 \times 10^{-5}) \\ &= 4.82 \end{aligned}$$

Thus the pH of the buffer is 4.82.

Is our answer reasonable?

We can check the answer in the usual way by substituting our calculated equilibrium values into the expression for K_a.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(1.5 \times 10^{-5})(0.11)}{0.090} = 1.8 \times 10^{-5}$$

This equals K_a, so the values we have obtained are correct equilibrium concentrations.

PRACTICE EXERCISE 11.24

Calculate the pH of the buffer solution in the preceding example by using the K_b for CH_3COO^-. Be sure to write the chemical equation for the equilibrium as the reaction of CH_3COO^- with water. Then use the chemical equation as a guide in setting up the equilibrium expression for K_b. If you work through the problem correctly, you should obtain the same answer as above.

We can rearrange the expression for K_a into a form that is particularly useful for calculations involving buffer solutions, and which also removes the need to write a concentration table for each calculation.

We know that, for the equilibrium:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

we can write K_a as:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

If we multiply both sides of the equation by [HA] and divide both sides by [A^-], we obtain:

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

If we take the negative logarithm (p) of both sides, realising that the logarithm of a product of two numbers is the sum of the logarithms of those numbers, and that $-\log\frac{x}{y}$ $\log\frac{y}{x}$, we obtain:

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

This rearrangement of the K_a expression is called the **Henderson–Hasselbalch equation**. This form of the K_a expression emphasises the fact that the pH of a buffer solution depends on both the pK_a of the weak acid and the ratio of conjugate base to acid. Recalling that $c = \frac{n}{V}$, we can rewrite the equation as:

$$pH = pK_a + \log\left[\frac{\frac{n_{A^-}}{V}}{\frac{n_{HA}}{V}}\right]$$

and therefore:

$$pH = pK_a + \log\frac{n_{A^-}}{n_{HA}}$$

Therefore we can express this relationship in terms of either a concentration ratio or a mole ratio. Note that, under the special condition where [HA] = [A^-] (or $n_{HA} = n_{A^-}$), $\frac{[A^-]}{[HA]} = 1$, log(1) = 0, and therefore pH = pK_a.

A further consequence of the relationship derived above is that the pH of a buffer should not change if the buffer undergoes moderate dilution. Dilution changes the volume of a solution but it does not change the amounts of the solutes, so their mole ratio remains constant and so does [H_3O^+].

WORKED EXAMPLE 11.18

Calculating the pH of an Ammonia/Ammonium Ion Buffer

To study the influence of an alkaline medium on the rate of a reaction, a student prepared a buffer solution by dissolving 0.12 mol of NH_3 and 0.095 mol of NH_4Cl in 250 mL of water. What is the pH of the buffer at 25 °C?

Analysis

The pH of the buffer is determined by the mole ratio of the members of the acid–base pair; so to calculate the pH we use the amounts of NH_3 and NH_4^+ directly in the Henderson–Hasselbalch equation. We also require the pK_a of NH_4^+.

Solution

Given that pK_a(NH_4^+) = 9.26, we can insert the values directly into the Henderson–Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log\frac{^n\text{A}^-}{^n\text{HA}} = 9.26 + \log\frac{0.12}{0.095} = 9.36$$

Note that we assumed that the initial concentrations of the acid and conjugate base are the equilibrium concentrations. We are usually justified in doing this.

Is our answer reasonable?

There is more base than acid in the buffer. Therefore the ratio $\frac{[A^-]}{[HA]}$ is greater than 1, and the log of this ratio will be positive. We would therefore expect a pH greater than the pK_a, which we have obtained.

PRACTICE EXERCISE 11.25

Determine the pH of the buffer in worked example 11.18 when [NH_3] = 0.08 M and [NH_4Cl] = 0.15 M.

Buffer solutions function most efficiently when the ratio $\frac{[A^-]}{[HA]}$ is close to 1. When this is the case, the concentrations of both the weak acid and its conjugate base are essentially equal, and the buffer can therefore resist change in pH on the addition of either acid or base. As we showed above, when $\frac{[A^-]}{[HA]} = 1$, pH = pK_a, and therefore the pK_a of the weak acid determines where, on the pH scale, a buffer can work best. Thus, to prepare a specific buffer for use at a particular pH, we first select a weak acid with a pK_a near the desired pH. Then, by experimentally adjusting the ratio $\frac{[A^-]}{[HA]}$. we can make a final adjustment to obtain the desired pH.

If the ratio $\frac{[A^-]}{[HA]}$ is significantly different from 1, then the concentrations of the weak acid and its conjugate base in solution are no longer similar. If, for example, [HA] > [A^-], the buffer will resist change in pH well on the addition of base, but it will be less effective at resisting change in pH on addition of acid, as there is less A^- present for the added acid to react with. Once all the A^- has reacted, the pH of the solution will change rapidly. As long as the ratio $\frac{[A^-]}{[HA]}$ in a buffer solution is between

$\frac{1}{10}$ and $\frac{10}{1}$, the buffer will maintain pH effectively. If we substitute these values into the Henderson–Hasselbalch equation, we obtain pH = pK_a - 1 and pH = pK_a + 1, respectively. This means that the operational range of any buffer is 1 pH unit either side of the pK_a of the weak acid, i.e. pH = pK_a ± 1.

WORKED EXAMPLE 11.19

Preparing a Buffer Solution with a Predetermined pH

A solution buffered at a pH of 5.00 is needed in an experiment. Can we use acetic acid and sodium acetate to prepare the buffer? If so, what amount of $NaOOCCH_3$ must be added to 1.0 L of a solution that contains 1.0 mol $NaOOCCH_3$ at 25 °C?

Analysis

There are two parts to this problem. To answer the first, we check the pK_a of acetic acid to see if it is in the desired range of pH = pK_a ± 1. If it is, we can calculate the necessary mole ratio. Once we have this, we can proceed to calculate the amount of CH_3COO^- needed and then the amount of $NaOOCCH_3$.

Solution

The pK_a of acetic acid (4.74) falls in the desired range and therefore acetic acid can be used with the acetate ion to make the buffer.

We find the required mole ratio of solutes by using the Henderson–Hasselbalch equation.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{{}^{n}\mathrm{A}^-}{{}^{n}\mathrm{HA}}$$

$$5.00 = 4.74 + \log\frac{{}^{n}\mathrm{CH_3COO}^-}{{}^{n}\mathrm{CH_3COOH}}$$

Therefore:

$$\log\frac{{}^{n}\mathrm{CH_3COO}^-}{{}^{n}\mathrm{CH_3COOH}} = 0.26$$

and hence:

$$\frac{{}^{n}\mathrm{CH_3COO}^-}{{}^{n}\mathrm{CH_3COOH}} = 1.82$$

$${}^{n}\mathrm{CH_3COO}^- = 1.82 \times {}^{n}\mathrm{CH_3COOH}$$

We know that $n_{CH_3COOH} = 1.0$ mol and so $n_{CH_3COO^-} = 1.82$ mol mol.

Because each mole of $NaOOCCH_3$ contains 1 mole of CH_3COO^-, we require 1.82 mol $NaOOCCH_3$.

Is our answer reasonable?

A 1 : 1 mole ratio of CH_3COO^- to CH_3COOH would give pH = pK_a = 4.74. The desired pH

of 5.00 is slightly more basic than 4.74, so the amount of conjugate base should be larger than the amount of conjugate acid. Our answer of 1.82 mol of $NaOOCCH_3$ appears to be reasonable.

PRACTICE EXERCISE 11.26

A chemist needs an aqueous buffer with a pH of 3.90. Would formic acid, HCOOH, and its salt, sodium formate, NaOOCH, make a good pair for this purpose? If so, what mole ratio of the acid to the anion of the salt is needed? What mass of NaOOCH would have to be added to a solution that contains 0.10 mol HCOOH at 25 °C?

Once we have prepared a buffer solution, we can calculate the pH change on addition of a specified amount of strong acid or base by assuming that the added strong acid or base reacts quantitatively with the weak acid or base component of the buffer solution. This is illustrated in worked example 11.20.

WORKED EXAMPLE 11.20

Calculating the pH Change in a Buffer Solution

What pH change will occur after the addition of 0.10 L of 0.10 M HCl to 1.0 L of a buffer solution containing 0.10 mol CH_3COOH and 0.10 mol $NaOOCCH_3$ at 25 °C? How does this compare with the pH change that would occur after the addition of the same amount of HCl to 1.0 L of pure water?

Analysis

We are asked for a pH *change*, which means we have to calculate the pH of the initial buffer solution. We then calculate the amount of HCl added and assume that this reacts completely with CH_3COO^- to form CH_3COOH. We then use the new amounts of CH_3COO^- and CH_3COOH in the Henderson–Hasselbalch equation to calculate the final pH. The question involving pure water is a straightforward calculation of the pH of a strong acid.

Solution

The initial pH can be obtained from the initial $[CH_3COOH]$ and $[CH_3COO^-]$ values using the Henderson–Hasselbalch equation.

$$\begin{aligned} \mathrm{pH} &= \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \\ &= 4.74 + \log\frac{0.1}{0.1} \\ &= 4.74 \end{aligned}$$

We now carry out a stoichiometric calculation to determine the equilibrium $^{n}CH_3COOH$ and $^{n}CH_3COO^-$ values. The reaction which will occur on addition of the strong acid is:

$$HCl(aq) + CH_3COO^-(aq) \rightarrow CH_3COOH(aq) + Cl^-(aq)$$

We assume this reaction goes to completion, so that:

$$\begin{aligned} ^{n}HCl(\text{added}) &= {}^{n}CH_3COO^-(\text{used}) = {}^{n}CH_3COOH(\text{formed}) \\ ^{n}HCl(\text{added}) &= c \times V \\ &= 0.10\ \text{mol}\,L^{-1} \times 0.10\ L \\ &= 0.010\ \text{mol} \end{aligned}$$

Therefore, 0.010 mol HCl(aq) reacts with 0.010 mol CH_3COO^-(aq) to form 0.010 mol CH_3COOH(aq). Initially we had 0.10 mol CH_3COOH and 0.10 mol CH_3COO^-, and so the final amounts are:

$$\begin{aligned} n_{CH_3COOH(\text{final})} &= 0.10\ \text{mol} + 0.010\ \text{mol} = 0.11\ \text{mol} \\ n_{CH_3COO^-(\text{final})} &= 0.10\ \text{mol} - 0.010\ \text{mol} = 0.090\ \text{mol} \end{aligned}$$

We now substitute these values into the Henderson–Hasselbalch equation.

$$\begin{aligned} \text{pH} &= 4.74 + \log\frac{0.090}{0.11} \\ &= 4.65 \end{aligned}$$

Therefore, the *change* in pH is - 0.09 pH units, the negative sign showing that this is a decrease in pH.

When we add 0.10 L of 0.10 mol L^{-1} HCl to 1.0 L of water, the final solution contains 0.010 mol HCl in 1.1 L. As HCl is a strong acid, it reacts completely with water to form H_3O^+ and hence:

$$\left[H_3O^+\right] = \frac{0.010\ \text{mol}}{1.1\ L} = 0.0091\ \text{mol}\,L^{-1}$$

Thus, pH = –log[H_3O^+] = –log(0.0091) = 2.04.

We started with pure water, and so the initial pH was 7.00. Hence, the pH change is - 4.96 pH units.

Is our answer reasonable?

We started with the buffer solution at pH 4.74 and added a small amount of strong acid to it. We expect that the final pH should be slightly less than this, which it is.

PRACTICE EXERCISE 11.27

Calculate the pH change on the addition of 0.10 L of 0.10 M NaOH to 1.0 L of a buffer solution containing 0.08 mol NH_3(aq) (pK_b = 4.74) and 0.12 mol NH_4Cl(aq) at 25 °C.

Worked example 11.20 illustrates the effectiveness of a buffer solution. When the strong acid is added to water, the solution becomes 4.96 pH units more acidic, whereas the buffer solution is little affected, becoming only 0.09 pH units more acidic.

If enough strong acid is added to react with all of the base component of a buffer solution, the mixture is no longer able to neutralise any more strong acid. We can illustrate this with reference to worked example 11.20. Initially there is 0.10 mol CH_3COO^- in the buffer solution; if 0.10 mol HCl is added, this will react completely with the 0.10 mol CH_3COO^- to give 0.10 mol CH_3COOH. When this happens, the concentration of CH_3COO^- is very small (all of the CH_3COO^- in solution at this point will come from dissociation of CH_3COOH) and the solution no longer functions as a buffer towards the addition of more acid. Similarly, if we added 0.10 mol NaOH to the original buffer solution in the example, it would react completely with the 0.10 mol CH_3COOH present to form 0.10 mol CH_3COO^-, thereby leaving essentially no CH_3COOH in the solution to react with any further added NaOH. This means that there is a limit to the amount of added acid or base that a buffer solution can absorb. The **buffer capacity** of any buffer is a measure of the amount of H_3O^+ or OH^- that can be added without significant change in the pH. In the example, the addition of ˜0.10 mol HCl or ˜0.10 mol NaOH would exhaust the capacity of the buffer solution.

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11.7 Acid–base Titrations

We often encounter solutions of acid or bases with unknown concentrations in chemistry. One method of determining the concentration of an acid or a base is to carry out an **acid–base titration** (figure 11.16). This involves gradual addition of an acid or base of known concentration (the **titrant**) from a **burette** to an accurately known volume of the unknown solution. An **acid–base indicator** changes colour when the **endpoint** of the titration is reached, and, if we have chosen the indicator correctly, the endpoint will be a good approximation of the **equivalence point** of the titration. The equivalence point is the point at which the reaction stoichiometry is satisfied, or, in other words, where the amount of titrant added exactly equals the amount of acid or base initially present. The equivalence point is sometimes called the stoichio-metric point. In all acid–base titrations, regardless of the strengths of the acid or base involved, the essential reaction that occurs is:

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$$



FIGURE 11.16 An acid–base titration. Phenolphthalein is often used as an indicator to detect the endpoint.

Knowledge of both the stoichiometry of the reaction and the volume of acid or base added allows us to calculate the concentration of the unknown solution. We will now examine acid– base titrations in a little more detail, with particular emphasis on the variations in pH that occur as the titrations proceed.

Strong Acid–Strong Base and Strong Base–Strong Acid Titrations

Figure 11.17 shows a plot of pH versus volume of titrant added for the titration of 25.00 mL of 0.200 M HCl(aq) with 0.200 M NaOH(aq). We call such a plot a **titration curve**, and it has the same general shape for the titration of any strong acid with any strong base. Likewise, the titration curve for the titration of 25.00 mL of 0.200 M NaOH with 0.200 M HCl is depicted in figure 11.18, and this too is general for the titration of any strong base with any strong acid. We will consider the strong acid–strong base (note that the titrant comes last when describing a titration) titration curve in detail, realising that analogous arguments apply for the strong base–strong acid titration.

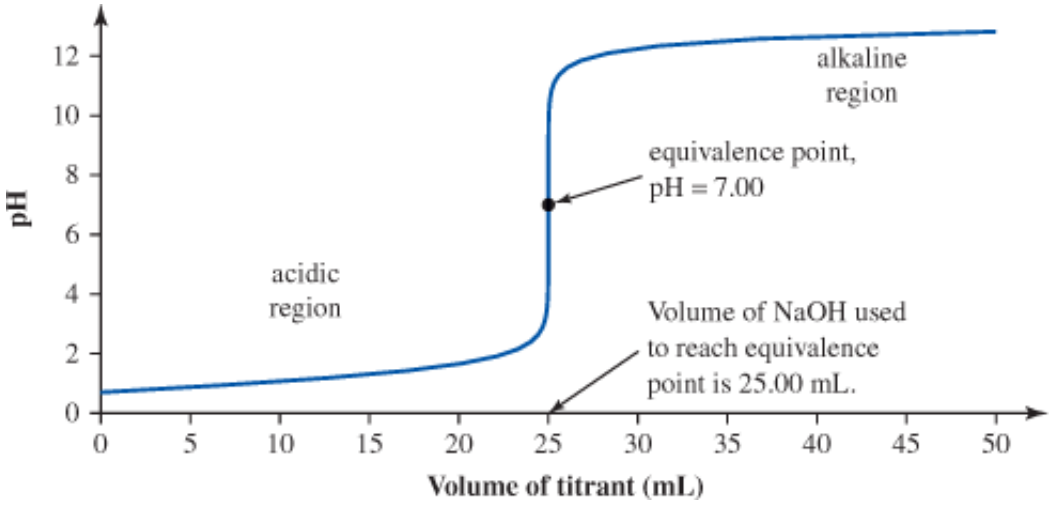


FIGURE 11.17 Titration curve for the titration of a strong acid with a strong base. Here we follow how the pH changes during the titration of 25.00 mL of 0.200 M HCl(aq) with 0.200 M NaOH(aq).

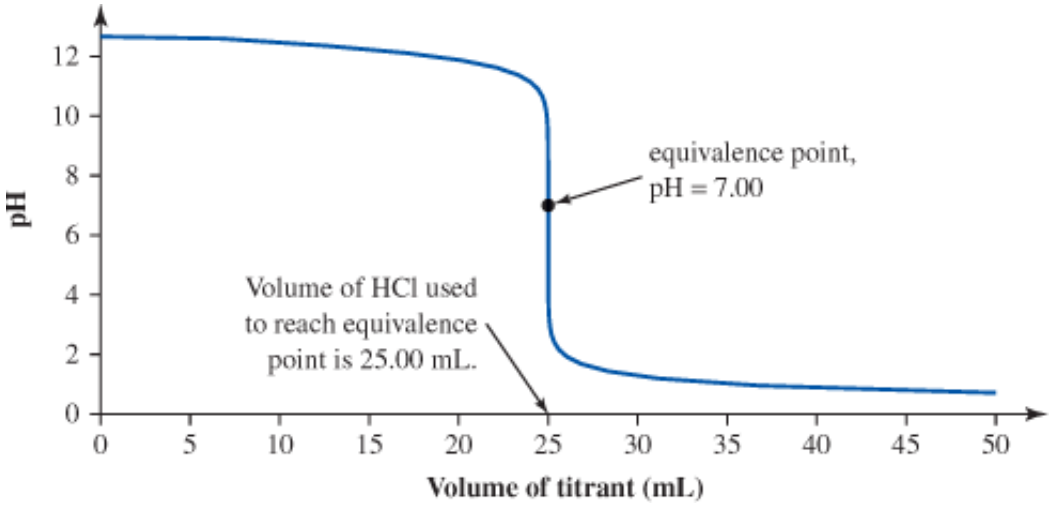


FIGURE 11.18 Titration curve for the titration of a strong base with a strong acid (25.00 mL 0.200 M NaOH(aq) with 0.200 M HCl(aq)).

There are four important points and regions to consider for a strong acid–strong base titration curve:

1. the initial pH
2. the acidic region
3. the equivalence point
4. the alkaline region.

The initial pH

The initial pH in a strong acid–strong base titration is the pH of the strong acid being titrated. Because the acid is strong, it will react completely with water to generate H_3O^+, and therefore we can calculate the pH by taking the negative logarithm of the acid concentration. For the titration curve in figure 11.17, the initial pH will be:

$$\begin{aligned} \text{pH} &= -\log\left[H_3O^+\right] \\ &= -\log(0.200) \\ &= 0.70 \end{aligned}$$

The acidic region

In the acidic region, we are adding OH^- to a solution of H_3O^+, and the essential reaction that occurs is:

$$OH^-(aq) + H_3O^+(aq) \rightarrow 2H_2O(l)$$

As you can see from figure 11.17, the pH initially changes very slowly on addition of NaOH(aq), and it is not until the equivalence point is approached that the pH starts to increase significantly. In the acidic region, the solution contains H_3O^+ and Cl^- ions from the acid, and Na^+ ions from the base, and the pH is governed by the amount of unreacted H_3O^+ in the solution. The concentration of H_3O^+decreases as NaOH is added, and, at any point in this region, it can be calculated from the equation:

$$\begin{aligned} \left[H_3O^+\right] &= \frac{{}^{n}H_3O^+(\text{initial}) - {}^{n}OH^-(\text{added})}{V_{\text{total}}} \\ &= \frac{\left(c_{H_3O^+(\text{initial})} \times V_{(\text{initial})}\right) - \left(c_{OH^-(\text{added})} \times V_{(\text{added})}\right)}{V_{\text{total}}} \end{aligned}$$

where $c_{H_3O^+(\text{initial})}$ is the initial concentration of the acid, $c_{OH^-(\text{added})}$ is the concentration of the NaOH solution, *V*initial is the initial volume of the acid solution, *V*added is the volume of the NaOH solution added and *V*total is the total volume of the solution ($V_{\text{total}} = V_{\text{initial}} + V_{\text{added}}$). Although this equation looks somewhat formidable, careful inspection reveals that it is merely $c = \frac{n}{V}$ in another form; the top line is the amount of H_3O^+ in the solution, calculated by subtracting the amount of OH^- added from the amount of H_3O^+ present initially. Notice that, even though the pH changes little on addition of NaOH in the acidic region, the resulting solution is not a buffer solution — the pH of this solution will change significantly on moderate dilution, in contrast to a solution containing significant amounts of a weak acid and its conjugate base.

The equivalence point

We defined the equivalence point as the point where the reaction stoichiometry is satisfied. This means that we have added exactly the same amount of OH^- as there were moles of H_3O^+ in the initial solution of acid. As we originally had 25.00 mL of 0.200 M HCl, this point occurs when we have added 25.00 mL of 0.200 M NaOH. Therefore, at this point on the titration curve, the reaction:

$$OH^-(aq) + H_3O^+(aq) \rightarrow 2H_2O(l)$$

has gone to completion, and the solution contains only Na^+ and Cl^- ions in water. The pH of the solution

at the equivalence point is exactly 7.00, because Cl^- is the conjugate base of a very strong acid and therefore has essentially no basic properties. The pH at the equivalence point will *always* be 7.00 for the titration of any strong monoprotic acid with a strong base.

The alkaline region

Beyond the equivalence point, we are adding excess NaOH(aq) to a solution containing Na^+(aq) and Cl^-(aq), so there is no chemical reaction occurring. The pH in this region is governed by the amount of excess NaOH(aq) added to the solution and will always be > 7. The concentration of OH^-, and hence the pH, can be calculated from the following equation:

$$[OH^-] = \frac{{}^{n}OH^-(\text{total}) - {}^{n}OH^-(\text{equiv})}{V_{\text{total}}} = \frac{(c_{OH^-(\text{initial})} \times V_{\text{added}}) - (c_{OH^-(\text{initial})} \times V_{\text{equiv}})}{V_{\text{total}}}$$

where $c_{OH^-(\text{initial})}$ is the concentration of the NaOH solution, V_{added} is the total volume of NaOH solution added, V_{equiv} is the volume of NaOH solution added at the equivalence point (in this case, 25.00 mL) and *V*total is the total volume of the solution. The top line gives the amount of OH^- in excess of that required to reach the equivalence point; this is obtained by subtracting the amount of OH^- used to reach the equivalence point from the total amount of OH^- added.

Weak Acid–Strong Base and Weak Base–Strong Acid Titrations

Figure 11.19 shows the titration curve for the titration of 25.00 mL of 0.200 M CH_3COOH(aq) with 0.200 M NaOH(aq), while the titration curve for the titration of 25.00 mL of 0.200 M $NH_3$with 0.200 M HCl is given in figure 11.20. We will focus on the weak acid–strong base curve, realising that analogous arguments can be made for the weak base–strong acid case. As you can see, the weak acid–strong base curve looks rather different from the strong acid–strong base curve (figure 11.17), especially in the acidic region. We will again consider in detail the four important points and regions on this curve.

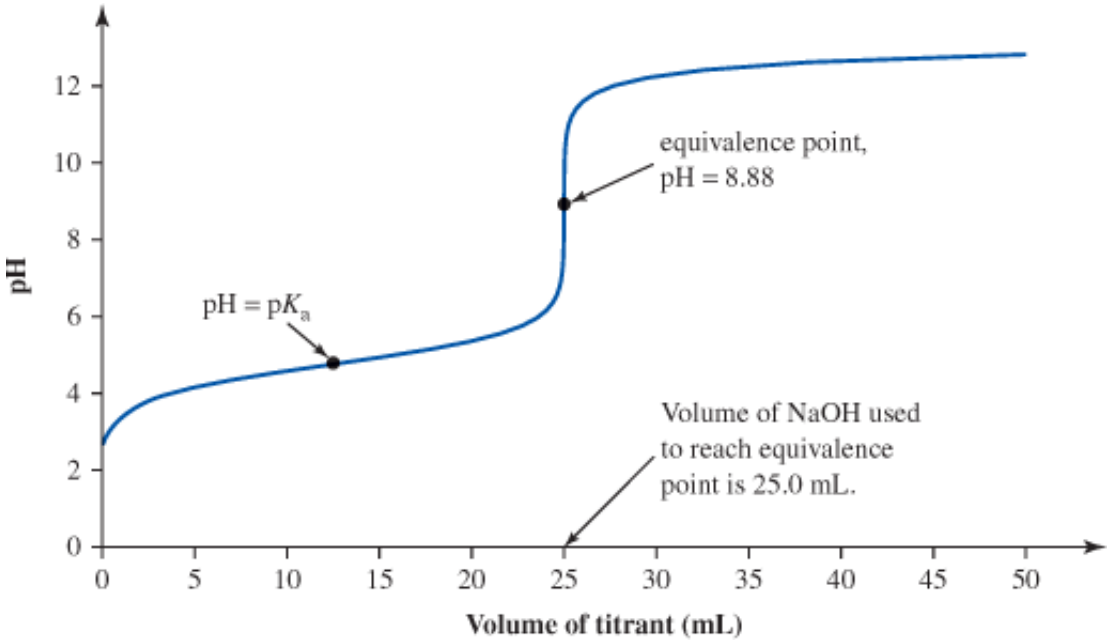


FIGURE 11.19 Titration curve for the titration of a weak acid with a strong base. In this titration, we follow the pH as 25.00 mL of 0.200 M $CH_3COOH(aq)$ is titrated with 0.200 M NaOH(aq).

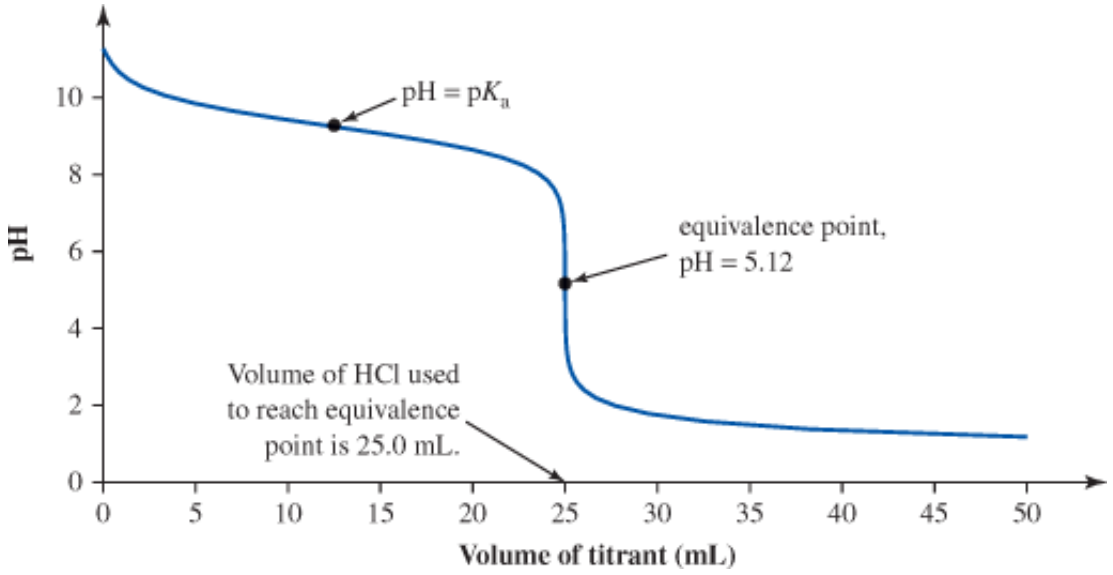


FIGURE 11.20 Titration curve for the titration of a weak base with a strong acid. Here we follow the pH as 25.00 mL of 0.200 M $NH_3(aq)$ is titrated with 0.200 M HCl(aq).

The Initial pH

The initial pH of 2.72 in this titration is significantly higher than that for the strong acid–strong base titration. This is to be expected as CH_3COOH is a weak acid and dissociates only to a small extent. We can calculate the initial pH of the acid solution in a weak acid–strong base titration with the method that was used for the calculation of the pH of a solution of a weak acid. We therefore set up a concentration table for a 0.200 M CH_3COOH solution. The balanced chemical equation is:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

and the equilibrium constant expression is:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

The concentration table can then be written as:

	$H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$		
Initial concentration (mol L^{-1})	0.200	0	0
Change in concentration (mol L^{-1})	$-x$	$+x$	$+x$
Equilibrium concentration (mol L^{-1})	0.200 - x	x	x

We make the usual assumption that x is small compared with 0.200, and therefore (0.200 - x) ≈ 0.200. Substituting the equilibrium concentrations into the equilibrium constant expression gives:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.200} = 1.8 \times 10^{-5}$$

and solving for x gives:

$$x^2 = (0.200)\left(1.8 \times 10^{-5}\right) = 3.6 \times 10^{-6}$$

$$x = \sqrt{3.6 \times 10^{-6}} = 1.9 \times 10^{-3}$$

As $x = [H_3O^+]$, we obtain the pH of the solution by:

$$pH = -\log\left[H_3O^+\right] = -\log\left(1.9 \times 10^{-3}\right) = 2.72$$

The Acidic Region

The general shape of the titration curve in this region differs from that for the strong acid–strong base titration in that there is an initial rapid increase in pH. The curve also lies at higher pH values than the analogous points of the strong acid–strong base titration. While the only reaction of note in the strong acid–strong base titration was $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$, the situation is more complicated when weak acids or bases are involved. In this case, initial addition of NaOH(aq) to $CH_3COOH(aq)$ forms $CH_3COO^-(aq)$ according to the equation:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaOOCCH_3(aq) + H_2O(l)$$

Initially, the pH of the solution changes rapidly, but, once the concentration of CH_3COO^- has increased sufficiently, the solution contains appreciable amounts of a weak acid and its conjugate base — in other words, we have a buffer solution. The pH in this region will therefore be governed by the ratio $\frac{[CH_3COO^-]}{[CH_2COOH]}$ through the Henderson–Hasselbalch equation $pH = pK_a + \log\frac{[A^-]}{[HA]}$. At the point halfway to the equivalence point, this ratio will be 1, and therefore pH = pK_a. Therefore, a titration of a weak acid with a strong base tells us not only the concentration of the weak acid but also its pK_a; we simply take the pH reading at the volume halfway to the equivalence point. While we can calculate the pH at any point in the acidic region using the Henderson–Hasselbalch equation, it can be more conveniently written in terms of concentrations and volumes of the solutions involved in the titration. The amount of CH_3COO^- is equal to the amount of NaOH added, and the amount of CH_3COOH in the solution at any point is equal to the initial amount of CH_3COOH minus the amount of NaOH added, so we can rewrite this equation as follows:

$$\begin{aligned}
\mathrm{pH} &= \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \\
&= \mathrm{p}K_\mathrm{a} + \log\frac{{}^{n}\mathrm{OH}^-(\text{added})}{{}^{n}\mathrm{HA}\ (\text{initial}) \ - {}^{n}\mathrm{OH}^-(\text{added})} \\
&= \mathrm{p}K_\mathrm{a} + \log\frac{(c_{\mathrm{OH}^-}(\text{initial}) \times V_{\mathrm{OH}^-(\text{added})})}{(c_{\mathrm{HA}}(\text{initial}) \times V_{\text{initial}}) - (c_{\mathrm{OH}^-}(\text{initial}) \times V_{\mathrm{OH}^-(\text{added})})}
\end{aligned}$$

where $c_{\text{OH-(initial)}}$ is the initial concentration of the NaOH solution, $V_{\mathrm{OH}^-(\text{added})}$ is the volume of the NaOH solution added, $c_{\text{HA (initial)}}$ is the initial concentration of the acid solution and V_{initial} is the initial volume of the acid solution.

Note that this equation is not exact, as it does not take into account the dissociation of the acid or the reaction of the conjugate base with water. However, as both of these reactions are suppressed by the common ion effect in a buffer solution, it gives a very good approximation, especially when the concentrations of the acid and conjugate base are similar. You should not attempt to memorise the previous equation, as it can be derived from the Henderson–Hasselbalch equation, which itself is derived from the K_a expression for a weak acid.

As we approach the equivalence point of the titration, the reaction:

$$\mathrm{CH_3COOH(aq) + NaOH(aq) \rightarrow NaOOCCH_3(aq) + H_2O(l)}$$

proceeds further towards completion and the pH starts to increase rapidly. This is because we have exhausted the capacity of the buffer solution; nearly all the CH_3COOH has been used up, and there is no longer sufficient acid present to be able to react with any added OH^-.

The Equivalence Point

At the equivalence point, the reaction:

$$\mathrm{CH_3COOH(aq) + NaOH(aq) \rightarrow NaOOCCH_3(aq) + H_2O(l)}$$

has gone to completion and the solution contains 0.100 M $Na^+(aq)$ and 0.100 M $CH_3COO^-(aq)$. In other words, at this point we have a 0.1 M aqueous solution of $NaOOCCH_3$. We have seen previously that CH_3COO^-, being the conjugate base of a weak acid, is appreciably basic, and therefore the following reaction will occur:

$$\mathrm{CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)}$$

This means that, at the equivalence point, there is a small amount of OH^- in the solution, and therefore the pH is greater than 7.00 (in this case it is 8.88, as we show below). In the titration of any weak acid with any strong base, the pH at the equivalence point is always greater than 7, because the conjugate base of the weak acid is measurably basic. The exact pH depends on both the K_b and the concentration of the conjugate base; the weaker the acid, the stronger its conjugate base, and therefore the more basic the solution at the equivalence point. Calculation of the pH at the equivalence point follows the method we outlined previously for the determination of the pH of a salt of a weak acid. The balanced chemical equation we need to consider is:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

We will use K_b to determine [OH^-], and hence pH:

$$K_b = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} = 5.6 \times 10^{-10}$$

The concentration table is as follows. Note that the initial concentration of CH_3COO^- is 0.100 m; this is because at the equivalence point the solution has twice its starting volume due to the added NaOH solution.

	$H_2O + CH_3COOH^- \rightleftharpoons$	CH_3COOH	$+ OH^-$
Initial concentration (mol L^{-1})	0.100	0	0
Change in concentration (mol L^{-1})	$-x$	$+x$	$+x$
Equilibrium concentration (mol L^{-1})	0.100 - x	x	x

We make the assumption that x will be small compared with 0.100, because CH_3COO^- is a weak base. Therefore (0.100 - x) ≈ 0.100. We then substitute values into the K_b expression:

$$K_b = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} = \frac{(x)(x)}{0.100} = 5.6 \times 10^{-10}$$

Solving this for x gives:

$$x^2 = (1.100)\left(5.6 \times 10^{-10}\right) = 5.6 \times 10^{-11}$$

$$x = \sqrt{5.6 \times 10^{-11}} = 7.5 \times 10^{-6}$$

As x = [OH^-], we obtain the pH of the solution as follows:

$$\text{pOH} = -\log[OH^-] - \log\left(7.5 \times 10^{-6}\right) = 5.12$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.12 = 8.88$$

Analogous arguments apply for the titration of a weak base with a strong acid, and the pH at the equivalence point in such titrations is < 7. The exact pH can be calculated using the K_a for the conjugate acid of the weak base.

The Alkaline Region

Beyond the equivalence point, we are simply adding excess OH^- to a solution of a weak base, and the pH in this region is controlled by the excess amount of NaOH. The titration curve in this region is essentially identical to that for a strong acid–strong base titration, and the pH at any point in this region may therefore be calculated using the same method as described previously for such titrations.

Diprotic Acids

When a weak diprotic acid such as ascorbic acid (vitamin C) is titrated with a strong base, there are two protons available to react with the base and there are therefore two equivalence points. Provided that the values of pK_{a1} and pK_{a2} differ by several powers of 10, the neutralisation takes place stepwise and the resulting titration curve shows two sharp increases in pH as shown in figure 11.21. Calculations involving acids containing two or more acidic protons can be difficult, and lie outside the scope of this book.

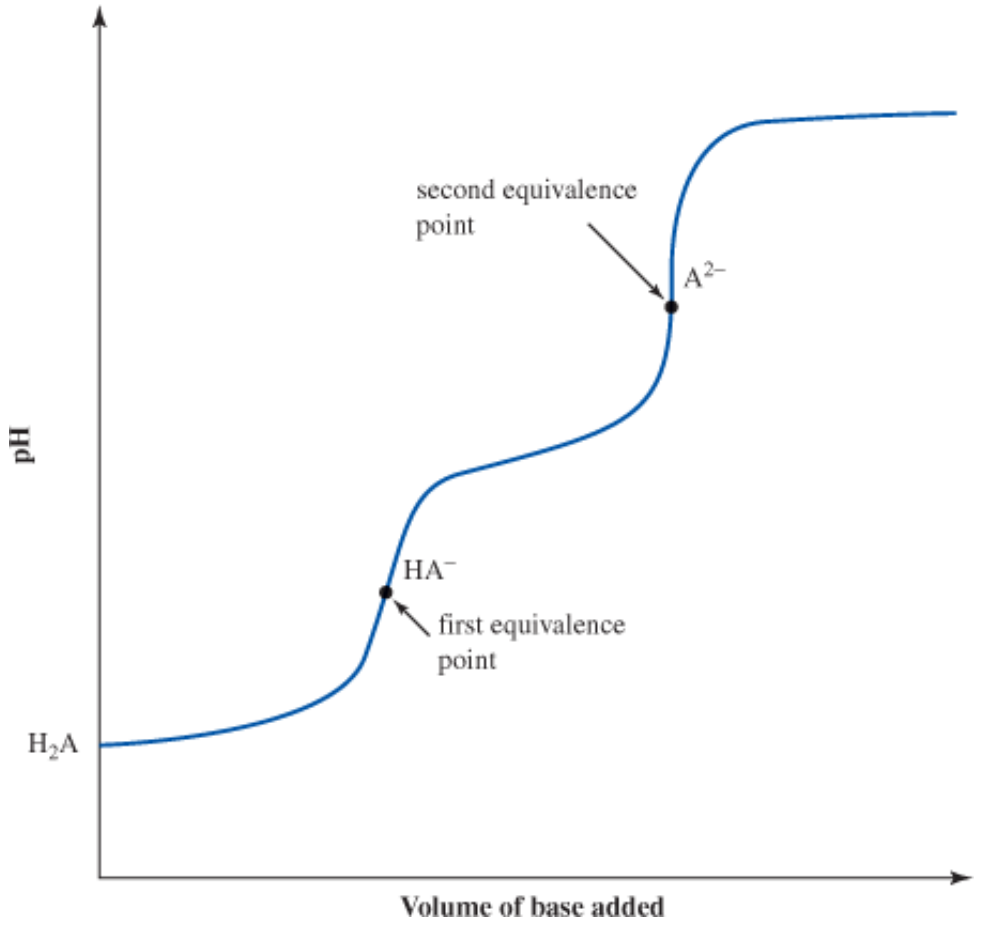


FIGURE 11.21 Titration of a diprotic acid, H_2A, by a strong base. As each equivalence point is reached, there is a sharp rise in the pH.

Speciation Diagrams

It is often useful to know the relative amounts of a weak acid and its conjugate base that are present in an aqueous solution having a particular pH. We can do this with the aid of a speciation diagram, which is a plot of mole ratio versus pH. From the speciation diagram for acetic acid in figure 11.22, we can see at a glance that undissociated CH_3COOH predominates at pH values less than 4.74 (the pK_a of acetic acid). At the point where pH = pK_a, there are equal amounts of CH_3COOH and CH_3COO^-, and the two lines therefore intersect. At higher pH values, the conjugate base, CH_3COO^-, is present in greater amounts than the undissociated acid; beyond pH 8, there is essentially no CH_3COOH present in the solution.

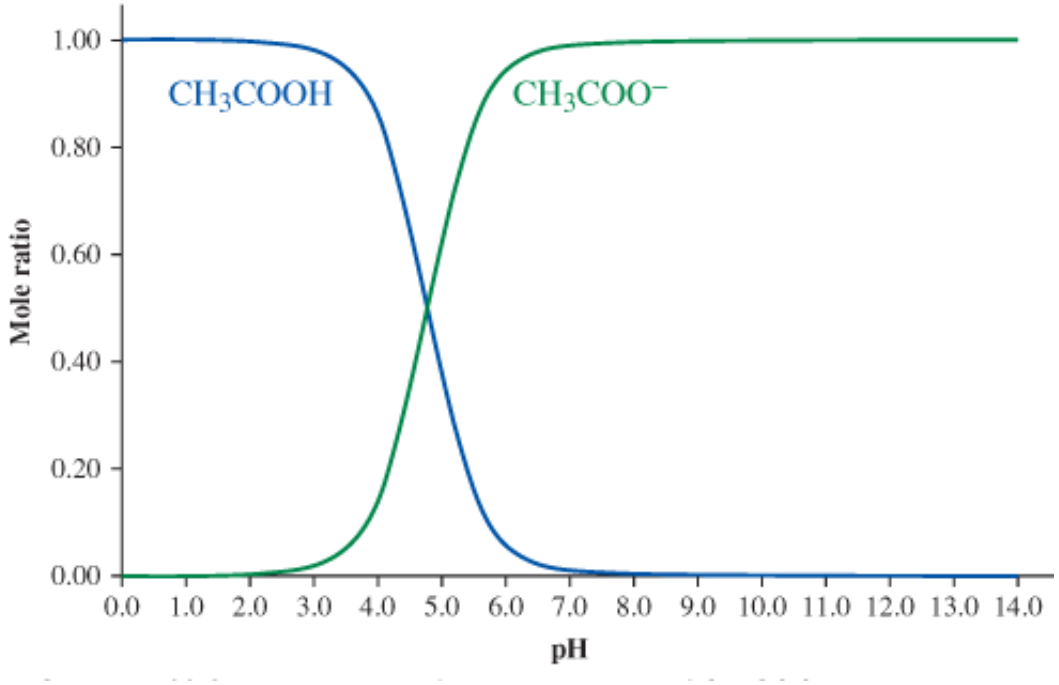


FIGURE 11.22 Speciation diagram for the dissociation of CH_3COOH in aqueous solution.

Speciation diagrams are relatively simple for monoprotic acids, but become somewhat more complicated, and consequently somewhat more useful, for polyprotic acids. Figure 11.23 shows the speciation diagram for H_3PO_4, a triprotic acid, which yields the anions $H_2PO_4^{2-}$, HPO_4^{2-} and PO_4^{3-} on successive deprotonations. The pK_a values:

$$\begin{aligned} pK_a(H_3PO_4) &= 2.15 \\ pK_a(H_3PO_4^-) &= 7.20 \\ pK_a\left(H_3PO_4^{2-}\right) &= 12.3 \end{aligned}$$

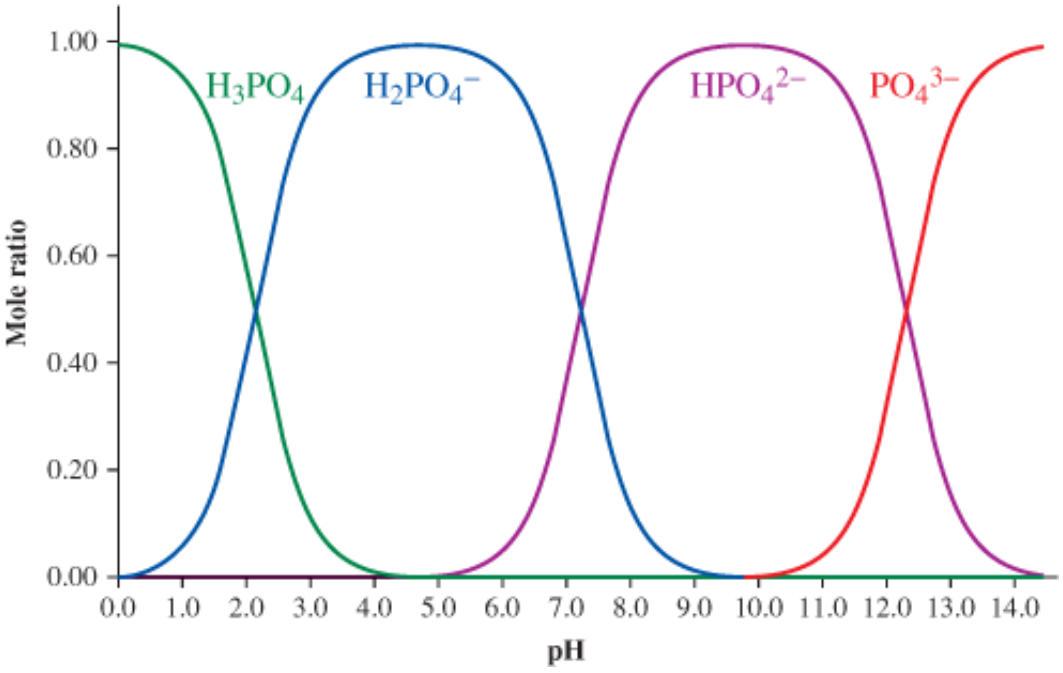


FIGURE 11.23 Speciation diagram for the dissociation of H_3PO_4 in aqueous solution.

It can be seen that H_3PO_4 predominates in very acidic regions, but, by pH 4, it has mostly been deprotonated to form $H_2PO_4^-$. As we proceed past the pK_a of $H_2PO_4^-$ (7.20), its conjugate base,

HPO_4^{2-}, is present in the largest amount until the pH increases past 12.3, the pK_a of HPO_4^{2-}. Under these conditions, PO_4^{3-} then becomes the dominant species in solution.

Speciation diagrams are extremely useful not only in situations involving polyprotic acids, but also in systems where metal ions react with ligands (see chapter 13), which them-selves contain acidic protons. The calculations involved can be rather complex, especially in systems involving a number of components, but can usually be carried out satisfactorily using spreadsheets.

Acid–base Indicators

The indicators used in acid–base titrations are themselves weak acids, which we can represent by the formula H *In*. A requirement of an acid–base indicator is that its 'acid form' H *In* and conjugate 'base form' In^- have different colours. In solution, the indicator is involved in a typical acid–base equilibrium.

$$\underset{\text{acid form}}{\underset{\text{colour 1}}{HIn(aq)}} + H_2O(1) \rightleftharpoons H_3O^+(aq) + \underset{\text{base form}}{\underset{\text{colour 2}}{In^-(aq)}}$$

The corresponding acid ionisation constant K_{In} is given by:

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$

In a strongly acidic solution, when $[H_3O^+]$ is high, the equilibrium is shifted to the left, and most of the indicator exists in its acid form. Under these conditions, the colour we observe is that of H *In*. If base is added to the solution, the $[H_3O^+]$ drops and the equilibrium shifts to the right, towards In^-. The colour we then observe is that of the base form of the indicator (figure 11.24).

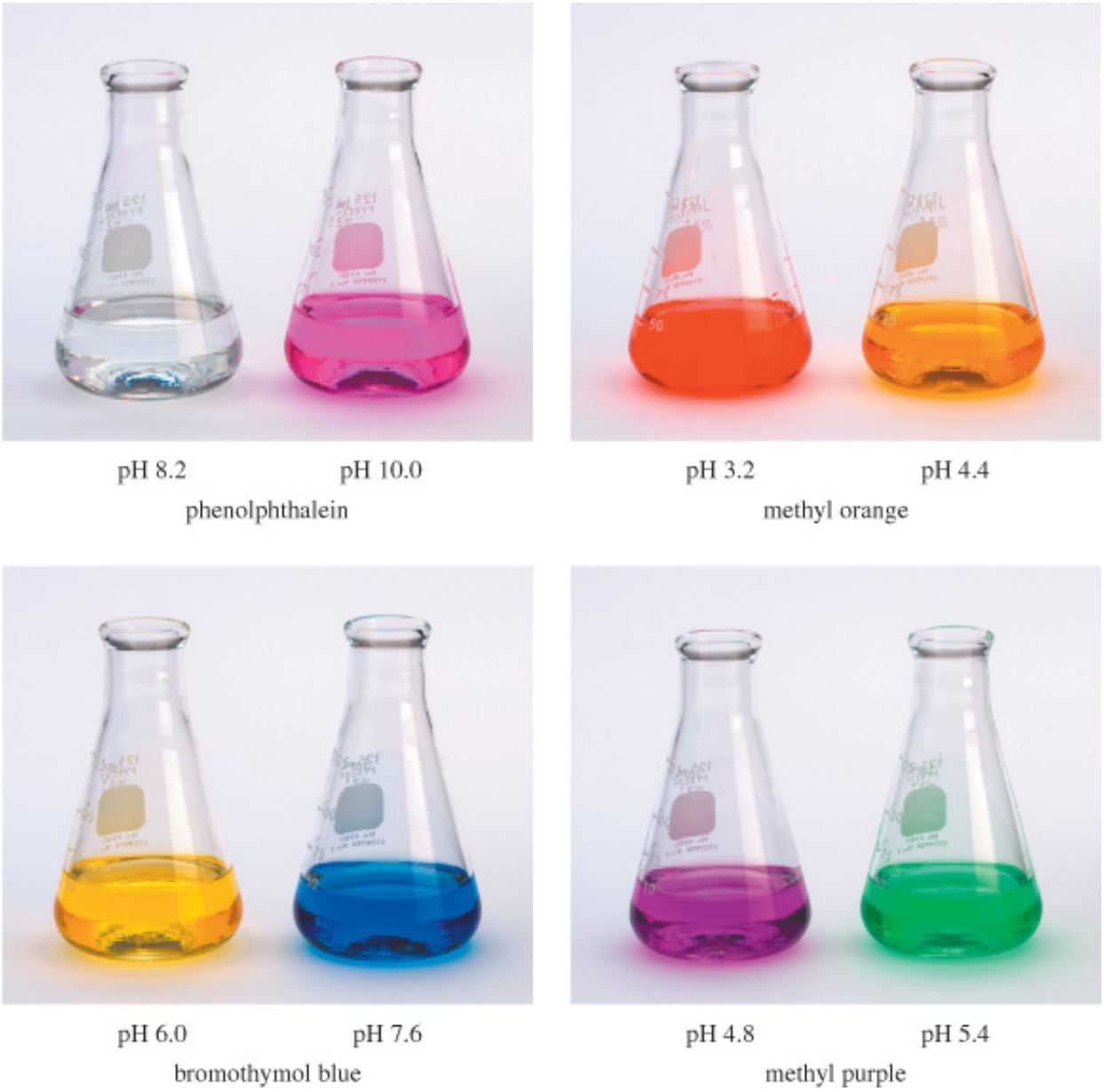


FIGURE 11.24 Colours of the acid form and base form of some common acid–base indicators. Andy Washnik

How Acid–base Indicators Work

In a typical acid–base titration, as we pass the equivalence point, there is a sudden and large change in the pH. For example, in the titration of HCl with NaOH described earlier (figure 11.17), the pH just before the equivalence point (when 24.97 mL of the base has been added) is 3.92. Just one drop later (when 25.03 mL of base has been added), we have passed the equivalence point and the pH has risen to 10.08. This large swing in pH causes a sudden shift in the position of equilibrium for the indicator, and we go from a condition where most of the indicator is in its acid form to a condition in which most is in the base form. As a result, the solution changes colour and we say that the endpoint has been reached.

Selecting the Best Indicator for an Acid–base Titration

The explanation in the preceding paragraph assumes that the *midpoint* of the colour change range of the indicator corresponds to the pH at the equivalence point. At this midpoint, we expect that there are equal amounts of both forms of the indicator, which means that [In^-] = [H *In*]. If this condition is true, then

from the equation:

$$\mathrm{pH} = \mathrm{p}K_{In} + \log\frac{[In^-]}{[\mathrm{H}In]}$$

we find that $\mathrm{p}K_{In}$ = pH at the equivalence point.

This important result tells us that, once we know the pH of the solution at the equivalence point, we also know the $\mathrm{p}K_{In}$ that the indicator should have to function most effectively. Thus, we want an indicator with a $\mathrm{p}K_{In}$ equal to (or as close as possible to) the pH at the equivalence point. This will ensure that the observed endpoint will be as close as possible to the equivalence point. Phenolphthalein, for example, changes a solution from colourless to pink as the pH of the solution changes over a range of 8.2 to 10.0 (see table 11.9). Phenolphthalein is therefore a nearly perfect indicator for the titration of a weak acid by a strong base, where the pH at the equivalence point is on the basic side (figure 11.19).

TABLE 11.9 Common acid–base indicators

Indicator	Approximate pH range for colour change	Colour change (lower to higher pH)
methyl green	0.2–1.8	yellow to blue
thymol blue	1.2–2.8	red to yellow
methyl orange	3.2–4.4	red to yellow
ethyl red	4.0–5.8	colourless to red
methyl purple	4.8–5.4	purple to green
bromocresol purple	5.2–6.8	yellow to purple
bromothymol blue	6.0–7.6	yellow to blue
phenol red	6.4–8.2	yellow to red/violet
litmus	4.7–8.3	red to blue
cresol red	7.0–8.8	yellow to red
thymol blue	8.0–9.6	yellow to blue
phenolphthalein	8.2–10.0	colourless to pink
thymolphthalein	9.4–10.6	colourless to blue
alizarin yellow R	10.1–12.0	yellow to red
clayton yellow	12.2–13.2	yellow to amber

Phenolphthalein also works very well for the titration of a strong acid with a strong base. As discussed earlier, just one drop of titrant can bring the pH from below 7 to nearly 10, which spans the pH range for phenolphthalein.

When we perform a titration, we want to use as little indicator as possible. The reason for this is that indicators are weak acids and also react with the titrant. If we were forced to use a lot of indicator, it would affect our measurements and make the titration less precise. Therefore, the best indicators are those with the most intense colours. Then, even extremely small amounts can give striking colour changes without consuming too much of the titrant.

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11.8 Lewis Acids and Bases

We stated earlier in this chapter that there was more than one definition of acids and bases, and, while we have used the Brønsted–Lowry definition throughout this chapter, there is a more general definition first proposed by the American chemist Gilbert Lewis. He stated that:

- A **Lewis acid** is an electron-pair acceptor.
- A **Lewis base** is an electron-pair donor. To illustrate these definitions, we will consider the reaction between BF_3 and NH_3.

$$BF_3(g) + NH_3(g) \rightarrow F_3B{-}NH_3(s)$$

In this reaction, NH_3 formally donates an electron pair to BF_3, resulting in formation of a B—N covalent bond, as shown in figure 11.25.

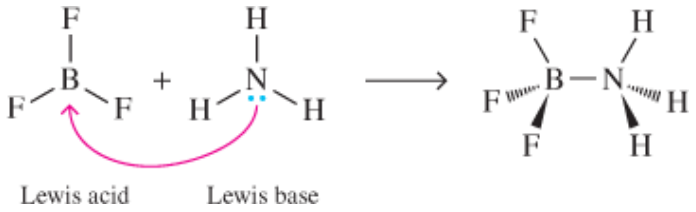


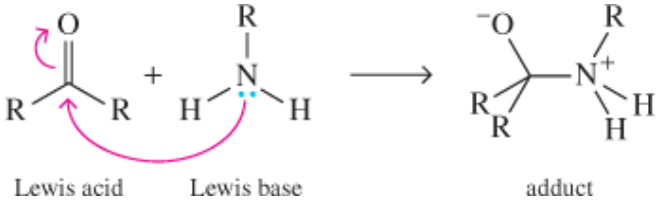
FIGURE 11.25 The Lewis acid–base reaction of BF_3 with NH_3. A covalent bond between B and N is formed, with both electrons in the bond formally deriving from the Lewis basic N atom.

Thus, BF_3 is a Lewis acid and accepts an electron pair from the Lewis base NH_3 in this reaction. Compounds such as F_3BNH_3, which are products of the reaction between a Lewis acid and a Lewis base, are sometimes called Lewis adducts, or simply **adducts**. As we will see in chapter 13, the chemistry of transition metal ions is dominated by Lewis adducts called coordination complexes. The formation of these involves the reaction of a Lewis acidic transition metal ion with one or more Lewis basic species called ligands, each containing lone pairs of electrons. For example, the coordination complex $[Ni(NH_3)_4]^{2+}$ is formed from reaction of Ni^{2+} with four NH_3 ligands, according to the equation:

$$Ni^{2+}(aq) + 4NH_3(aq) \rightarrow [Ni(NH_3)_4]^{2+}(aq)$$

Lewis acid Lewis base Lewis adduact (coordion complex)

Organic chemistry, as we will see from chapters 16 to 26, is full of examples of Lewis acids and bases. Much of organic chemistry is concerned with the making and breaking of covalent bonds involving carbon, and such reactions can be considered from a Lewis acid–Lewis base perspective. For example, the reaction of a ketone with a primary amine gives an imine and involves the formation of a C═N bond (see chapter 21, p. 953). The first step of this reaction involves the reaction of the Lewis basic amine with the Lewis acidic ketone, as follows:



The similarity to the BF_3/NH_3 reaction is obvious. The nomenclature of organic chemistry dictates that Lewis acids are called **electrophile** and Lewis bases are called **nucleophile**.

As the Lewis definition of acids and bases is the most general of the three we have met so far, it follows that all Brønsted–Lowry acids and bases must be Lewis acids and bases. However, the reverse does not necessarily hold; for example, the Lewis acid BF_3 has no protons to donate and therefore cannot be a Brønsted–Lowry acid.

The strengths of Lewis acids and bases are not as readily quantified as those of their Brønsted–Lowry counterparts. While the latter are measured relative to a single solvent (water), the large variety of solvents in which Lewis acids and bases are used makes a single scale of strengths difficult to achieve. However, it is known that a mixture of the Brønsted–Lowry acid HF and the Lewis acid antimony pentafluoride, SbF_5, is capable of protonating extremely weak

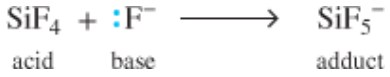
bases, such as alkanes, and is in fact one of the strongest acids known. Such mixtures are called superacids.

The concept of Lewis acids and bases is particularly useful in understanding the reactivities of *p*-block elements. As we will see in chapters 13 and 14, in nature, *p*-block elements such as oxygen, sulfur and the halogens tend to be found in combination with particular metals. For example, copper, lead and mercury are most often found as sulfide ores; sodium and potassium are found as their chloride salts; magnesium and calcium exist as carbonates; and aluminium, titanium and iron are all found as oxides. The underlying principle that determines which particular combination is favoured is the strength with which the atoms involved bind their valence electrons. This is related to the Lewis acid and base characteristics of the atoms and we can therefore use the Lewis acid–base model to describe the many different affinities that exist among elements. This notion not only explains the natural distribution of minerals, but also can be used to predict patterns of chemical reactivity.

Recognising Lewis Acids and Bases

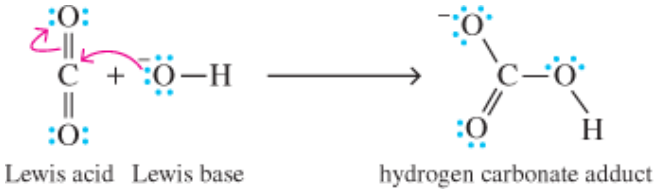
A Lewis base must have valence electrons available for bond formation. Any molecule with a Lewis structure that shows nonbonding electron pairs can act as a Lewis base. Ammonia, phosphorus trichloride and dimethyl ether, each of which contains lone pairs, are Lewis bases. Anions can also act as Lewis bases.

For example, in the reaction:



the fluoride ion, with eight valence electrons in its 2*s* and 2*p* orbitals, acts as a Lewis base. A Lewis acid must be able to accept electrons to form a new bond. Because bond formation can occur in several ways, compounds with several different structural characteristics can act as Lewis acids. Nevertheless, most Lewis acids fall into the following categories:

1. *A molecule that has vacant valence orbitals*. A good example is BF_3, which uses a vacant 2*p* orbital on boron to form an adduct with ammonia. The elements in the *p* block beyond period 2 of the periodic table have *d* orbitals which can potentially accept an electron pair, thus allowing them to act as Lewis acids. The silicon atom in SiF_4 is an example.
2. *A molecule with delocalised*π *bonds involving oxygen*. Examples are CO_2, SO_2 and SO_3. Each of these molecules can form a σ bond between its central atom and a Lewis base, at the expense of a π bond. For example, the hydroxide anion, a good Lewis base, attacks the carbon atom of CO_2 to form hydrogen carbonate.



   In this reaction, the oxygen atom of the hydroxide ion donates a pair of electrons to make a new C—O bond. Because all the valence orbitals of the carbon atom in CO_2 are involved in bonding to oxygen, one of the C—O π bonds must be broken to make an orbital available to overlap with the occupied orbital of the hydroxide anion.
3. *A metal cation*. Removing electrons from a metal atom always generates vacant valence orbitals. As described on the previous page, many transition metal cations form complexes with ligands in aqueous solution. In these complexes, the ligands act as Lewis bases, donating pairs of electrons to form metal–ligand bonds. The metal cation accepts these electrons, so it acts as a Lewis acid. Metal cations from the *p* block also act as Lewis acids. For example, Pb^{2}+(aq) (group 14) forms a Lewis acid–base adduct with four CN^- anions, each of which donates a pair of electrons.

$$Pb^{2}(aq) + 4CN^{-}(aq) \rightarrow [Pb(CN)_4]^{2-}(aq)$$

Worked example 11.21 provides practice in recognising Lewis acids and bases.

WORKED EXAMPLE 11.21

Lewis Acids and Bases

Identify the Lewis acids and bases in each of the following reactions and draw the structures of the resulting adducts.

(a) $AlCl_3 + Cl^- \rightarrow AlCl_4^-$

(b) $Co^{3+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{3+}$

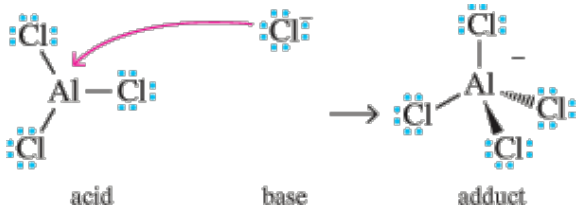
(c) $SO_2 + OH^- \rightarrow HSO_3^-$

Analysis

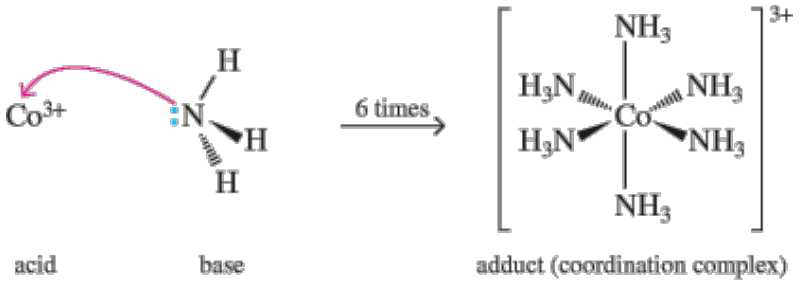
Every Lewis base has one or more lone pairs of valence electrons. A Lewis acid can have vacancies in its valence shell, or it can sacrifice a π bond to make a valence orbital available for adduct formation. To decide whether a molecule or ion acts as a Lewis acid or base, examine its Lewis structure for these features. Review pp. 171–4 in chapter 5 for procedures used to determine Lewis structures.

Solution

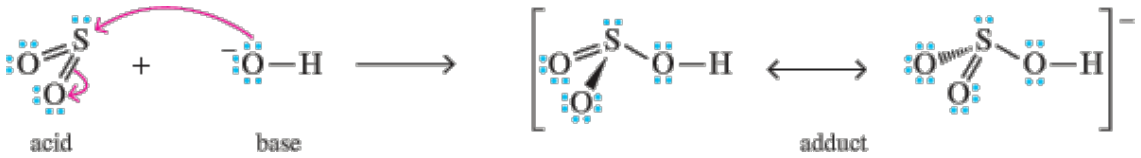
(a) Both reactants contain chlorine atoms with lone pairs, so either might act as a Lewis base if a suitable Lewis acid is present. The aluminium atom of $AlCl_3$ has a vacant 3*p* orbital perpendicular to the molecular plane. The empty *p* orbital accepts a pair of electrons from the Cl^- anion to form the fourth Al—Cl bond. The Lewis acid is $AlCl_3$, and the Lewis base is Cl^-.



(b) As already noted, ammonia is a Lewis base because it has a lone pair of electrons on the nitrogen atom. Like other transition metal cations, Co^{3+} is a Lewis acid and uses vacant 3*d* orbitals to form bonds to NH_3.



(c) Sulfur dioxide contains delocalised π bonds, indicating the potential for Lewis acidity. The sulfur atom of SO_2 has a set of 3*d* orbitals that can be used to form an adduct. In this case, the hydroxide ion acts as a Lewis base. The anion uses one lone pair of electrons to form a new bond to sulfur.



Is our answer reasonable?

The Lewis structures verify that each species identified as a Lewis base possesses lone pairs of electrons and that the Lewis acids have orbitals available to accept electrons.

PRACTICE EXERCISE 11.28

Draw a reaction scheme showing all electron transfers for the formation of the $SnCl_6^{2-}$ ion from the reaction of $SnCl_4$ with Cl^-. Identify the Lewis acid and Lewis base in this reaction.

Polarisability

Polarisability, described in chapter 6, is a measure of the ease with which the electron cloud of an atom, ion or molecule can be distorted by an electrical charge. An electron cloud is polarised towards a positive charge and away from a negative charge, as shown in figure 11.26. Pushing the electron cloud to one side of an atom causes a polarisation of charge. The side with the concentrated electron density has a small negative charge; the protons in the nucleus give the opposite side a small positive charge.

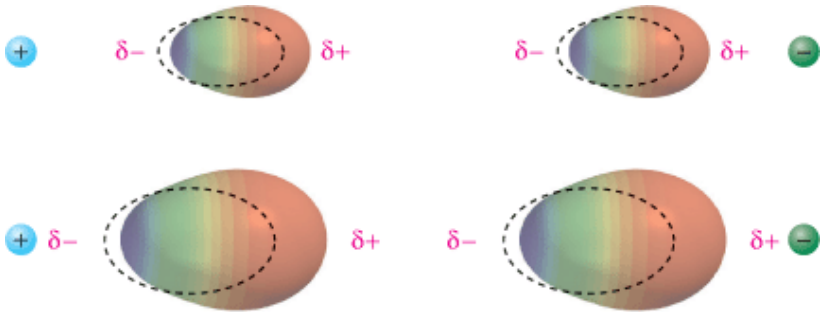


FIGURE 11.26 The electron cloud of an atom is polarised towards a positive charge and away from a negative charge. A smaller atom binds its valence electrons more tightly and is less polarisable than a larger atom, which binds its electrons loosely.

Polarisability shows periodic variations that correlate with periodic trends in how tightly valence electrons are bound to the nucleus (figure 11.27).

1. Polarisability decreases from left to right in any period of the periodic table. As the effective nuclear charge (Z_{eff}) increases, the nucleus holds the valence electrons more tightly.
2. Polarisability increases from top to bottom in any group of the periodic table. As the principal quantum number (n) increases, the valence orbitals become larger. This reduces the net attraction between valence electrons and the nucleus.

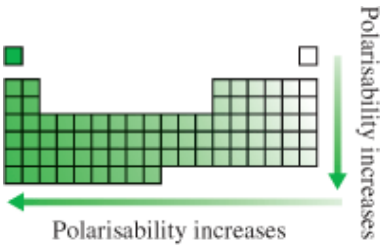


FIGURE 11.27 Polarisability decreases across a period and increases down a group.

The Hard–soft Concept

Lewis acids and bases can be organised according to their polarisability. If polarisability is low, the species is categorised as ‘hard’. If polarisability is high, the species is ‘soft’.

A **hard Lewis base** has electron pairs of low polarisability. This characteristic correlates with high electronegativity. Fluoride, the anion of the most electronegative element, is the hardest Lewis base because it contains a small, dense sphere of negative charge. Molecules and ions that contain oxygen or nitrogen atoms are usually also hard bases, although not as hard as fluorine. Examples include H_2O, CH_3OH, OH^-, NH_3 and H_2NCH_3.

A **soft Lewis base** has a large donor atom of high polarisability and low electronegativity. The iodide ion has its valence electrons in large $n = 5$ orbitals, making this anion highly polarisable and a very soft base. Other molecules and polyatomic anions with donor atoms from periods 3 to 6 are usually also soft bases. To summarise, the donor atom becomes softer from top to bottom of a group of the periodic table (figure 11.28).

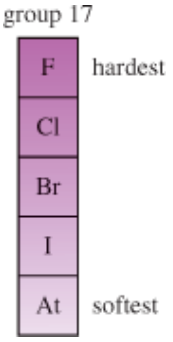


FIGURE 11.28 The donor atom becomes softer down a group.

A **hard Lewis acid** has an acceptor atom with low polarisability. Most metal atoms and ions are hard acids. In general, the smaller the ionic radius and the larger the charge, the harder the acid. The Al^{3+} ion, with an ionic radius of only 67 pm, is a prime example of a hard Lewis acid. The nucleus exerts a strong pull on the compact electron cloud, giving the ion very low polarisability.

The designation of hard acids is not restricted to metal cations. For example, in BF_3 the small boron atom in its +3 oxidation state is bonded to three highly electronegative fluorine atoms. All the B—F bonds are polarised away from a boron centre that is already electron deficient. Boron trifluoride is therefore a hard Lewis acid.

A **soft Lewis acid** has a relatively high polarisability. Large atoms and low oxidation states often convey softness. Contrast the hard acid Al^{3+} with Hg^{2}+, a typical soft acid (figure 11.29). The ionic radius of Hg^{2+} is 116 pm, almost twice that of Al^{3+}, because the valence orbitals of Hg^{2+} have a high principal quantum number, $n = 6$. Consequently, Hg^{2+} is a highly polarisable, very soft Lewis acid. The relatively few soft Lewis acid transition metal ions are located around gold in the periodic table.

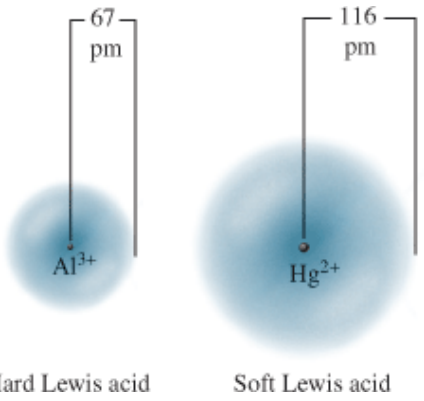


FIGURE 11.29 The Al^{3+} ion is a harder Lewis acid than Hg^{2+} because of its smaller ionic radius and higher charge.

The terms 'hard' and 'soft' are relative, so there is no sharp dividing line between the two, and many Lewis acids and bases are intermediate between hard and soft. Worked example 11.22 shows how to categorise Lewis acids and bases according to their hard–soft properties.

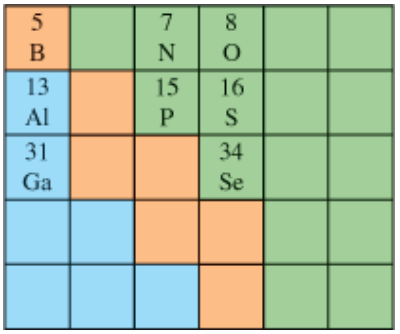
WORKED EXAMPLE 11.22

Ranking Hardness and Softness

Rank the following groups of Lewis acids and bases from softest to hardest: (a) H_2S, H_2O and H_2Se, (b) Fe^0, Fe^{3+} and Fe^{2+} and (c) BCl_3, $GaCl_3$ and $AlCl_3$.

Analysis

The first task is to decide whether the members of a given group are Lewis acids or bases. Then evaluate the relative softness and hardness based on polarisability, taking into account correlations with electronegativity, size and charge. Refer to the periodic table to assess the trends.



Solution

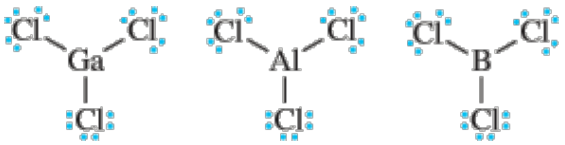
(a)



These three molecules have lone pairs, so they are Lewis bases. The central atoms are in the same group of the periodic table, so their polarisability and the softness of the molecules increases moving down the group. Thus, H_2Se is softer than H_2S, which is softer than H_2O.

(b) Fe^0 Fe^{2+} Fe^{3+} Metal atoms and cations are Lewis acids. As valence electrons are removed from a metal atom, the remaining electron cloud undergoes an ever larger pull from the nuclear charge. This decreases the size of the ion as well as its polarisability. Thus, Fe^0 is softer than Fe^{2+}, which is softer than Fe^{3+}.

(c)



These three molecules have trigonal planar geometries with sp^2 hybridised central atoms. Each has a vacant valence *p* orbital perpendicular to the molecular plane, making the molecules Lewis acids. The size, polarisability and softness of the central acceptor atom increases going down the group. A gallium atom is larger and more polarisable than an aluminium atom. Thus, $GaCl_3$ is softer than $AlCl_3$, which is softer than BCl_3. We have already noted that the Al^{3+} ion is a hard Lewis acid, and is therefore likely to form compounds which are themselves hard Lewis acids. Thus gallium trichloride is a soft Lewis acid, whereas $AlCl_3$ and BCl_3 are both hard.

Is our answer reasonable?

Hardness and softness are primarily determined by atomic size, and the order of hardness in each of these sets is consistent with the size trends among the species.

PRACTICE EXERCISE 11.29

Identify H_2O, NH_3, and PH_3 as Lewis acids or Lewis bases, and rank them in order of increasing hardness.

The hard–soft Acid–base Principle

The concept of hard and soft acids and bases can be used to interpret many trends in chemical reactivity. These trends are summarised in the hard–soft acid–base principle (HSAB principle), an empirical summary of results collected from many chemical reactions:

- Hard Lewis acids tend to combine with hard Lewis bases.
- Soft Lewis acids tend to combine with soft Lewis bases.

The geochemical distribution of metals conforms to the HSAB principle. Metals that form hard acid cations have strong affinities for hard bases such as oxide, fluoride and chloride. Most metal ions that are hard acids are found bonded to the oxygen atoms of various silicate anions. These elements are concentrated in the Earth's mantle. Hard acid metals also occur in combinations with other hard bases, including oxides or, less often, halides, sulfates and carbonates. Examples include rutile, TiO_2, limestone, $CaCO_3$, gypsum, $CaSO_4$, and sylvite, KCl.

Metals that are soft acids, such as gold and platinum, have low affinities for hard oxygen atoms, so they are not affected by O_2 in the atmosphere. Consequently, these metals, including Ru, Rh, Pd, Os, Ir, Pt and Au, are often found in the crust of the Earth in their elemental form. Other soft metals occur in nature as sulfides. The sulfide anion is a soft base, so this category includes some soft acids and many intermediate cases. Soft acids may also occur either in elemental form or as arsenide or telluride minerals. Examples include galena, PbS, cinnabar, HgS, chalcopyrite, $CuFeS_2$, argentite, Ag_2S, calaverite, $AuTe_2$, and sperrylite, $PtAs_2$.

The group 13 elements illustrate the trend in hardness and softness among Lewis acids. At the top of the group, boron is a hard Lewis acid and so is aluminium. Moving down the group, the valence orbitals increase in size and polarisability. Thus, gallium is a borderline acid, and indium is soft. The order of reactivity for the trihalides of these elements depends on the Lewis base. For a hard base such as ammonia, the reactivity trend for adduct formation is:

$$BCl_3 > AlCl_3 > GaCl_3 > InCl_3$$

reflecting the preference that the hard base has for the harder acid. The order is reversed when the trihalides form adducts with dimethylsulfide, $(CH_3)_2S$, a soft base.

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SUMMARY

The Brønsted–Lowry Definition of Acids and Bases

A Brønsted–Lowry acid is a proton donor; a Brønsted–Lowry base is a proton acceptor. According to the Brønsted–Lowry approach, an acid–base reaction is a proton transfer event. In an equilibrium involving a Brønsted–Lowry acid and base, there are two conjugate acid–base pairs. The members of any given pair differ from each other by only one proton. A solvent that can be either an acid or a base, depending on the nature of the other reactant, is amphiprotic.

Acid–base Reactions in Water

Water reacts with itself to produce small amounts of H_3O^+ and OH^- ions. The concentrations of these ions in both pure water and in dilute aqueous solutions are related by the expression:

$$\left[H_3O^+\right][OH^-] = K_w = 1.0 \times 10^{-14} \quad (\text{at } 25°C)$$

K_w is the autoprotolysis constant of water. In pure water:

$$\left[H_3O^+\right] = [OH^-] = 1.0 \times 10^{-7} M \quad (\text{at } 25°C)$$

The pH of a solution is a measure of acidity and is normally measured with a pH meter. As the pH decreases, the acidity increases. The defining equation for pH is pH = –log[H_3O^+]. In exponential form, this relationship between [H_3O^+] and pH is given by [H_3O^+] = 10^{-pH}.

Comparable expressions can be used to describe low OH^- ion concentrations in terms of pOH values: pOH = –log[OH^-] and [OH^-] = 10^{-pOH}. At 25 °C, pH + pOH = 14.00. A solution is acidic if its pH is less than 7.00 and basic if its pH is greater than 7.00. A neutral solution has a pH of 7.00.

Strong Acids and Bases

In calculating the pH of solutions of strong acids and bases, we assume that they react completely with water. The autoprotolysis of water contributes negligibly to [H_3O^+] in a solution of an acid. It also contributes negligibly to the [OH^-] in a solution of a base.

Weak Acids and Bases

An acid HA reacts with water according to the general equation:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The equilibrium constant is called the acidity constant, K_a.

$$K_a = \frac{\left[H_3O^+\right][A^-]}{[HA]}$$

A base B reacts by the general equation:

$$B + H_2O \rightleftharpoons BH^+ + OH$$

The equilibrium constant is called the basicity constant, K_b.

$$K_b = \frac{[HO^-]\left[BH^+\right]}{[B]}$$

The smaller the value of K_a or K_b, the weaker the substances are as Brønsted–Lowry acids or bases.

Another way to compare the relative strengths of acids or bases is to use the negative logarithms of K_a and K_b, called pK_a and pK_b, respectively.

$$pK_a = -\log K_a$$
$$pK_b = -\log K_b$$

The *smaller* the p K_a or pK_b, the *stronger* the acid or base. For a conjugate acid–base pair:

$$K_a K_b = K_w$$

and:

$$pK_a + pK_b = 14.00 \quad (\text{at } 25^\circ\text{C})$$

The values of K_a and K_b can be obtained from initial concentrations of the acid or base and the pH of the solution. The measured pH gives the equilibrium value for $[H_3O^+]$.

Problems fall into one of three categories:

1. the only solute is a weak acid (we must use the K_a expression)
2. the only solute is a weak base (we must use the K_b expression)
3. the solution contains both a weak acid and its conjugate base (we can use either K_a or K_b, or the Henderson–Hasselbalch equation).

When the initial concentration of the acid (or base) is larger than 400 times the value of K_a (or K_b), it is safe to use initial concentrations of acid or base as though they were equilibrium values in the equilibrium constant expression. When this approximation cannot be used, we use the quadratic formula.

The weaker an acid, the stronger its conjugate base, and vice versa. Anions of strong acids, such as Cl^- and NO_3^-, are such weak Brønsted–Lowry bases that they cannot affect the pH of a solution.

If a salt is derived from a weak acid *and* a weak base, its net effect on pH has to be established on a case-by-case basis by determining which of the two ions reacts with water to a greater extent.

The Molecular Basis of Acid Strength

Binary acids contain only hydrogen and another nonmetal. Their strengths increase from top to bottom within a group and left to right across a period. Oxoacids, which contain oxygen atoms in addition to hydrogen and another element, increase in strength as the number of oxygen atoms on the same central atom increases. Oxoacids with the same number of oxygen atoms generally increase in strength as the central atom moves from bottom to top within a group and from left to right across a period.

Buffer Solutions

A solution that contains appreciable amounts of both a weak acid and a weak base (usually an acid–base conjugate pair) is called a buffer solution, because it is able to absorb H_3O^+ from a strong acid or OH^- from a strong base without suffering large changes in pH.

For the general acid–base pair, HA and A^-, the following reactions occur in a buffer solution:

H_3O^+ is added to the buffer: $A^- + H_3O^+ \longrightarrow HA + H_2O$

OH^- is added to the buffer: $HA + OH^- \longrightarrow A^- + H_2O$

The pH of a buffer is controlled by the ratio of weak acid to weak base, expressed either in terms of concentration or amount.

Because the $[H_3O^+]$ is determined by the mole ratio of HA to A^-, dilution does not change the pH of a buffer. The equation:

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

can be used to calculate the pH directly from the pK_a of the acid and the concentrations of the conjugate acid HA and base A^-.

In performing buffer calculations, the usually valid simplifications are:

$$[HA]_{equilibrium} = [HA]_{initial}$$
$$[A^-]_{equilibrium} = [A^-]_{initial}$$

Buffers are most effective when the pK_a of the acid member of the buffer pair lies within ±1 unit of the desired pH.

Although the mole ratio of A^- to HA determines the pH at which a buffer works, the amounts of the acid and its conjugate base give the buffer its capacity for taking on strong acid or base with little change in pH.

Acid–base Titrations

The pH at the equivalence point depends on the ions of the salt formed during the titration. In the titration of a strong acid with a strong base, the pH at the equivalence point is 7 because neither of the ions produced in the reaction affects the pH of an aqueous solution.

For the titration of a weak acid with a strong base, the approach towards calculation of the pH varies depending on which stage of the titration is considered.

1. Before the titration begins, the only solute is the weak acid, and so K_a is used.
2. After starting, but before the equivalence point, the solution is a buffer. Either K_a or K_b can be used.
3. At the equivalence point, the active solute is the conjugate base of the weak acid. K_b for the conjugate base must be used.
4. After the equivalence point, excess strong base determines the pH of the mixture. No equilibrium calculations are required. At the equivalence point, the pH is above 7.

Similar calculations apply in the titration of a weak base by a strong acid. In such titrations, the pH at the equivalence point is below 7.

The indicator chosen for a titration should have the centre of its colour change range near the pH at the equivalence point. For the titration of a strong or weak acid with a strong base, phenolphthalein is the best indicator. When a weak base is titrated with a strong acid, several indicators, including methyl orange, work satisfactorily.

Lewis Acids and Bases

A Lewis acid is an electron-pair acceptor, while a Lewis base is an electron-pair donor. Electrophiles are Lewis acids and nucleophiles are Lewis bases.

A Lewis base must have one or more pairs of valence electrons available for bond formation. A Lewis acid must be able to accept an electron pair to form a new bond. Most Lewis acids are one of the following: a molecule with vacant valence orbitals, a molecule with delocalised π bonds involving oxygen, or a metal cation.

The polarisability of an atom, ion or molecule is the ease with which its electron cloud can be distorted by an electrical charge. Polarisability decreases from left to right in any period of the periodic table (as the effective nuclear charge, Z_{eff}, increases). Polarisability increases from top to bottom of any group of the periodic table (as the principal quantum number, n, increases).

A hard Lewis base has electron pairs of low polarisability and high electronegativity. A soft Lewis base has a large donor atom of high polarisability and low electronegativity. A hard Lewis acid has an acceptor atom with low polarisability. A soft Lewis acid has a relatively high polarisability. The hard–soft acid–base (HSAB) principle states that hard Lewis acids tend to combine with hard Lewis bases, while soft Lewis acids tend to combine with soft Lewis bases. This is reflected in nature, where hard metal ions tend to be found bonded to hard bases, and vice versa.

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KEY CONCEPTS AND EQUATIONS

Autoprotolysis constant for water $[H_3O^+][OH^-] = K_W$ *(section 11.2)*

This equation is used to calculate $[H_3O^+]$ if $[OH^-]$ is known, and vice versa.

$$\left[H_3O^+\right][OH^-] = K_w$$

pH and pOH *(section 11.2)*

These provide a convenient method for representing $[H_3O^+]$ and $[OH^-]$ in aqueous solution.

Relationship between pH and pOH: pH + pOH = 14.00 at 25°C *(section 11.2)*

This relationship can be used to calculate pH if pOH is known, and vice versa.

$$pH + pOH = 14.00 (\text{at } 25^\circ C)$$

$K_aK_b = K_W$ *(section 11.4)*

This equation is used to calculate K_a given K_b, or vice versa.

Periodic trends in strengths of binary acids *(section 11.5)*

Periodic trends can be used to predict the relative acidities of *X*—H bonds, both for the binary hydrids themselves and for molecules that contain *X*—H bonds.

Periodic trends in strengths of oxoacids *(section 11.5)*

Periodic trends can be used to predict the relative acidities of oxoacids according to the nature of the central nonmetal as well as the number of oxygen atoms attached to a given nonmetal. The principles involved also let you compare the acidities of compounds containing different electronegative elements.

$pH = pK_a + \log\frac{[A^-]}{[HA]}$ *(section 11.6)*

This equation can be used to calculate the pH of a buffer solution.

Hard–soft acid–base principle *(section 11.8)*

Hard Lewis acids tend to combine with hard Lewis bases. Soft Lewis acids tend to combine with soft Lewis bases.

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REVIEW QUESTIONS

The Brønsted–Lowry Definition of Acids and Bases

11.1 How is a Brønsted–Lowry acid defined? How is a Brønsted– Lowry base defined?

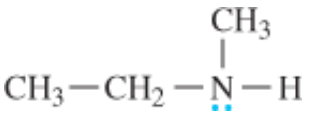
11.2 How are the formulae of the members of a conjugate acid– base pair related to each other? Within the pair, how can you tell which is the acid?

11.3 Is H_2SO_4 the conjugate acid of SO_4^{2-}? Explain your answer.

11.4 Define the term 'amphiprotic'.

11.5 Write the structural formulae for the conjugate acids of the following structures.

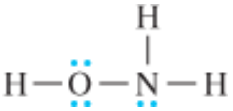
(a)



(b)

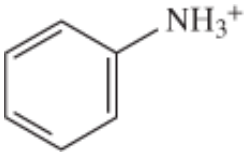


(c)

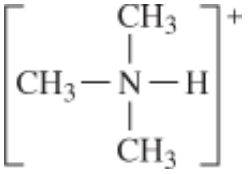


11.6 Write the structural formulae for the conjugate bases of the following structures.

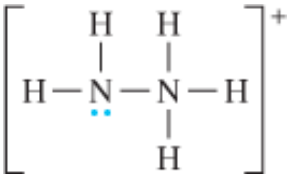
(a)



(b)



(c)



Acid–base Reactions in Water

11.7 Explain why, in pure water at 25 °C, the concentration of H_3O^+ cannot be greater than 1×10^{-7} M.

11.8 At 40.0 °C, $K_w = 3.0 \times 10^{-14}$. Calculate the pH of pure water at this temperature. Comment on the statement 'pure water always has a pH of 7' with reference to your answer.

Strong Acids and Bases

11.9 What is the definition of a strong acid?

11.10 Will the conjugate acid of a strong base be very strong, strong, weak or very weak? Give your reasoning.

11.11 The NH_2^- ion (sometimes called the amide ion) is a very strong base; it is even stronger than OH^-. Write an equation that shows the reaction that occurs when the amide ion is placed in water,

and use this to explain why the amide ion cannot exist in aqueous solution.

Weak Acids and Bases

11.12 Write the general equation for the reaction of a weak acid with water. Give the expression for K_a.

11.13 Write the chemical equation for the reaction of each of the following weak acids with water and write the appropriate K_a expression. (Some are polyprotic acids; for these, write only the equation for the first step in the ionisation.)

(a) HNO_2

(b) H_3PO_4

(c) $HAsO_4^{2-}$

(d) $(CH_3)_3NH^+$

11.14 Write the general equation for the reaction of a weak base with water. Give the expression for K_b.

11.15 Write the chemical equation for the reaction of each of the following weak bases with water and write the appropriate K_b expression.

(a) $(CH_3)_3N$

(b) AsO_4^{3-}

(c) NO_2^-

(d) $(CH_3)_2NNH_2$

11.16 The pK_a of HCN is 9.21 and that of HF is 3.17. Which is the stronger Brønsted–Lowry base, CN^- or F^-?

11.17 Aspirin is acetylsalicylic acid, a monoprotic acid with a K_a value of 3.27×10^{-4}. Is a solution of the sodium salt of aspirin in water acidic, basic or neutral? Explain.

11.18 Consider the following compounds and suppose that a 0.1 M solution is prepared of each: NaI, KF, $(NH_4)_2SO_4$, KCN, $KOOCCH_3$, $CsNO_3$ and KBr. Write the formulae of those that have solutions that are:

(a) acidic

(b) basic

(c) neutral.

11.19 Ammonium nitrate is commonly used in fertiliser mixtures as a source of nitrogen for plant growth. What effect, if any, will this compound have on the acidity of the moisture in the ground? Explain.

11.20 A solution of hydrazinium acetate is slightly acidic. Without looking at the tables of equilibrium constants, is K_a for acetic acid larger or smaller than K_b for hydrazine? Justify your answer.

11.21 What criterion do we use to determine whether we are able to use the initial concentration of an acid or base as though it were the equilibrium concentration when we calculate the pH of the solution?

11.22 For which of the following are we permitted to use the initial concentration of the acid or base to calculate the pH of the solution specified?

(a) 0.020 M CH_3COOH

(b) 0.10 M CH_3NH_2

(c) 0.002 M N_2H_4

(d) 0.050 M HCOOH

The Molecular Basis of Acid Strength

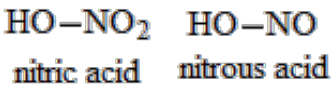
11.23 Within the periodic table, how do the strengths of the binary acids vary from left to right across a period? How do they vary from top to bottom within a group?

11.24 Astatine, At, atomic number 85, is radioactive and does not occur in appreciable amounts in nature. Based on what you have learned in this chapter, answer the following.

(a) How would the acidity of HAt compare with HI?

(b) How would the acidity of $HAtO_3$ compare with $HBrO_3$?

11.25 Explain why nitric acid is a stronger acid than nitrous acid.



11.26 Explain why $HClO_4$ is a stronger acid than H_2SeO_4.

11.27 Explain why the NO_2^- ion is a stronger base than the SO_3^{2-} ion.

11.28 The position of equilibrium in the equation below lies far to the left. Identify the conjugate acid–base pairs. Which of the two acids is stronger?

$$HOCl(aq) + H_2O \rightleftharpoons H_3O^+(aq) + OCl^-(aq)$$

11.29 Consider the following: CO_3^{2-} is a weaker base than hydroxide ion, and HCO_3^- is a stronger acid than water. In the equation below, would the position of equilibrium lie to the left or to the right? Justify your answer.

$$CO_3^{2-}(aq) + H_2O \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

11.30 Acetic acid, CH_3COOH, is a weaker acid than nitrous acid, HNO_2. How do the strengths of the bases CH_3COO^- and NO_2^- compare?

11.31 Nitric acid, HNO_3, is a very strong acid. It is 100% ionised in water. In the reaction below, would the position of equilibrium lie to the left or right?

$$NO_3^-(aq) + H_2O \rightleftharpoons HNO_3(aq) + OH^-(aq)$$

11.32 $HClO_4$ is a stronger proton donor than HNO_3, but in water both acids appear to be of equal strength; they are both 100% ionised. Why is this so? What solvent property would be necessary in order to distinguish between the acidities of these two Brønsted–Lowry acids?

11.33 Formic acid, HCOOH, and acetic acid, CH_3COOH, are classified as weak acids, but in water HCOOH is more dissociated than CH_3COOH. However, if we use liquid ammonia as a solvent for these acids, they both appear to be of equal strengths and 100% dissociated. Explain why this is so.

Buffer Solutions

11.34 Write ionic equations that illustrate how each pair of compounds below can serve as a buffer pair.

(a) H_2CO_3 and $NaHCO_3$ (the 'carbonate' buffer in blood)

(b) NaH_2PO_4 and Na_2HPO_4 (the 'phosphate' buffer inside body cells)

(c) NH_4Cl and NH_3

11.35 Buffer 1 is a solution containing 0.10 M NH_4Cl and 1.0 M NH_3. Buffer 2 is a solution containing 1.0 M NH_4Cl and 0.10 M NH_3. Which buffer is better able to maintain a steady pH on the

addition of strong acid? Explain.

Acid–base Titrations

11.36 **11.36** When a formic acid solution is titrated with sodium hydroxide, will the solution be acidic, neutral or basic at the equivalence point?

11.37 When a solution of hydrazine is titrated by hydrochloric acid, will the solution be acidic, neutral or basic at the equivalence point?

11.38 Define the terms ‘equivalence point’ and ‘endpoint’ as they apply to an acid–base titration.

11.39 Qualitatively, describe how an acid–base indicator works. Why do we want to use a minimum amount of indicator in a titration?

11.40 Explain why ethyl red is a better indicator than phenolphthalein in the titration of dilute ammonia by dilute hydrochloric acid.

11.41 What is a good indicator for titrating potassium hydroxide with hydrobromic acid? Explain.

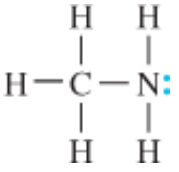
11.42 If you use methyl orange in the titration of CH_3COOH with NaOH, will the end point of the titration correspond to the equivalence point? Justify your answer.

Lewis Acids and Bases

11.43 Define the terms ‘Lewis acid’ and ‘Lewis base’.

11.44 Explain why the addition of a proton to a water molecule to give H_3O^+ is a Lewis acid–base reaction.

11.45 Methylamine has the formula CH_3NH_2 and the structure:



Use Lewis structures to illustrate the reaction of methylamine with boron trifluoride, BF_3.

11.46 Explain why the oxide ion, O^{2-}, can function as a Lewis base but not as a Lewis acid.

11.47 Draw the Lewis structures of each of the reactants in the following reactions.

(a) $SO_3 + OH^- \rightarrow HSO_4^-$

(b) $SnCl_2 + Cl^- \rightarrow [SnCl_3]^-$

(c) $AsF_3 + SbF_5 \rightarrow [AsF_2]^+[SbF_6]^-$

11.48 Identify the Lewis acid and the Lewis base in each of the reactions that appears in question 11.47.

11.49 Draw mechanistic arrows that show the donation of electrons that takes place in each reaction in question 11.47 and draw the Lewis structures of the products.

11.50 State the hard–soft acid–base (HSAB) principle. Define and give examples of hard and soft acids and bases.

11.51 Rank the three molecules or ions in each of the following groups from softest to hardest.

(a) NCl_3, NH_3 and NF_3

(b) ClO_4^-, ClO_2^- and ClO_3^-

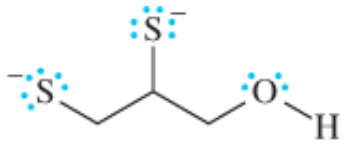
(c) Pb^{2+}, Pb^{4+} and Zn^{2+}

(d)

PCl_3, $SbCl_3$ and PF_3

11.52 Iron is always found in nature in compounds, often with oxygen. The other members of group 8 in the periodic table, ruthenium and osmium, occur in elemental form. Explain these observations using the HSAB principle.

11.53 Lead poisoning can be treated using the dianion of 2,3-dimercaptopropanol. Two ions bind one Pb^{2+} ion in a soluble tetrahedral complex that can be excreted from the body. Using hard– soft acid–base concepts, draw the expected structure of this complex.



2,3-dimercaptopropanol dianion

11.54 The anion present in aqueous solutions of boric acid is $[B(OH)_4]^-$ rather than $H_2BO_3^-$. This is because H_3BO_3 undergoes Lewis acid–base adduct formation with one water molecule, and the adduct then transfers a proton to a second water molecule to generate $[B(OH)_4]^-$ and a hydronium ion. Draw Lewis structural diagrams illustrating these two transfer reactions. Show all formal charges, and include arrows that show the movement of electrons.

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REVIEW PROBLEMS

11.55 Write the formula for the conjugate acid of each of the following.

(a) F^-

(b) N_2H_4

(c) C_5H_5N

(d) O_2^{2-}

(e) $HCrO_4^-$

11.56 Write the formula for the conjugate base of each of the following.

(a) NH_2OH

(b) HSO_3^-

(c) HCN

(d) H_5IO_6

(e) HNO_2

11.57 Identify the conjugate acid–base pairs in the following reactions.

(a) $HNO_3 + N_2H_4 \rightleftharpoons NO_3^- + N_2H_5^+$

(b) $NH_3 + N_2H_5^+ \rightleftharpoons NH_4^+ + N_2H_4$

(c) $H_2PO_4^- + CO_3^{2-} \rightleftharpoons HPO_4^{2-} + HCO_3^-$

(d) $HIO_3 + HC_2O_4^- \rightleftharpoons IO_3^- + H_2C_2O_4$

11.58 Identify the conjugate acid–base pairs in the following reactions.

(a) $HSO_4^- + SO_3^{2-} \rightleftharpoons HSO_3^- + SO_4^{2-}$

(b) $S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$

(c) $CN^- + H_3O^+ \rightleftharpoons HCN + H_2O$

(d) $H_2Se + H_2O \rightleftharpoons HSe^- + H_3O^+$

11.59 Calculate $[H_3O^+]$ in each of the following aqueous solutions in which the hydroxide ion concentrations are:

(a) 0.0024 M

(b) 1.4×10^{-5} M

(c) 5.6×10^{-9} M

(d) 4.2×10^{-13} M

11.60 Calculate $[OH^-]$ in each of the following aqueous solutions in which the H_3O^+ concentrations are:

(a) 3.5×10^{-8} M

(b) 0.0065 M

(c) 2.5×10^{-13} M

(d) 7.5×10^{-5} M

11.61 Calculate the pH of each solution in question 11.59.

11.62 Calculate the pH of each solution in question 11.60.

11.63 Calculate $[H_3O^+]$ and $[OH^-]$ in solutions that have the following pH values.

(a) 8.26

(b) 10.25

(c) 4.65

(d) 6.18

(e) 9.70

11.64 What is the $[H_3O^+]$ in 0.030 M HNO_3? What is the pH of the solution? What is the OH^- concentration in the solution?

11.65 A sodium hydroxide solution is prepared by dissolving 6.0 g NaOH in 1.00 L of aqueous solution. What is the molar concentration of OH^- in the solution? What are the pOH and the pH of the solution? What is the H_3O^+ concentration in the solution?

11.66 An aqueous solution was made by dissolving 0.837 g $Ba(OH)_2$ in water to give a final volume of 100 mL. What is the molar concentration of OH^- in the solution? What are the pOH and the pH? What is the H_3O^+ concentration in the solution?

11.67 What volume of 0.100 M KOH is needed to completely neutralise the HCl in 300 mL of a hydrochloric acid solution that has a pH of 2.25?

11.68 The K_a for HF is 6.8×10^{-4}. What is K_b for F^-?

11.69 The barbiturate ion, $C_4H_3N_2O_3^-$, has $K_b = 1.0 \times 10^{-10}$. What is K_a for barbituric acid?

11.70 Hydrogen peroxide, H_2O_2, is a weak acid with $K_a = 1.8 \times 10^{-12}$. What is the value of K_b for the HO_2^- ion?

11.71 Methylamine, CH_3NH_2, resembles ammonia in odour and basicity. Its K_b is 4.4×10^{-4}. Calculate the K_a of its conjugate acid.

11.72 Lactic acid, $CH_3CH(OH)COOH$, is responsible for the sour taste of sour milk. At 25 °C, its $K_a = 1.4 \times 10^{-4}$. What is the K_b of its conjugate base, the lactate ion, $CH_3CH(OH)COO^-$?

11.73 Iodic acid, HIO_3, has a pK_a of 0.23. (a) What are the formula and the K_b of its conjugate base? (b) Is its conjugate base a stronger or weaker base than the acetate ion?

11.74 At the temperature of the human body, 37 °C, the value of K_w is 2.4×10^{-14}. Calculate the $[H_3O^+]$, $[OH^-]$, pH and pOH of pure water at this temperature. What is the relation between pH, pOH and K_w at this temperature? Is water neutral at this temperature?

11.75 Periodic acid, HIO_4, is an important oxidising agent and a moderately strong acid. In a 0.10 M solution, $[H_3O^+] = 3.8 \times 10^{-2}$ mol L^{-1}. Calculate the K_a and pK_a for periodic acid.

11.76 Chloroacetic acid, $ClCH_2COOH$, is a stronger monoprotic acid than acetic acid. In a 0.10 M solution, the pH is 1.96. Calculate the K_a and pK_a for chloroacetic acid.

11.77 Hydroxylamine, NH_2OH, like ammonia, is a Brønsted– Lowry base. A 0.15 M solution has a pH of 10.12. What are K_b and pK_b for hydroxylamine?

11.78 What are the concentrations of all the solute species in 0.150 M lactic acid, $CH_3CH(OH)COOH$?

What is the pH of the solution? This acid has $K_a = 1.4 \times 10^{-4}$.

11.79 What is the pH of 0.15 M hydrazoic acid, HN_3? For HN_3, $K_a = 1.8 \times 10^{-5}$.

11.80 Phenol, also known as carbolic acid, is sometimes used as a disinfectant. What are the concentrations of all of the solute species in a 0.050 M solution of phenol, C_6H_5OH? For this acid, $K_a = 1.3 \times 10^{-10}$.

11.81 Codeine, a cough suppressant extracted from crude opium, is a weak base with a pK_b of 5.79. What is the pH of a 0.020 M solution of codeine?

11.82 Pyridine, C_5H_5N, is a bad-smelling liquid that is a weak base in water. Its pK_b is 8.82. What is the pH of a 0.20 M aqueous solution of this compound?

11.83 What amount of NH_3 must be dissolved in water to give 500 mL of solution with a pH of 11.22?

11.84 Calculate the pH of 0.20 M NaCN. What is the concentration of HCN in the solution?

11.85 Calculate the pH of 0.40 M KNO_2. What is the concentration of HNO_2 in the solution?

11.86 Calculate the pH of 0.15 M methylammonium chloride, CH_3NH_3Cl. For methylamine, CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.

11.87 Calculate the pH of 0.10 M hydrazinium chloride, N_2H_5Cl. Hydrazine, N_2H_4, is a weak base with $K_b = 1.7 \times 10^{-6}$.

11.88 A 0.18 M solution of the sodium salt of nicotinic acid (also known as niacin) has a pH of 9.05. What is the value of K_a for nicotinic acid?

11.89 A weak base B forms the salt BHCl, composed of the ions BH^+ and Cl^-. A 0.15 M solution of the salt has a pH of 4.28. What is the value of K_b for the base B?

11.90 Calculate the mass of NH_4Br that has to be dissolved in 1.00 L of water at 25 °C to give a solution with a pH of 5.16.

11.91 Liquid chlorine bleach is essentially a solution of sodium hypochlorite, NaOCl, in water. Usually, the concentration is approximately 5% NaOCl by weight. Use this information to calculate the approximate pH of a bleach solution, assuming NaOCl is the only solute. (Assume the bleach has a density of 1.0 g mL^{-1}.)

11.92 What is the pH of a 0.0050 M solution of sodium cyanide? The K_b of NaCN is 1.62×10^{-5}.

11.93 What is the pH of a 0.020 M solution of chloroacetic acid, for which $K_a = 1.36 \times 10^{-3}$?

11.94 The compound *para*-aminobenzoic acid (PABA) is a powerful sunscreening agent whose salts were once used widely in suntan and sunscreen lotions. The parent acid is a weak acid with a pK_a of 4.92 (at 25 °C). What is the $[H_3O^+]$ and pH of a 0.030 M solution of this acid?

11.95 Barbituric acid, $HC_4H_3N_2O_3$, was discovered by the Nobel Prize-winning organic chemist Adolph von Baeyer and named after his friend Barbara. It is the parent compound of widely used sleeping drugs, the barbiturates. Its pK_a is 4.01. What is the $[H_3O^+]$ and pH of a 0.020 M solution of barbituric acid?

11.96 Choose the stronger acid in each of the following:

(a) H_2S or H_2Se,

(b) H_2Te or HI,

(c) PH_3 or NH_3.

11.97 Choose the stronger acid in each of the following:

(a) HBr or HCl,

(b) H_2O or HF,

(c) H_2S or HBr.

11.98 Choose the stronger acid in each of the following:

(a) HIO_3or HIO_4,

(b) H_3AsO_4 or H_3AsO_3.

11.99 Choose the stronger acid in each of the following:

(a) HOCl or $HClO_2$,

(b) H_2SeO_4 or H_2SeO_3.

11.100 Choose the stronger acid in each of the following:

(a) H_3AsO_4 or H_3PO_4,

(b) H_2CO_3 or HNO_3,

(c) H_2SeO_4 or $HClO_4$.

11.101 Choose the stronger acid in each of the following:

(a) $HClO_3$ or HIO_3,

(b) HIO_2 or $HClO_3$,

(c) H_2SeO_3 or $HBrO_4$.

11.102 What is the pH of a solution that contains 0.15 M CH_3COOH and 0.25 M CH_3COO^-? $K_a = 1.8 \times 10^{-5}$ for CH_3COOH.

11.103 A buffer contains 0.25 M NH_3 and 0.45 M NH_4^+. Calculate the pH of the buffer.

11.104 Suppose 25.0 mL of 0.10 M HCl is added to 250 mL of a buffer composed of 0.25 M NH_3 and 0.20 M NH_4Cl. By how much will the concentrations of the NH_3 and NH_4^+ ions change after the addition of the strong acid?

11.105 A student added 100 mL of 0.10 M NaOH to 250 mL of a buffer that contained 0.15 M CH_3COOH and 0.25 M CH_3COO^-. By how much did the concentrations of CH_3COOH and CH_3COO^-change after the addition of the strong base?

11.106 What mole ratio of NH_4Cl to NH_3 would buffer a solution at pH 9.25?

11.107 What mass of sodium acetate, $NaOOCCH_3$, needs to be added to 1.0 L of 0.15 M acetic acid (pK_a4.74) to make a buffer solution with pH 5.00?

11.108 What mass of sodium formate, NaOOCH, needs to be dissolved in 1.0 L of 0.12 M formic acid (pK_a 3.74) to make a buffer solution with pH 3.80?

11.109 What mass of ammonium chloride has to be dissolved in 500 mL of 0.20 M NH_3 to prepare a buffer solution with pH 10.00?

11.110 What mass of ammonium chloride has to be dissolved in 125 mL of 0.10 M NH_3 to make it a buffer with a pH of 9.15?

11.111 Suppose 25.00 mL of 0.100 M HCl is added to an acetate buffer, which was prepared by dissolving 0.100 mol of acetic acid and 0.110 mol of sodium acetate in water. What are the initial and final pH values? What would the pH be if the same volume of the HCl solution was added to 125 mL of pure water?

11.112 What volume of 0.15 M HCl has to be added to 100 mL of the buffer described in question 11.111 to make the pH decrease by 0.05 pH units? What volume of the same HCl solution would, if added to 100 mL of pure water, make the pH decrease by 0.05 pH units?

11.113 An 18.5 mL sample of a lactic acid solution required 17.25 mL of 0.155 M NaOH to reach an endpoint in a titration. What amount of lactic acid was in the sample?

11.114 Ascorbic acid (vitamin C) is a diprotic acid with the formula $H_2C_6H_6O_6$. A sample of a vitamin supplement was analysed by titrating a 0.1000 g sample dissolved in water with 0.0200 M NaOH. A volume of 15.20 mL of the base was required to react completely with the ascorbic acid. What was the percentage by mass of ascorbic acid in the sample?

11.115 To a mixture of NaCl and Na_2CO_3, with a mass of 1.243 g, was added 50.00 mL of 0.240 M HCl (an excess of HCl). The mixture was warmed to expel all of the CO_2 and then the unreacted HCl was titrated with 0.100 M NaOH. The titration required 22.90 mL of the NaOH solution. What was the percentage by mass of NaCl in the original mixture of NaCl and Na_2CO_3?

11.116 Aspirin is the common name of a monoprotic acid called acetylsalicylic acid. Its formula is $HOOCC_6H_4OCOCH_3$. A certain pain reliever was analysed for aspirin by dissolving 0.250 g of it in water and titrating it with 0.0300 M KOH solution. The titration required 29.40 mL of base. What is the percentage by mass of aspirin in the drug?

11.117 When 50 mL of 0.10 M formic acid, HCOOH, is titrated with 0.10 M sodium hydroxide, what is the pH at the equivalence point? (Be sure to take into account the change in volume during the titration.) Select a good indicator for this titration from table 11.9.

11.118 When 25 mL of 0.10 M aqueous ammonia is titrated with 0.10 M hydrobromic acid, what is the pH at the equivalence point? Select a good indicator for this titration from table 11.9.

11.119 What is the pH of a solution prepared by mixing 25.0 mL of 0.180 M CH_3COOH with 35.0 mL of 0.250 M NaOH?

11.120 What is the pH of a solution prepared by mixing 30.0 mL of 0.200 M CH_3COOH with 15.0 mL of 0.400 M KOH?

11.121 For the titration of 25.00 mL of 0.1000 M acetic acid with 0.1000 M NaOH, calculate the pH:

(a) before the addition of any NaOH solution

(b) after 10.00 mL of the base has been added

(c) after half of the acetic acid has been neutralised

(d) at the equivalence point.

11.122 For the titration of 25.00 mL of 0.1000 M ammonia with 0.1000 M HCl, calculate the pH:

(a) before the addition of any HCl solution

(b) after 10.00 mL of the acid has been added

(c) after half of the NH_3 has been neutralised

(d) at the equivalence point.

11.123 Use Lewis symbols to represent the reaction:

$$NH_2^- + H_3O^+ \rightarrow NH_3 + H_2O$$

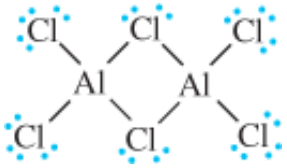
Identify the Lewis acid and Lewis base in the reaction.

11.124 Use Lewis symbols to represent the reaction:

$$BF_3 + F^- \rightarrow BH_4^-$$

Identify the Lewis acid and Lewis base in the reaction.

11.125 Aluminium chloride, $AlCl_3$, forms molecules with the formula Al_2Cl_6. The structure of these molecules is:



Use Lewis structures to show how the reaction $2AlCl_3 \rightarrow Al_2Cl_6$ is a Lewis acid–base reaction.

11.126 In each of the following reactions, identify the Lewis acid and the Lewis base.

(a) $Ni + 4CO \rightarrow [Ni(CO)_4]$

(b) $SbCl_3 + 2Cl^- \rightarrow [SbCl_5]^{2-}$

(c) $(CH_3)_3P + AlBr_3 \rightarrow (CH_3)_3P\text{-}AlBr_3$

(d) $BF_3 + ClF_3 \rightarrow [ClF_2]^+[BF_4]^-$

11.127 In each of the following reactions, identify the Lewis acid and the Lewis base.

(a) $AlCl_3 + CH_3Cl \rightarrow CH_3^+ + [AlCl_4]^-$

(b) $Zn^{2+} + 4CN^- \rightarrow [Zn(CN)_4]^{2-}$

(c) $I_2 + I^- \rightarrow I_3^-$

(d) $CaO + CO_2 \rightarrow CaCO_3$

11.128 Using liquid ammonia, NH_3, as a solvent, sodium amide, $NaNH_2$, reacts with ammonium chloride, NH_4Cl, in an acid–base neutralisation reaction. Assuming that these compounds are completely dissociated in liquid ammonia, write molecular, ionic and net ionic equations for the reaction. Which substance is the acid and which is the base?

11.129 Rank the following ions in order of increasing polarisability, and explain your reasoning: Fe^{3+}, Fe^{2+}, Pb^{2+} and V^{3+}.

11.130 Rank the following ions in order of increasing polarisability, and explain your reasoning: SO_3^{2-}, NO_3^-, CO_3^{2-} and ClO_3^-.

11.131 Rank the three Lewis acids in each of the following groups from hardest to softest, and explain your reasoning.

(a) BCl_3, BF_3 and $AlCl_3$

(b) Al^{3+}, Tl^{3+} and Tl^+

(c) $AlCl_3$, AlI_3 and $AlBr_3$

11.132 Rank the three Lewis bases in each of the following groups from hardest to softest, and explain your rankings.

(a) NH_3, SbH_3 and PH_3

(b) PO_4^{3-}, ClO_4^- and SO_4^{2-}

(c) O^{2-}, Se^{2-} and S

11.133 Explain why SO_3 is a harder Lewis acid than SO_2.

11.134 Explain why iodide is a soft base but chloride is a hard base.

11.135 Determine the Lewis structure of $SnCl_4$ and explain how it functions as a Lewis acid.

11.136 Determine the Lewis structure of SbF_5 and explain how it functions as a Lewis acid.

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11.137 What is the formula of the conjugate acid of dimethylamine, $(CH_3)_2NH$? What is the formula of its conjugate base?

11.138 Hydrazine, N_2H_4, is a weaker Brønsted–Lowry base than ammonia. In the following reaction, would the position of equilibrium lie to the left or to the right? Justify your answer.

$$N_2H_5^+ + NH_3 \rightleftharpoons N_2H_4 + NH_4^+$$

11.139 Suppose 38.0 mL of 0.00200 M HCl is added to 40.0 mL of 0.00180 M NaOH. What is the pH of the final mixture?

11.140 What is the pH of a solution that is 0.100 M in HCl and also 0.125 M in CH_3COOH? What is the concentration of acetate ion in this solution?

11.141 A solution is prepared by mixing 300 mL of 0.500 M $NH_3$and 100 mL of 0.500 M HCl. Assuming that the volumes are additive, what is the pH of the resulting mixture?

11.142 What is the pH of 0.120 M NH_4NO_3?

11.143 Predict whether the pH of 0.120 M NH_4CN is greater than, less than or equal to 7.00. Give your reasons.

11.144 Some people who take megadoses of ascorbic acid will drink a solution containing as much as 6.0 g of ascorbic acid dissolved in a glass of water. Assuming the volume to be 250 mL, calculate the pH of this solution.

11.145 For the titration of 25.00 mL of 0.1000 M HCl with 0.1000 M NaOH, calculate the pH of the reaction mixture after each of the following total volumes of base has been added to the original solution. (Remember to take into account the change in total volume.) Construct a graph showing the titration curve for this experiment.

(a) 0 mL
(b) 10.00 mL
(c) 24.90 mL
(d) 24.99 mL
(e) 25.00 mL
(f) 25.01 mL
(g) 25.10 mL
(h) 26.00 mL
(i) 50.00 mL

11.146 The fluorides BF_3, AlF_3, SiF_4 and PF_5 are Lewis acids. They all form very stable fluoroanions when treated with lithium fluoride. In contrast, three other fluorides, CF_4, NF_3 and SF_6, do not react with lithium fluoride. Use Lewis acid–base concepts to explain this behaviour.

11.147 Complete each of the following reactions by considering the Lewis acid and base characteristics of the starting materials.

(a) $AlCl_3 + LiCH_3 \rightarrow ?$
(b) SO_3 + excess $H_2O \rightarrow ?$
(c) $SbF_5 + LiF \rightarrow ?$
(d) $SF_4 + AsCl_5 \rightarrow ?$

11.148 Certain proteolytic enzymes react in alkaline solutions. One of these enzymes produces 1.8

micromoles of hydrogen ions per second in a 2.50 mL portion of a buffer composed of 0.25 M $NH_3$and 0.20 M NH_4Cl. By how much will the concentrations of the NH_3 and NH_4^+ ions change after the reaction has run for 35 seconds?

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KEY TERMS

acid
acid–base indicator
acid–base reactions
acid–base titration
acidic
acidity constant(Ka)
adduct
alkaline
amphiprotic
autoprotolysis
Kw
base
basic
basicity constant(Kb)
Brønsted–Lowry
buffer capacity
buffer solution
burette
conjugate acid
conjugate acid–base pair
conjugate base
diprotic acid
diprotic base
electrophile
endpoint
equivalence point
hard Lewis acid
hard Lewis base
Henderson–Hasselbalch equation
heterolytic cleavage
homolytic cleavage
hydronium ion
hydroxide ion
Lewis acid
Lewis base
monoprotic acid
monoprotic base
neutral
nucleophiles
pH
pK_a
pK_b
pK_w
pOH
polyprotic acid
polyprotic base
resonance stabilisation
soft Lewis acid
soft Lewis base
strong acid
strong base
titrant
titration curve
triprotic acid
weak acid
weak base
zwitterion

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CHAPTER

12 Oxidation and Reduction

In the preceding chapters, we learned about some important reactions that take place in aqueous solutions. In this chapter, we will expand on that knowledge with a discussion of a class of reactions that involve the transfer of one or more electrons from one chemical species to another. Chemists call these electron transfer processes oxidations and reductions or, simply, redox reactions. Redox reactions are very common. For example, the photo on this page shows a rusty iron anchor, all that remains of the *Marie Gabrielle* (1880) on the 'Shipwreck Coast' at Moonlight Head in Victoria, Australia. The *Marie Gabrielle* was en route from China with a load of tea when she hit the reef in strong winds. Formation of rust is a redox process in which electrons are transferred from iron to oxygen.

In this chapter, we will learn how to recognise and analyse the changes that occur in these reactions. We will also learn that redox reactions can be used to generate electricity in galvanic cells (commonly called batteries) and that, by reversing this process, electricity can be used to cause nonspontaneous redox reactions. Because electricity plays a role in these systems, the processes involved are electrochemical changes. The study of such changes is called electrochemistry.



KEY TOPICS

12.1 Oxidation and reduction
12.2 Balancing net ionic equations for redox reactions
12.3 Galvanic cells
12.4 Reduction potentials
12.5 Relationship between cell potential, concentration and Gibbs energy
12.6 Corrosion

12.7 Electrolysis
12.8 Batteries

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12.1 Oxidation and Reduction

Among the first reactions studied by early scientists were those that involved oxygen. According to the original definition, *oxidation* is a reaction with oxygen. If a metal atom M reacts with molecular oxygen, O_2, according to the equation $M + \frac{1}{2}O_2 \rightarrow MO$, formation of the metal oxide MO occurs through transfer of electrons (e^-) from the metal atom:

$$M \rightarrow M^{2+} + 2e^-$$

to the oxygen atom:

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$

Hence:

$$M + \frac{1}{2}O_2 \rightarrow M^{2+} + O^{2-}$$

By taking up two electrons, oxygen acquires a completely filled valence shell with eight electrons. On the other hand, the reverse reaction (removal of oxygen from the metal oxide to give the metal in its elemental form) was described as *reduction*.

Only much later did chemists realise that the reactions of oxygen constitute a special case of a more general phenomenon, one in which electrons are transferred from one substance to another. For example, the reaction between sodium and chlorine to give sodium chloride proceeds through transfer of electrons from sodium (*oxidation* of sodium) to chlorine (*reduction* of chlorine):

$$\begin{aligned} Na &\rightarrow Na^+ + e^- && \text{(oxidation)} \\ \frac{1}{2}Cl_2 + e^- &\rightarrow Cl^- && \text{(reduction)} \end{aligned}$$

Notice that the electron appears as a 'product' if the process is oxidation and as a 'reactant' if the process is reduction.

Based on our understanding of this process, we define **oxidation** as the loss of electrons. An **oxidising agent** (or oxidant) is then a substance that has the ability to remove electrons from a substance. **Reduction** is the gain of electrons. A **reducing agent** (or reductant) is a substance with the ability to donate electrons to another substance. Thus, the oxidising agent is in fact reduced, and the reducing agent is oxidised. Collectively, *electron transfer* reactions are called **reduction–oxidation reactions** or **redox reactions**.

Redox reactions are summarised in the following equation:

$$\text{reducing agent} \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftarrows}} \text{oxidising agent} + \text{electron(s)}$$

To help remember, think of the mnemonic OIL RIG, which stands for 'oxidation is loss, reduction is gain'. Since positive and negative charges must always be balanced in a reaction, *oxidation and reduction always occur together*. No substance is ever oxidised unless something else is reduced, and the total number of electrons lost by one substance is always the same as the total number gained by the other. In the reaction of sodium with chlorine, for example, the overall reaction is:

$$2Na + Cl_2 \rightarrow 2NaCl$$

When two sodium atoms are oxidised, two electrons are lost, which is exactly the number of electrons gained when one Cl_2 molecule is reduced.

WORKED EXAMPLE 12.1

Identifying Reduction–oxidation

The bright light produced by the reaction between magnesium and oxygen is often used in fireworks displays (figure 12.1). The product of the reaction is magnesium oxide, MgO:

$$2Mg + O_2 \rightarrow 2MgO$$

Which element is oxidised and which is reduced? What are the oxidising and reducing agents?



FIGURE 12.1 The reaction between magnesium and oxygen produces bright white light.ST Yiap

Analysis

Magnesium oxide is an ionic substance consisting of a metal and a nonmetal. The locations of the elements in the periodic table (groups 2 and 16) tell us that the ions in MgO are Mg^{2+} and O^{2-}.

Solution

When a magnesium atom becomes a magnesium ion, it must lose two electrons:

$$Mg \rightarrow Mg^{2+} + 2e^-$$

Because magnesium is oxidised, it must be the reducing agent. Oxygen can gain these two electrons to give an O^{2-} ion:

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$

O^2 is reduced and so it must be the oxidising agent.

Is our answer reasonable?

There are two things we can do to check our answers. First, we can check to be sure that we have placed electrons on the correct sides of the equations. As with ionic equations, the number of atoms of each kind and net charge must be the same on both sides. We see that this is true for both equations. (If we had placed the electrons on the wrong side, the charges would not balance.) As oxidation reactions always have electrons on the right-hand side, and reduction reactions always have electrons on the left-hand side, by observing the locations of the electrons in the equations, we come to the same conclusions that Mg is oxidised and O_2 is reduced.

Another check is noting that we have identified one substance as being oxidised and the other as being reduced. If we had made a mistake, we might have found that both were oxidised, or both were reduced. That is impossible because, in every reaction in which there is oxidation, there must also be reduction, and vice versa.

PRACTICE EXERCISE 12.1

Identify the substances oxidised and reduced and the oxidising and reducing agents in there action of copper and chlorine to form $CuCl_2$.

Oxidation Numbers

The reaction of magnesium with oxygen in worked example 12.1 is clearly a redox reaction. However, not all reactions with oxygen produce ionic products. For example, the reaction of sulfur with oxygen is a redox reaction, but the product sulfur dioxide, SO_2, is covalent. To help us follow electron transfers in such reactions, we use the convenient concept of the oxidation number. (Note that oxidation numbers in covalent compounds are used for convenience and should not be misinterpreted as ionic charges.) The **oxidation number** (or **oxidation state**) is the hypothetical charge that an atom in a molecule *would* possess *if* the shared electron pairs in each covalent bond were assigned to the more electronegative element in the bond. Thus, the oxidation number is the charge that each atom would have if the compound were divided into monatomic ions.

The oxidation number of an element in a particular compound is assigned according to the following set of rules.

1. The oxidation number of any free element (an element not combined chemically with a different element) is 0. For example, Ar, Fe, O in O_2, P in P_4 and S in S_8 all have oxidation numbers of 0.
2. The oxidation number for any simple, monatomic ion (e.g. Na^+ and Cl^-) is equal to the charge on the ion.
3. The sum of all the oxidation numbers of the atoms in a neutral molecule must equal zero. The sum of all the oxidation numbers in a polyatomic ion must equal the charge on the ion.
4. In all of its compounds, fluorine has an oxidation number of -1.
5. In most of its compounds, hydrogen has an oxidation number of +1.
6. In most of its compounds, oxygen has an oxidation number of -2.

In addition to these basic rules, some other chemical knowledge is required. As shown in chapter 4, the periodic table can be used to determine the charges on certain ions of the elements. For instance, all the metals in group 1 form ions with a 1+ charge, and all those in group 2 form ions with a 2+ charge. This means that when we find sodium in a compound, we can assign it an oxidation number of +1 because its simple ion, Na^+, has a charge of 1+. Similarly, calcium in a compound exists as Ca^{2+} and has an oxidation number of +2. In binary ionic compounds with metals, the nonmetals have oxidation numbers that are equal to the charges on their anions. For example, the compound Fe_2O_3 contains the oxide ion, O^{2-}, which is assigned an oxidation number of -2. Similarly, Mg_3P_2 contains the phosphide ion, P^{3-}, which has an oxidation number of -3.

It is important to realise that the oxidation number does not actually equal a charge on an atom. To differentiate oxidation numbers from actual electrical charges, the following convention is used; oxidation numbers are given with the sign *before* the number, whereas electrical charges specify the sign *after* the number. For example, the sodium ion has a charge of 1+ and an oxidation number of +1. In a molecular formula, oxidation numbers are placed as a small Arabic numeral above the corresponding element symbol:

$$\overset{+6}{H_2}\overset{}{S}\overset{}{O_4} \quad \overset{+7}{K}\overset{}{M}\overset{}{n}\overset{}{O_4} \quad \overset{+5}{N}\overset{}{a}\overset{}{N}\overset{}{O_3} \quad \overset{-3}{N}\overset{+1}{H_4}\overset{}{Cl}$$

Sometimes it is convenient to specify the oxidation number of an element when its name is written out. This is done by writing the oxidation number as a Roman numeral in parentheses after the name of the element. For example, 'iron(III)' means iron with an oxidation number of +3.

The numbered rules given on the previous page usually come into play when an element can have more than one oxidation number, such as transition metals. Iron can form Fe^{2+} and Fe^{3+} ions so, in an iron compound, the rules help to determine which one is present. Nonmetals can also exhibit more than one oxidation number, especially when they are combined with hydrogen and oxygen in compounds or polyatomic ions, and their oxidation numbers must be calculated using the rules.

WORKED EXAMPLE 12.2

Assigning Oxidation Numbers

Molybdenum disulfide, MoS_2, has a structure that allows it to be used as a dry lubricant, much like graphite. What are the oxidation numbers of the atoms in MoS_2?

Analysis

This is a binary compound of a metal and a nonmetal so, for the purposes of assigning oxidation numbers, we assume it to contain ions. Molybdenum is a transition metal, so there is no simple rule to tell what its ions are. However, sulfur is a nonmetal in group 16, and its ion is S^{2-}.

Solution

Because S^{2-} is a simple monatomic ion, its charge equals its oxidation number, so sulfur has an oxidation number of -2. Now we can use rule 3 (the summation rule) to determine the oxidation number of molybdenum, which we will represent by *x*.

$$\begin{aligned} &\text{S} \quad (2\,\text{atoms}) \times (-2) = -4 \quad \text{(rule 2)} \\ &\text{Mo} \quad \underline{(1\,\text{atom}) \times (x) = x} \\ &\qquad\qquad \text{Sum} = 0 \quad \text{(rule 3)} \end{aligned}$$

The value of *x* must be +4 for the sum to be 0. Therefore, the oxidation numbers are Mo = +4 and S = -2.

PRACTICE EXERCISE 12.2

Assign oxidation numbers to each atom in (a) $NiCl_2$, (b) Mg_2TiO_4, (c) $K_2Cr_2O_7$, (d) HPO_4^{2-}, (e) $(NH_4)_2Ce(NO_3)_6$, (f) $K_4[Fe(CN)_6]$ and (g) $Na_3[Fe(CN)_6]$.

Some classes of compounds have atoms in oxidation states that are exceptions to the rules on p. 491, but these are rare. The usual examples are the oxygen atoms in peroxides (for example, in hydrogen peroxide, H_2O_2, which is used for bleaching hair, the oxygen atoms have an oxidation number of -1, instead of -2) and the hydrogen atoms in hydrides (for example, in calcium hydride, CaH_2, the hydrogen atoms have an oxidation number of -1, instead of +1). Oxidation numbers calculated by the rules on p. 491 can have fractional values (for example, the nitrogen atoms in the ionic compound sodium azide, NaN_3 (see figure 12.2), have an oxidation number of $+\frac{1}{3}$).



FIGURE 12.2 The airbags used as safety devices in modern cars are inflated by the explosive decomposition of sodium azide, which gives elemental sodium and gaseous nitrogen through the reaction:

$$2NaN_3 \rightarrow 2Na + 3N_2$$

Sodium metal, which is highly reactive, is converted into a harmless silicate glass through reaction with additives, such as potassium nitrate and silicon dioxide. Because of the high toxicity of sodium azide, it is now sometimes replaced by less harmful nitrogen-rich compounds, such as tetrazoles (five-membered rings with one carbon and four nitrogen atoms).Richard Olivier

Using the concept of oxidation numbers, we can now view a redox reaction as a chemical reaction in which changes in oxidation numbers

occur. *Oxidation is an increase in oxidation number. Reduction is a decrease in oxidation number.*

WORKED EXAMPLE 12.3

Using Oxidation Numbers to Analyse Redox Reactions

Identify the substance oxidised and the substance reduced as well as the oxidising and reducing agents in the reaction:

$$2KCl + MnO_2 + 2H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + Cl_2 + 2H_2O$$

Analysis

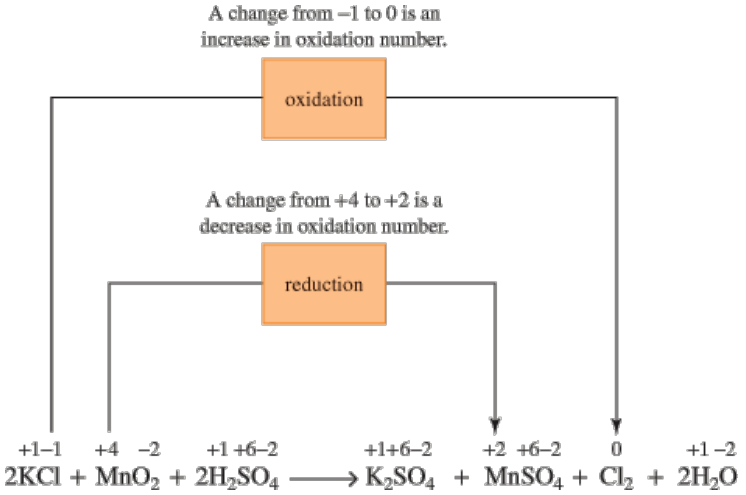
To identify the redox species, we need to consider what is happening with the oxidation numbers. This will tell us what is oxidised and reduced. Then we recall that the substance oxidised is the reducing agent, and the substance reduced is the oxidising agent.

Solution

To identify redox changes using oxidation numbers, we first assign an oxidation number to each atom on both sides of the equation:

$$\underset{+1-1}{2KCl} + \underset{+4-2}{MnO_2} + \underset{+1+6-2}{2H_2SO_4} \rightarrow \underset{+1+6-2}{K_2SO_4} + \underset{+2+6-2}{MnSO_4} + \underset{0}{Cl_2} + \underset{+1-2}{2H_2O}$$

Next we look for changes, keeping in mind that an increase in oxidation number is oxidation and a decrease is reduction.



Thus, the Cl in KCl is oxidised and the Mn in MnO_2 is reduced. The reducing agent is KCl and the oxidising agent is MnO_2. (Notice that, in identifying the oxidising and reducing agents, we specify the entire formulae for the substances containing the atoms changing oxidation numbers.)

Is our answer reasonable?

There are lots of things we could check here. We have found changes that lead us to identify an oxidation and a reduction process; this gives us confidence that we have done the rest of the work correctly.

PRACTICE EXERCISE 12.3

The reaction of concentrated hydrochloric acid, HCl, with potassium permanganate, $KMnO_4$, is a convenient method of preparing chlorine gas in the laboratory:

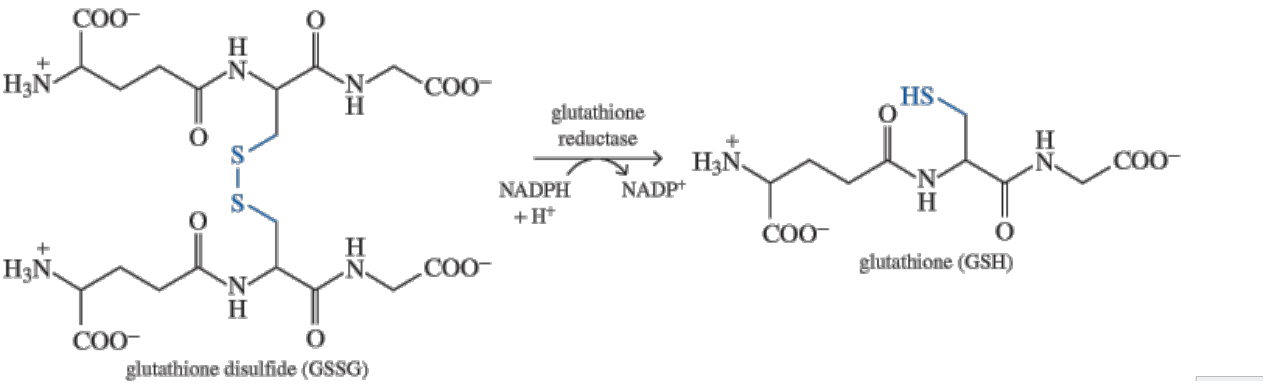
$$6HCl + 2KMnO_4 + 2H^+ \rightarrow 3Cl_2 + 2MNO_2 + 4H_2O + 2K^+$$

Identify the substances oxidised and reduced as well as the oxidising and reducing agents in this reaction.

Chemical Connections

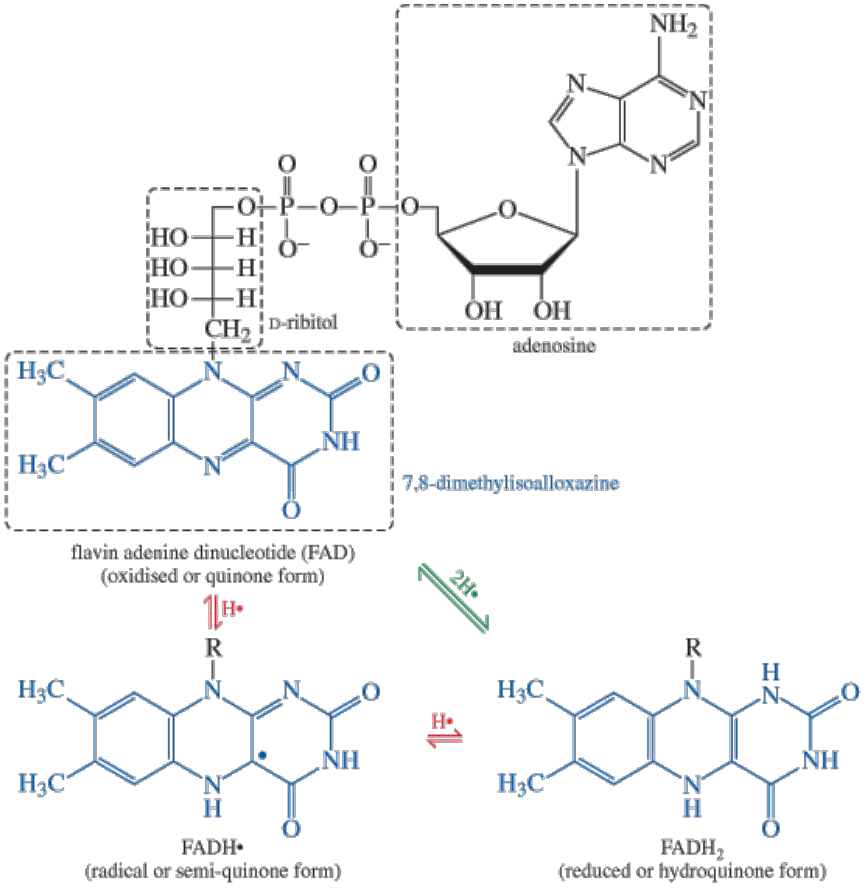
Biological Redox Processes

Redox reactions are extremely important in metabolic processes. Many of these processes involve the breaking of C—H bonds and the transfer of two electrons from C to an electron acceptor. Often, in biological processes, the redox process involves enzymes and the electrons are transferred to oxygen. Consider, for example, the redox process shown below.



In this process glutathione disulfide (GSSG) is reduced to the tripeptide (see chapter 24) glutathione (γ-L-glutamyl-L-cysteinylglycine, GSH). GSH is a reducing agent (antioxidant) that helps to protect cells from potentially damaging reactive oxygen species, such as oxygen radicals and peroxides. This process is catalysed by glutathione reductase. Glutathione reductase contains flavin adenine dinucleotide (FAD), which acts as the electron transfer group. Generally, electron transfers involving flavins can occur in two ways:

- Two sequential one-electron transfer processes involving the semiquinone or radical form FADH• and the fully reduced or hydroquinone form $FADH_2$, i.e. FAD → FADH• → $FADH_2$ (the red pathway shown below).
- A simultaneous two-electron transfer, i.e. FAD → $FADH_2$, which does not involve the semi-quinone intermediate FADH• (the green pathway shown below).



Photosynthesis

Another important biological redox process is photosynthesis. The energy we gain from the food we eat and the fossil fuels we burn can ultimately be tracked back to the complicated biochemical process of photosynthesis. Photosynthesis converts the energy in sunlight into chemical energy that biological systems can use. It occurs in many plants as well as in some bacteria.

Photosynthesis is a complex series of coordinated redox reactions but the overall effect is to reduce gaseous CO_2 to carbohydrates (if $x = 6$, the carbohydrate is most commonly glucose) and to oxidise H_2O to oxygen.

$$xCO_2 \quad xH_2O \xrightarrow{\text{light}} (CH_2O)_x \quad xO_2$$

The photosynthetic process takes place in compartments, or organelles, known as chloroplasts. The process has two components: *light reactions* and *dark reactions*. The light reactions use energy from light to create the substances required for the dark reactions. The absorption of light energy occurs in two types of reaction centres in structures known as thylakoids within the chloroplasts. The reaction centres are called photosystem I (PS I) and photo system II (PS II) (figure 12.3).

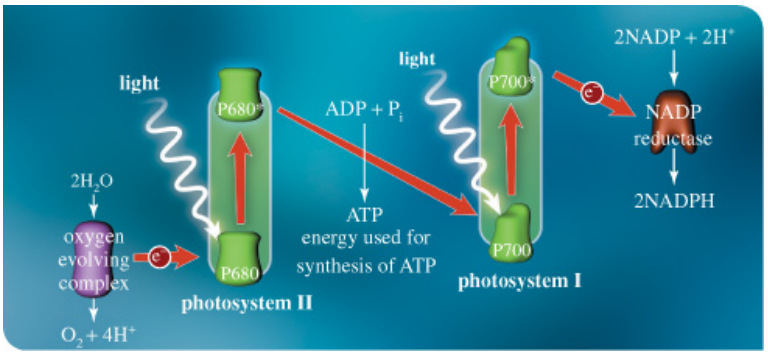


FIGURE 12.3 This scheme shows how electrons are shuttled through an electron transport chain in the light-driven component of photosynthesis.

In PS II, the pigment chlorophyll (which is what makes plants green) and several other 'accessory pigments', including carotenes and xanthophylls, absorb light and pass its energy to a central chlorophyll complex known as P680. The energy oxidises the central chlorophyll complex, releasing electrons. This triggers a series of redox reactions, where electrons are shuttled though an electron transport chain.

The electrons released from the chlorophyll complex are replaced by electrons from the oxidation of water.

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+$$

The electrons released from chlorophyll in PS II flow to the cytochrome b_6f complex (cyt b_6f) within the thylakoid membrane via another complex called plastoquinone (figure 12.4). This flow generates a proton gradient (a build-up of positive charge on one side of the membrane). The charge differential across the membrane then powers the synthesis of the high-energy molecule adenosine triphosphate, ATP, from adenosine diphosphate, ADP, and inorganic phosphate, P_i, catalysed by the enzyme ATP synthase according to the equation:

$$ADP + P_i \rightarrow ATP$$

ATP is one of the substances used in the dark reactions.

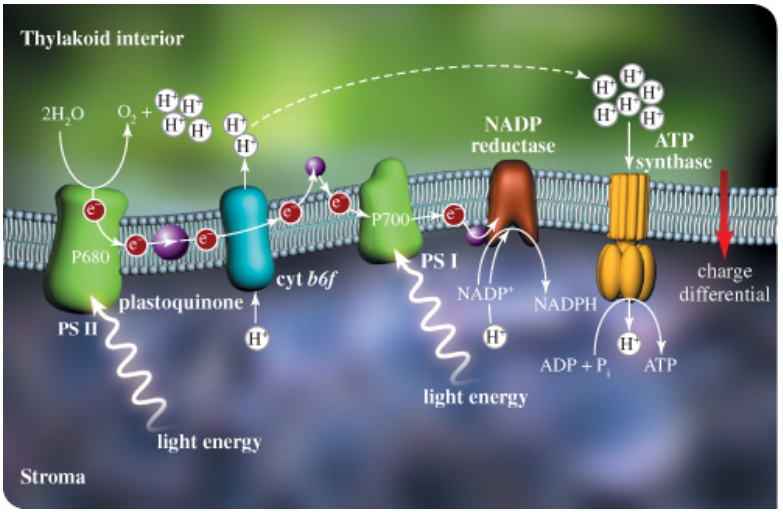


FIGURE 12.4 Overview of photosynthetic processes as they occur in plants, algae and cyanobacteria.

Electrons from cyt b_6f are transferred to PS I. At the chlorophyll complex in PS I (P700), energy from light excites the electrons to a higher energy state. The electrons reduce $NADP^+$ to NADPH in a reaction catalysed by the enzyme NADP reductase according to the equation:

$$2NADP^+ + 2H^+ + 4e \rightarrow 2NADPH$$

The dark reactions (also called the Calvin-Benson cycle) then use NADPH and ATP to produce glyceraldehyde-3-phosphate (G3P) from CO_2 and H_2O according to the equation:

$$3CO_2 + 6NADPH + 5H_2O + 9ATP \rightarrow G3P + 2H^+ + 6NADP^+ + 9ADP + 8P_i$$

G3P is a three-carbon sugar from which other carbohydrates (such as glucose) are produced through subsequent metabolic processes.

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12.2 Balancing Net Ionic Equations for Redox Reactions

Many redox reactions take place in aqueous solution and many of these involve ions; they are ionic reactions. In studying redox reactions, it is often helpful to write ionic and net ionic equations. We do this by dividing the oxidation and reduction processes into individual equations called **half-equations**, which are then balanced separately. We combine the balanced half-equations to obtain the fully balanced net ionic equation.

To illustrate the method, we will balance the net ionic equation for the reaction of iron(III) chloride, $FeCl_3$, with tin(II) chloride, $SnCl_2$, in aqueous solution, which changes the Fe^{3+} to Fe^{2+} and the Sn^{2+} to Sn^{4+}. In the reaction, the chloride ion is unaffected — it is a spectator ion.

We begin by writing an equation that shows only the species involved in the reaction. In this case, the reactants are Fe^{3+} and Sn^{2+}, and the products are Fe^{2+} and Sn^{4+}. The equation is therefore:

$$Fe^{3+} + Sn^{2+} \rightarrow Fe^{2+} + Sn^{4+}$$

Note that, while the equation is balanced in terms of mass, it is not yet balanced in terms of charge on either side of the arrow. To balance this equation in terms of both mass and charge, we must first identify the reactant and product of the two half-equations:

$$Sn^{2+} \rightarrow Sn^{4+}$$
$$Fe^{3+} \rightarrow Fe^{2+}$$

Next, we balance the half-equations so that each obeys both criteria for a balanced ionic equation; both atoms and charge have to balance. Obviously, the atoms are already balanced in each equation. The charge, however, is not. We add electrons as necessary to balance the charges. For the first half-equation, two electrons are added to the right, so the net charge on both sides will be 2+. In the second half-equation, one electron is added to the left, which makes the net charge on both sides equal to 2+.

$$\begin{aligned} Sn^{2+} &\rightarrow Sn^{4+} + 2e^- \\ Fe^{3+} + e^- &\rightarrow Fe^{2+} \end{aligned}$$

Note that an oxidation half-equation will *always* have the electrons on the right-hand side and a reduction half-equation will *always* have the electrons on the left-hand side. Therefore, the first half-equation corresponds to an oxidation reaction and the second to a reduction reaction.

In any overall redox reaction, the number of electrons gained always equals the number lost. Given that two electrons are lost by Sn^{2+} in the oxidation process:

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$$

two electrons must be used in the reduction process. Therefore, we need to multiply each of the coefficients in the reduction half-equation by 2:

$$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$$

We combine the balanced half-equations by adding them to give:

$$\begin{aligned} Sn^{2+} &\rightarrow Sn^{4+} + 2e^- \\ 2Fe^{3+} + 2e^- &\rightarrow 2Fe^{2} \\ \hline Sn^{2+} + Fe^{3+} + 2e^- &\rightarrow Sn^{4+} + 2Fe^{2+} + 2e^- \end{aligned}$$

Finally, we note that two electrons appear on each side of the equation. We can cancel these to give the final

balanced equation:

$$Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+}$$

Notice that both the charge *and* the number of each type of atom are now balanced.

PRACTICE EXERCISE 12.4

Balance the following redox equation:

$$Al(s) + Cu^{2+}(aq) \rightarrow Al^{3+}(aq) + Cu(s)$$

Redox Reactions in Acidic and Basic Solutions

In many redox reactions in aqueous solutions, H_3O^+ or OH^- ions play an important role, as do water molecules. For example, when solutions of $K_2Cr_2O_7$ and $FeSO_4$ are mixed, the acidity of the mixture decreases as the reaction proceeds, as dichromate ions, $Cr_2O_7^{2-}$, oxidise Fe^{2+}. This is because the reaction uses up H_3O^+ as a reactant and produces H_2O as a product. In other reactions, OH is consumed, while in still others H_2O is a reactant. Also, in many cases, the products (or even the reactants) of a redox reaction will depend on the acidity of the solution. For example, in an acidic solution, MnO_4^- is reduced to Mn^{2+} ions, but in a neutral or slightly basic solution the reduction product is insoluble MnO_2, with Mn having an oxidation number of +4. We will first learn how to balance acidic solutions. Balancing basic solutions uses the same concepts but requires an additional step at the end to ensure that the final equation does not show H^+.

Acidic Solutions

$Cr_2O_7^{2-}$ (orange-red) reacts with Fe^{2+} (almost colourless) in an acidic solution to give Cr^{3+} (green) and Fe^{3+} (orange) as products (figure 12.5). Therefore, the equation we must balance is:

$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

The oxidation number of Cr in $Cr_2O_7^{2-}$ is +6.



FIGURE 12.5 A solution of $K_2Cr_2O_7$ being added to an acidic solution containing Fe^{2+}. Note the green-orange swirl of products.Peter Lerman

The balanced equation can be found through the following steps.

Step 1: Identify the reactant and product of each of the oxidation and reduction processes.

$$\begin{aligned} Cr_2O_7^{2-} &\rightarrow Cr^{3+} \quad \text{(reduction)} \\ Fe^{2+} &\rightarrow Fe^{3+} \quad \text{(oxidation)} \end{aligned}$$

Step 2: Balance atoms other than H and O.

There are two Cr atoms on the left and only one on the right, so we place a coefficient of 2 in front of Cr^{3+}. The oxidation half-equation is already balanced in terms of atoms.

$$\begin{aligned} Cr_2O_7^{2-} &\rightarrow 2Cr^{3+} \\ Fe^{2+} &\rightarrow Fe^{3+} \end{aligned}$$

Step 3: Balance oxygen by adding H_2O.

There are seven oxygen atoms on the left of the reduction half-equation and none on the right. Therefore, we add $7H_2O$ to the right side of the reduction half-equation.

$$\begin{aligned} Cr_2O_7^{2-} &\rightarrow 2Cr^{3+} + 7H_2O \\ Fe^{2+} &\rightarrow Fe^{3+} \end{aligned}$$

Step 4: Balance hydrogen by adding H^+. Note that, for simplicity, we use H^+, rather than H_3O^+, when balancing redox equations.

After adding the water, we see that we have created an imbalance; the first half-equation has 14 hydrogen atoms on the right and none on the left. To balance these, we add $14H^+$ to the left side of the half-equation.

$$\begin{aligned} 14H^+ + Cr_2O_7^{2-} &\rightarrow 2Cr^{3+} + 7H_2O \\ Fe^{2+} &\rightarrow Fe^{3+} \end{aligned}$$

Now each half-equation is balanced in terms of number and type of atoms involved. Next we will balance the charge.

Step 5: Balance the charge by adding electrons.

First we calculate the net charge on each side. For the reduction half-equation, we have:

$$\underline{14H^+ + Cr_2O_7^{2-}} \rightarrow \underline{2Cr^{3+} + 7H_2O}$$

$$\text{net charge} = (14+) + (2-) = 12+ \qquad \text{net charge} = 2(3+) + 0 = 6+$$

To balance the net charge, we need to add six electrons to the left-hand side of the halfequation. Recall that, in balanced reduction half-equations, electrons always appear on the left-hand side.

$$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

To balance the oxidation half-equation, we need to add one electron to the right.

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

Step 6: Make the number of electrons gained equal to the number lost.

At this point we have the two balanced half-equations:

$$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$
$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

Because six electrons are gained in the reduction process, but only one is lost in the oxidation process, we multiply all of the coefficients of the oxidation half-equation by 6.

$$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$$

Step 7: Add the balanced half-equations.

$$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$
$$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$$
$$6e^- + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 6e^-$$

Step 8: Cancel any species that is the same on both sides.
Cancel six electrons from both sides to give the final balanced equation:

$$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

Step 9: Check that the final equation is balanced in terms of number and type of atoms and charge. In step 4, we used H^+ instead of H_3O^+. If you want to express your equation with H_3O^+, take note of the number of H^+ in the balanced equations and add the same number of H_2O to *both* sides. Then combine H^+ and H_2O as H_3O^+.

Summary of the steps for balancing an equation for a redox reaction in an acidic solution

Step 1: Identify reactants and products for each half-equation.

Step 2: Balance atoms other than H and O.

Step 3: Balance oxygen by adding H_2O.

Step 4: Balance hydrogen by adding H^+.

Step 5: Balance net charge by adding e^-.

Step 6: Make e^- gain equal e^- loss.

Step 7: Add the balanced half-equations.

Step 8: Cancel any species that is the same on both sides.

Step 9: Check that there are the same number and type of atoms and the same charge on each side of the reaction.

WORKED EXAMPLE 12.4

Balancing Redox Equations in Acidic Solutions

Balance the following equation. The reaction occurs in acidic solution.

$$MnO_4^- + H_2SO_3 \rightarrow SO_4^{2-} + Mn^{2+}$$

Solution

We follow the steps just given. The oxidation number of Mn in MnO_4^- is +7, of S in H_2SO_3 is +4

and of S in SO_4^{2-} is +6.

Step 1: Identify the reactants and products of the reduction and oxidation processes.

$$\begin{aligned} MnO_4^- &\rightarrow Mn^{2+} \quad \text{(reduction)} \\ H_2SO_3 &\rightarrow SO_4^{2-} \quad \text{(oxidation)} \end{aligned}$$

Step 2: There is nothing to do for this step. All the atoms except H and O are already balanced.

Step 3: Add H_2O to balance oxygen.

$$\begin{aligned} MnO_4^- &\rightarrow Mn^{2+} + 4H_2O \\ H_2O + H_2SO_3 &\rightarrow SO_4^{2-} \end{aligned}$$

Step 4: Add H^+ to balance hydrogen.

$$\begin{aligned} 8H^+ + MnO_4^- &\rightarrow Mn^{2+} + 4H_2O \\ H_2O + H_2SO_3 &\rightarrow SO_4^{2-} + 4H^+ \end{aligned}$$

Step 5: Balance the charge by adding electrons.

$$\begin{aligned} 5e^- + 8H^+ + MnO_4^- &\rightarrow Mn^{2+} + 4H_2O \\ H_2O + H_2SO_3 &\rightarrow SO_4^{2-} + 4H^+ + 2e^- \end{aligned}$$

Step 6: Make electron loss equal to electron gain by multiplying the first equation by 2 and the second equation by 5.

$$\begin{aligned} 10e^- + 16H^+ + 2MnO_4^- &\rightarrow 2Mn^{2+} + 8H_2O \\ 5H_2O + 5H_2SO_3 &\rightarrow 5SO_4^{2-} + 20H^+ + 10e^- \end{aligned}$$

Step 7: Add the balanced half-equations.

$$\begin{aligned} 10e^- + 16H^+ + 2MnO_4^- &\rightarrow 2Mn^{2+} + 8H_2O \\ 5H_2O + 5H_2SO_3 &\rightarrow 5SO_4^{2-} + 20H^+ + 10e^- \end{aligned}$$

$$10e^- + 16H^+ + 2MnO_4^- + 5H_2O + 5H_2SO_3 \rightarrow 2Mn^{2+} + 8H_2O + 5SO_4^{2-} + 20H^+ + 10e^-$$

Step 8: Cancel $10e^-$, $16H^+$ and $5H_2O$ from both sides. The final equation is:

$$2MnO_4^- + 5H_2SO_3 \rightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-} + 4H^+$$

Is our answer reasonable?

This is step 9. The check is simple. Notice that each side of the equation has the same number of atoms of each element and the same net charge. This is what makes it a balanced equation and confirms that we have completed the problem correctly.

PRACTICE EXERCISE 12.5

The element technetium (atomic number 43) is radioactive; one of its isotopes, ^{99m}Tc, is used in medicine for diagnostic imaging. The isotope is usually obtained in the form of the pertechnetate anion, TcO_4^-, but its use sometimes requires the

technetium to be in a lower oxidation state.

Reduction can be carried out using Sn^{2+} in an acidic solution. The equation is:

$$TcO_4^- + Sn^{2+} \rightarrow Tc^{4+} + Sn^{4+} \quad \text{(acidic solution)}$$

Balance the equation.

Basic Solutions

In basic solutions, the dominant species are H_2O and OH^-. Strictly speaking, these should be used to balance the half-equations. However, the simplest way to obtain a balanced equation for a basic solution is to first balance it as if it were in acidic solution. We balance the equation using the nine steps just described, and then we use the four-step procedure described below to convert the equation to the correct form for a basic solution. The conversion uses the fact that H^+ and OH^- react in a 1 : 1 ratio to give H_2O.

Additional steps for balancing an equation for a redox reaction in a basic solution

Step 10: Take note of the number of H^+ in the balanced equation and add the same number of OH^- to *each* side.

Step 11: Combine each pair of H^+ and OH^- to form one H_2O.

Step 12: Cancel any H_2O molecules that occur on both sides.

Step 13: Check that there are the same number and type of atoms and the same charge on each side of the reaction.

As an example, suppose we wanted to balance the following equation in a basic solution:

$$SO_3^{2-} + MnO_4^- \rightarrow SO_4^{2-} + MnO_2$$

Following steps 1 to 9 for acidic solutions gives:

$$2H^+ + 3SO_3^{2-} + 2MnO_4^- \rightarrow 3SO_4^{2-} + 2MnO_2 + H_2O$$

Conversion of this equation to one appropriate for a basic solution proceeds as follows.

Step 10: Take note of the number of H^+ in the balanced equation and add the same number of OH^- to *each* side.

The equation for an acidic solution has $2H^+$ on the left, so we add $2OH^-$ to *each* side.

$$2OH^- + 2H^+ + 3SO_3^{2-} + 2MnO_4^- \rightarrow 3SO_4^{2-} + 2MnO_2 + H_2O + 2OH^-$$

Step 11: Combine H^+ and OH^- to form H_2O.

The left side has $2OH^-$ and $2H^+$, which become $2H_2O$.

$$2OH^- + 2H^+ + 3SO_3^{2-} + 2MnO_4^- \longrightarrow 3SO_4^{2-} + 2MnO_2^- + H_2O + 2OH^-$$

$$2H_2O + 3SO_3^{2-} + 2MnO_4^- \longrightarrow 3SO_4^{2-} + 2MnO_2^- + H_2O + 2OH^-$$

Step 12: Cancel any H_2O molecules that occur on both sides.

In this equation, one H_2O can be eliminated from both sides. The final equation, balanced in a basic

solution, is:

$$H_2O + 3SO_3^{2-} + 2MnO_4^- \rightarrow 3SO_4^{2-} + 2MnO_2 + 2OH^-$$

Step 13: Check that the equation is balanced in terms of number and type of atoms and charge.

PRACTICE EXERCISE 12.6

Balance the following equation in a basic solution.

$$MnO_4^- + C_2O_4^{2-} \rightarrow MnO_2 + CO_3^{2-}$$

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12.3 Galvanic Cells

From the previous discussion, it is obvious that in chemical processes an oxidation cannot occur without a simultaneous reduction, and vice versa. This is because one substance has to release electrons (the reducing agent, which becomes the oxidised species after the reaction), which have to be taken up by another substance (the oxidising agent, which becomes the reduced species after the reaction). Because a specific substance cannot donate electrons to or take up electrons from every other compound, no absolute oxidising or reducing agents actually exist. In fact, whether a substance acts as an oxidant or reductant in a reaction depends on the nature of the reaction partner to be oxidised or reduced, respectively. We will illustrate this with three examples.

Example 1

If a strip of metallic zinc is dipped into a solution of copper sulfate, a reddish-brown deposit of metallic copper forms on the zinc (see figure 12.6). Analysis of the solution reveals that it now contains zinc ions, as well as some remaining unreacted copper ions.

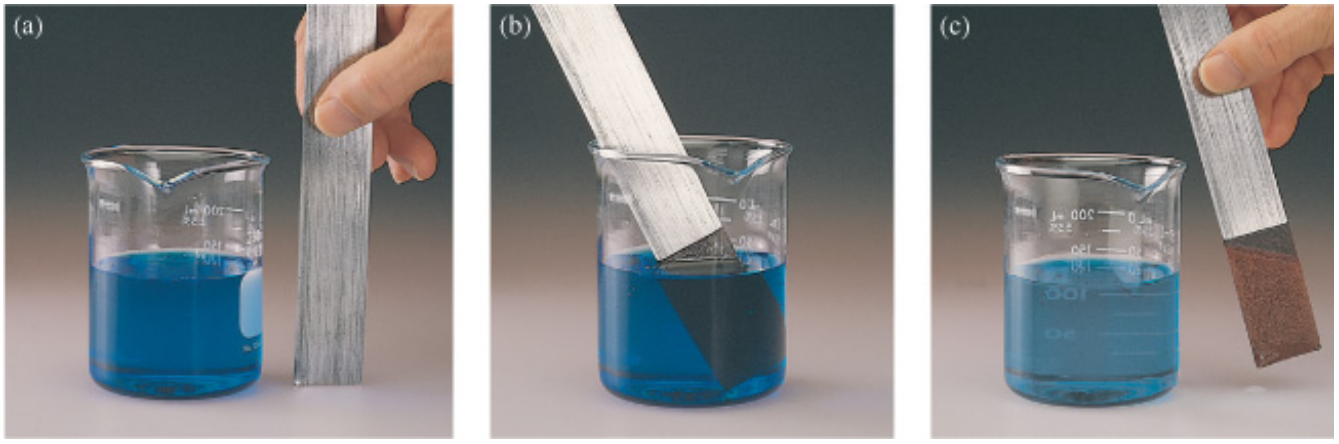


FIGURE 12.6 The reaction of zinc with copper ions:
(a) A piece of shiny zinc next to a beaker containing a copper sulfate solution.
(b) When the zinc is placed in the solution, copper ions are reduced to elemental copper while the zinc dissolves.
(c) After a while, the zinc becomes coated with a red-brown layer of copper. The blue colour of the solution fades as Cu^{2+} is reduced.

Zinc transfers electrons to copper ions, and the results of this experiment can be summarised by the equation:

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

The term '(aq)' expresses the fact that the molecules or ions are dissolved in water, where they become surrounded by water molecules (hydration).

The redox changes become clear if both half-equations are analysed. Both copper sulfate and zinc sulfate are soluble salts, and they are completely dissociated. The sulfate ion is a spectator ion and not involved in the redox process.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad \text{(oxidation)}$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad \text{(reduction)}$$

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+} + (aq) + Cu(s) \quad \text{(redox reaction)}$$

An atomic-level view of the processes at the surface of zinc during the reaction is depicted in figure 12.7.

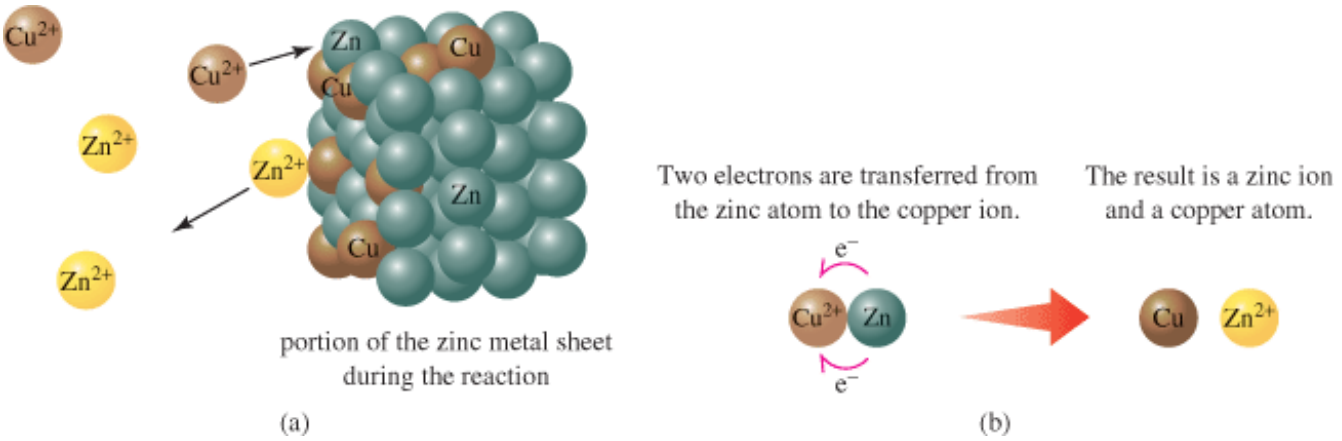


FIGURE 12.7 The reaction of copper ions with zinc, viewed at the atomic level:

(a) Copper ions (pale brown) collide with the zinc surface where they pick up electrons from zinc atoms (grey). The zinc atoms become zinc ions (yellow) and enter the solution. The copper ions become copper atoms (red-brown) and stick to the surface of the zinc. (For clarity, the water molecules of the solution and the sulfate ions are not shown.)

(b) A close-up view of the exchange of electrons that leads to the reaction.

Example 2

In contrast to example 12.3.1, when a piece of copper is dipped into a solution of zinc sulfate (see figure 12.8), no reaction occurs. Copper cannot reduce the zinc ions to metallic zinc.

$$Cu(s) + ZnSO_4(aq) \rightarrow \text{no reaction}$$

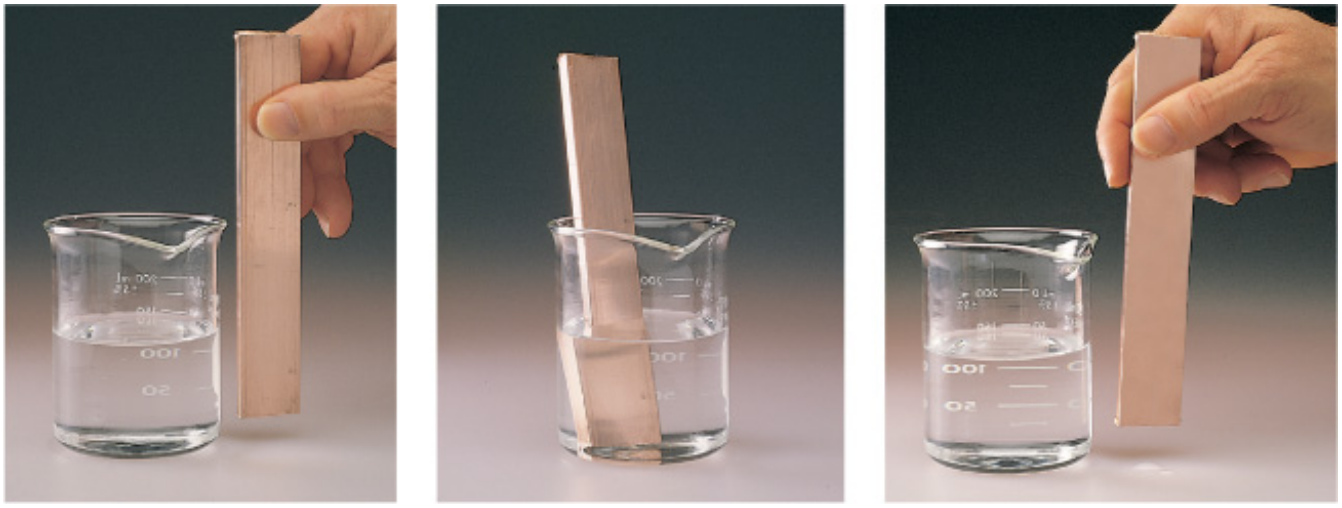


FIGURE 12.8 Copper cannot reduce zinc ions. Although metallic zinc will displace copper from a solution containing Cu^{2+} ions, metallic copper will not displace Zn^{2+} from its solutions. Here we see that the copper bar is unaffected by being dipped into a solution of zinc sulfate.

Example 3

When a coil of copper is dipped into a solution that contains silver ions, these are reduced to elemental silver and copper is oxidised (see figure 12.9). The redox processes are:

$$\begin{aligned} Cu(s) &\rightarrow Cu^{2+}(aq) + 2e^- && \text{(oxidation)} \\ 2Ag^+(aq) + 2e^- &\rightarrow 2Ag(s) && \text{(reduction)} \\ \hline Cu(s) + 2Ag^+(aq) &\rightarrow Cu^{2+} + (aq) + 2Ag(s) && \text{(redox reaction)} \end{aligned}$$

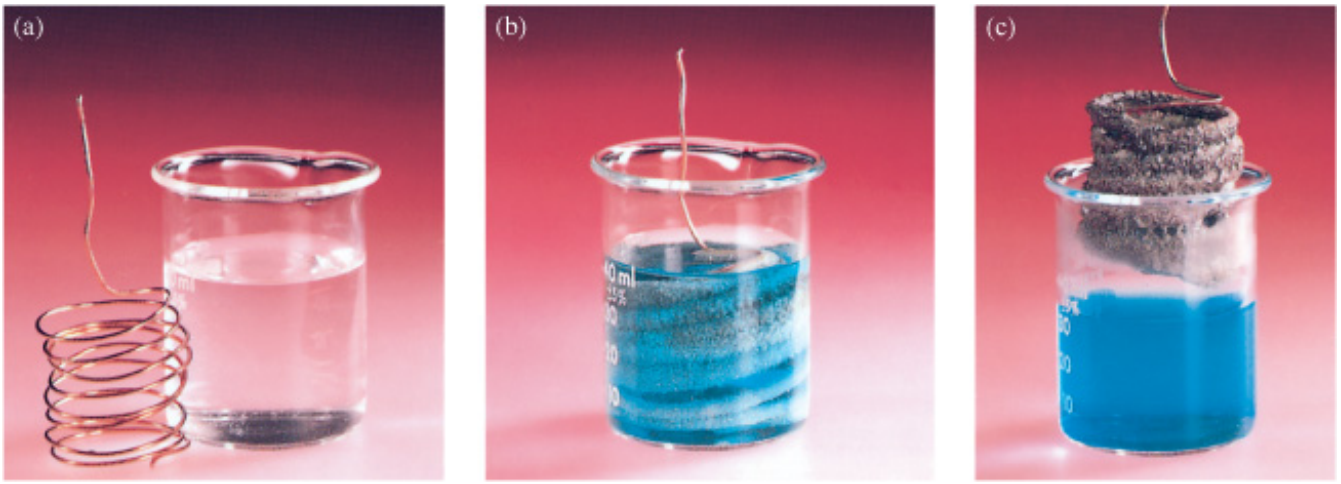


FIGURE 12.9 Reaction of copper with a solution of silver nitrate.

(a) A coil of copper wire stands next to a beaker containing a silver nitrate solution.

(b) When the copper wire is placed in the solution, copper dissolves, giving the solution its blue colour, and metallic silver deposits as glittering crystals on the wire.

(c) After a while, much of the copper has dissolved and nearly all of the silver has deposited in its elemental form.

To gain insights into the different oxidising and reducing behaviours of these substances, the driving force of the electron transfer needs to be understood. The finding that, in example 12.3.1, an electrical current (moving electrons) flows between the zinc and copper systems means that a **potential difference** exists between the two systems. (Remember that a current, e.g. water, heat, gas and electric current, can flow only if a difference in level of height, temperature, pressure or potential exists.)

The potential difference is expressed in the electrical unit **volt (V)**, which is a measure of the amount of energy, in **joules (J)**, that can be delivered per SI unit of charge, **coulomb (C)**, as the current moves through a circuit. Thus, a current flowing under a potential difference of 1 volt can deliver 1 joule of energy per coulomb.

$$1\,V = \frac{1\,J}{1\,C} = 1\,JC^{-1}$$

Setting Up a Galvanic Cell

The potential difference between zinc and copper cannot be determined experimentally simply by dipping zinc metal into a solution of copper ions, because the electron transfer takes place directly between Cu^{2+} and Zn, as shown in figure 12.7. Instead, if a zinc rod (electrode) is dipped into a solution of $ZnSO_4$ and a copper rod (electrode) is dipped into a solution of $CuSO_4$, and the solutions are connected with a salt bridge (its function will be described shortly), zinc can transfer its electrons to the copper ions only through an external circuit (see figure 12.10a). An arrangement where a metal, M, is dipped into a solution containing a salt of the respective metal ion, $M^{n+}X_n$, (if X is a monoanion) is called a **half-cell**. In a half-cell, oxidation and reduction can occur according to this equilibrium:

$$M \rightleftharpoons M^{n+} + ne^-$$

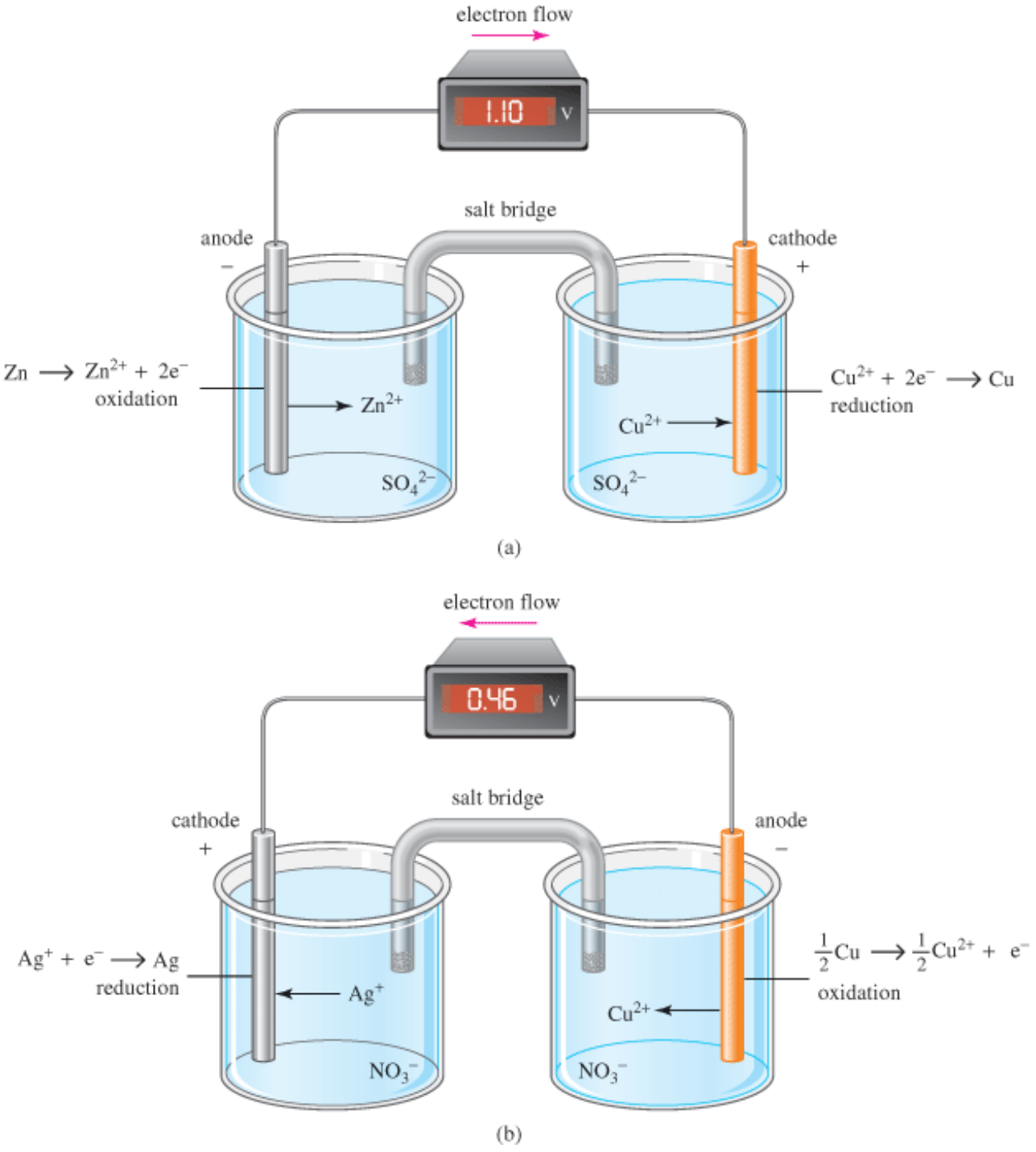


FIGURE 12.10 Galvanic cells.

(a) The zinc-copper cell and

(b) the silver-copper cell. At 25 °C under standard conditions (1×10^5 Pa and concentration of 1 M for all solutes), the potential is 1.10 V in the zinc-copper cell and 0.46 V in the silver-copper cell.

The chemical process is identical to that in example 12.3.1 (see p. 500 and figure 12.6). However, in this case, the existing potential difference can be measured using a highly sensitive current meter or by inserting a **voltmeter** with a very high resistance. Such a combination of two half-cells is called a **galvanic cell** (after Luigi Galvani, 1737-1798, an Italian anatomist who discovered that electricity can cause the contraction of muscles). The overall reaction that takes place in the galvanic cell is the **cell reaction**.

In the zinc-copper system, if the solutions have a concentration of 1.00 M Cu^{2+} and 1.00 M Zn^{2+}, the potential difference, or **electrochemical potential**, is 1.10 V. The potential difference between the electrodes can be compared with the pressure difference between two gas containers filled with gas at different pressures. If both containers were connected, the pressure in the system would be equalised by gas flow

from the container with the higher pressure to the container with the lower pressure. In a galvanic cell, the 'electron gas' flows from the electrode with the higher 'electron pressure' (zinc) to the electrode with the lower 'electron pressure' (copper), which is indicated by the direction of the arrow above the voltmeter in figure 12.10a. Thus, the potential difference is a measure of the electron pressure difference between two electrodes. The redox reaction between Zn and Cu^{2+} (example 12.3.1) is finished when the electron pressures between zinc and copper are in equilibrium. In many textbooks, the potential difference in a galvanic cell is called electromotive force. This term is discouraged, since potential difference is not a 'force'. The unit of potential difference in a galvanic cell is the volt (V).

When a copper electrode in a solution of $Cu(NO_3)_2$ is connected to a silver electrode in a solution of $AgNO_3$, the current flows in the opposite direction (see figure 12.10b). When the concentrations of the $Cu(NO_3)_2$ and $AgNO_3$ solutions are 1.00 m, the potential difference is 0.46 V. Likewise, a zinc electrode in a solution of $ZnSO_4$ connected to a silver electrode in a solution of $AgNO_3$ will form a galvanic cell with a potential difference of 1.56 V (the sum of the potential differences of the two previously discussed galvanic cells, 1.10 V + 0.46 V = 1.56 V) and in which the electrons flow from the zinc electrode to the silver electrode. We will explain this finding later.

Processes in Galvanic Cells

As we have seen, a redox system consisting of two metals and solutions of their salts (two half-cells) can be combined to form a galvanic cell, which produces electricity. In other words, a galvanic cell consists of an oxidising agent in one compartment (the first half-cell) that pulls electrons through a wire from a reducing agent in the other compartment (the other half-cell).

We will now have a closer look at the processes occurring in galvanic cells. The processes involved are described as **electrochemical changes**, and the study of such changes is called **electrochemistry**. Figure 12.11 shows schematically the processes that take place in the two half-cells of the copper–silver galvanic cell. At the copper electrode, Cu^{2+} ions *enter* the solution when copper atoms are oxidised, leaving electrons behind on the electrode. The solution around the copper electrode becomes positively charged, unless Cu^{2+} ions move away from the electrode or NO_3^- ions move towards it. At the silver electrode, Ag^+ ions *leave* the solution and become silver atoms by acquiring electrons from the electrode surface. The solution around the silver electrode becomes negatively charged, unless more Ag^+ ions move towards the electrode or NO_3^- ions move away.

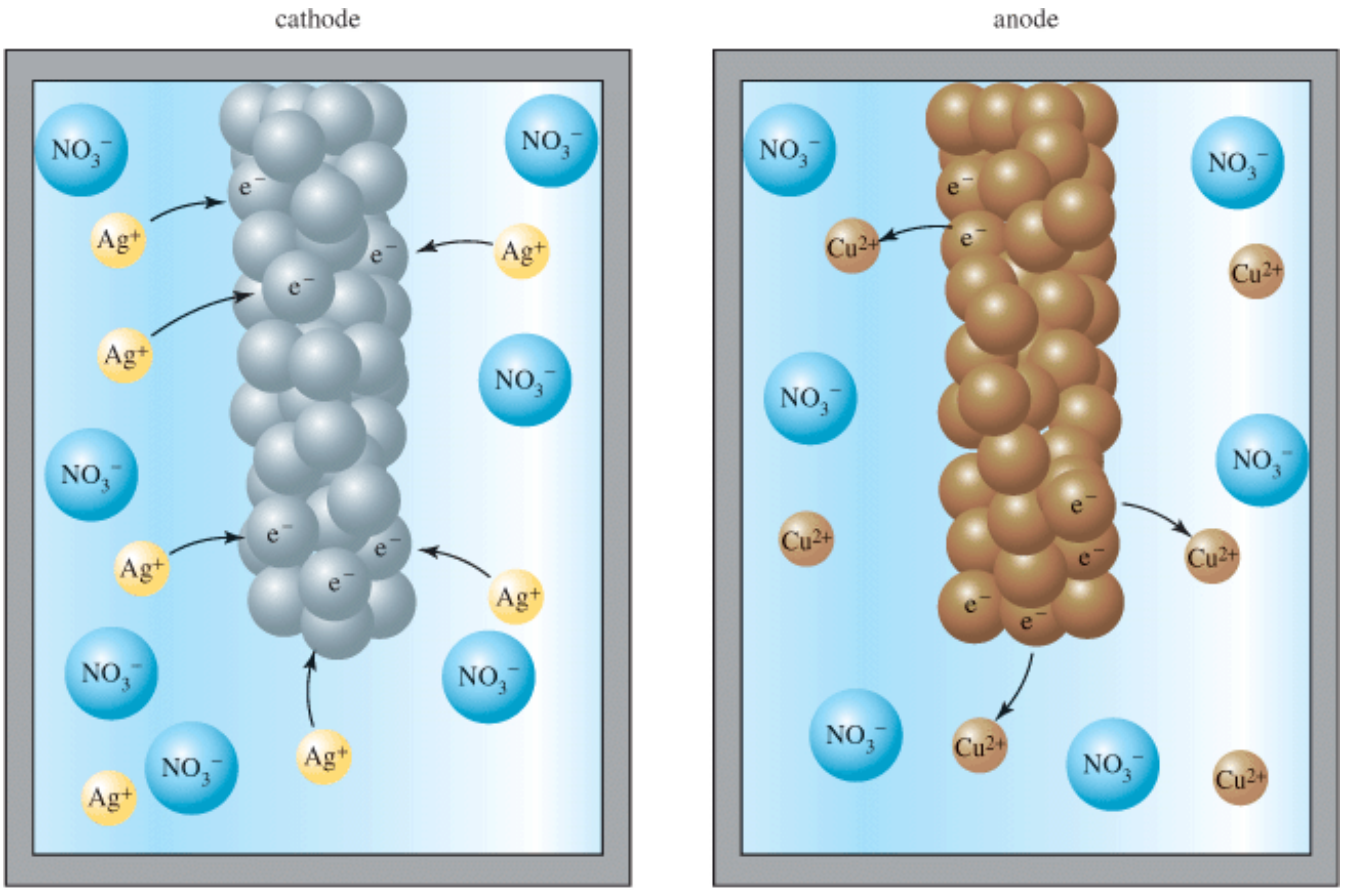


FIGURE 12.11 Changes that take place at the anode and cathode in the copper–silver galvanic cell (not drawn to scale).

In any electrochemical system, the electrode at which oxidation occurs is called the **anode**; the electrode at which reduction occurs is called the **cathode**. Thus, in the copper–silver galvanic cell, the silver electrode is the cathode and the copper electrode is the anode. At the anode, Cu^{2+} is released into the solution. The remaining electrons give the anode a slight negative charge; the anode has a *negative polarity*. At the cathode, electrons spontaneously join Ag^{+} ions to become a part of the electrode. However, this effect is the same as if Ag^{+} ions become a part of the electrode, so that the electrode acquires a slight positive charge. The cathode has a *positive polarity*.

If the production of Cu^{2+} at the anode and deposition of Ag^{+} at the cathode were to continue, the solution around the anode would quickly become positively charged; the solution around the cathode would acquire a negative charge because consumption of positive ions from the solution would leave an excess of negative ions.

Nature does not permit large amounts of positive and negative charge to accumulate, so, for the reactions to continue and for electricity to continue to flow through the external circuit, there must be a means of balancing the charges in the solutions around the electrodes. To understand how this happens, we will examine how electric charge is conducted in the cell.

In the external circuit of the cell, electric charge is transported from one electrode to the other by the movement of electrons through the wires. This type of conduction is called **electronic conduction** and is how metals in general, and other materials, conduct electricity. In the cell, electrons always travel from the negatively charged anode, where they are left behind by the oxidation process, to the positively charged cathode, where they are picked up by the substance being reduced.

In electrochemical cells, there is another kind of electrical conduction that also takes place to balance charges in the two half-cells. In a solution that contains ions (or in a molten ionic compound), *electric charge is carried through the liquid by the movement of ions, not electrons*. The transport of electric charge by ions is called **electrolytic conduction**.

For a galvanic cell to work, the solutions in both half-cells must remain electrically neutral. This requires that ions be permitted to enter or leave the solutions. For example, when copper is oxidised, the solution surrounding the electrode becomes filled with Cu^{2+} ions, so negative ions are needed to balance their charge. Similarly, when Ag^{+} ions are reduced, NO_3^- ions are left behind in the solution and positive ions are needed to maintain neutrality. The salt bridge shown in figure 12.10 allows the movement of ions required to keep the solutions neutral.

A **salt bridge** is a tube filled with a solution of a salt composed of relatively inert ions that are not involved in the cell reaction. Often KNO_3 or KCl are used. In the most simplified version, the tube is fitted with a porous plug at each end that prevents the solution from pouring out but, at the same time, enables the solution in the salt bridge to exchange ions with the solutions in the half-cells.

During operation of the cell, negative ions can diffuse from the salt bridge into the copper half-cell, or Cu^{2+} ions can leave the solution and enter the salt bridge. Both processes together keep the copper half-cell electrically neutral. At the silver half-cell, positive ions from the salt bridge can enter or negative NO_3^- ions can leave the half-cell also to keep this half electrically neutral, too.

Without the salt bridge, electrical neutrality could not be maintained and no electric current could be produced by the cell. Therefore, *electrolytic contact* — contact by means of a solution containing ions — must be maintained for the cell to function. A closer look at the overall ion movement during the operation of the galvanic cell shows that negative ions (*anions*) move away from the cathode, where they are present in excess, *towards the anode*, where they are needed to balance the charge of the positive ions (*cations*) formed. Similarly, cations move away from the anode, where they are in excess, *towards the cathode*, where they balance the anions left in excess. In summary, in galvanic cells:

- The *cathode* is the electrode at which reduction (electron gain) occurs. Cations move in the general direction of the cathode.
- The *anode* is the electrode at which oxidation (electron loss) occurs. Anions move in the general direction of the anode.

Figure 12.12 provides a summary of the components of, and processes in, a basic galvanic cell.

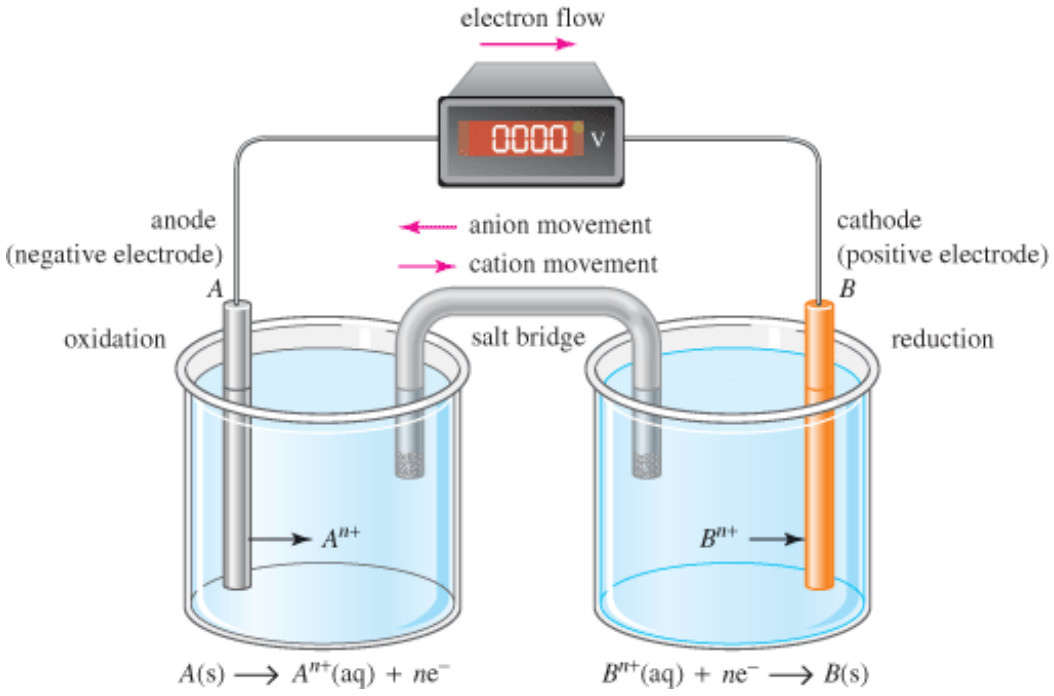


FIGURE 12.12 Schematic diagram of a galvanic cell. Electrons always flow from the negative electrode (anode) to the positive electrode (cathode). In this diagram, the anode is the left-hand electrode at which oxidation occurs, and the cathode is the right-hand electrode where reduction occurs.

After this theoretical description of galvanic cells, you may perhaps wonder where you would encounter galvanic cells in your daily life. Basically, a galvanic cell can be considered as a battery, and we will discuss batteries later in this chapter. (More precisely, a battery consists of several galvanic cells.) But you may have also created an unwanted galvanic cell in your mouth; if you have old fillings in your teeth, you may have experienced a strange and perhaps unpleasant sensation, like an electric shock, while accidentally biting on a piece of aluminium foil. Most old fillings are made of an amalgam of mercury and silver. When the aluminium foil touches the filling, a galvanic cell is created in the mouth, in which aluminium is the anode, the filling is the cathode and saliva is the electrolyte salt bridge. In essence, the contact short-circuits the galvanic cell and a small amount of current flows, which is sensed by the nerves in the teeth.

Notation of Galvanic Cells and Cell Reactions

As a matter of convenience, chemists use a **cell diagram** as a shorthand way of describing the make-up of a galvanic cell. The cell diagram, which is also known as **standard cell notation**, for the galvanic cell in figure 12.12 is:

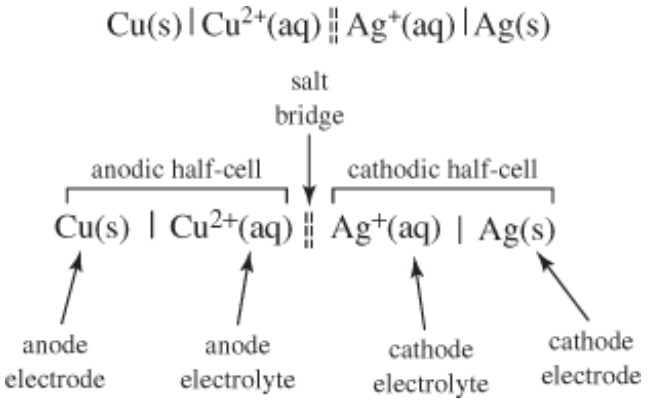
$$A(s)\,|\,A^{n+}(aq)\,\|\,B^{n+}(aq)\,|\,B(s)$$

By convention, *the half-cell containing the anode is specified on the left of a cell diagram*, with the electrode material of the anode given first. The single vertical line represents a *phase boundary* — here, between the solid electrode and the solution that surrounds it. The double vertical dashed lines represent the salt bridge, which connects the solutions in the two half-cells. On the right, the half-cell containing the cathode is described, with the material of the cathode given last. *The defined cell reaction for any cell diagram is obtained based on the fact that reduction occurs at the right-hand electrode (cathode).* Therefore, the defined cell reaction for the cell in figure 12.12 is:

$$A(s) + B^{n+}(aq) \rightarrow A^{n+}(aq) + B(s)$$

We will see in section 12.4 how to determine whether the defined cell reaction occurs spontaneously.

The copper–silver cell discussed on p. 503 is represented by the following cell diagram:



Sometimes, the oxidised and reduced forms of the reactants in a half-cell are both in solution. For example, a galvanic cell can be made using an anodic half-cell composed of a zinc electrode dipping into a solution containing Zn^{2+} and a cathodic half-cell composed of an inert (nonre-acting) platinum electrode dipping into a solution containing both Fe^{2+} and Fe^{3+} (figure 12.13). The cell reaction is:

$$2Fe^{3+}(aq) + Zn(s) \rightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$$

The cell diagram for this galvanic cell is:

$$Zn(s)\left|Zn^{2+}(aq)\right\|Fe^{3+}(aq), Fe^{2+}(aq)\left|Pt(s)\right.$$

where we have separated the formulae for the two iron ions by a comma. This is done when the species are in the same phase. In this cell, the reduction of Fe^{3+} to Fe^{2+} takes place at the surface of the inert platinum electrode.



FIGURE 12.13 The cathodic halfcell for the galvanic cell represented by the cell diagram on the left, showing the platinum gauze cathode in a solution of Fe^{2+} and Fe^{3+}.

WORKED EXAMPLE 12.5

Describing Galvanic Cells

The following spontaneous reaction occurs when metallic zinc is dipped into a solution of silver nitrate:

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$

Describe a galvanic cell that could take advantage of this reaction. What is the reaction in each half-cell? What is the cell diagram? Sketch the cell and label the cathode and anode, the charges on each electrode, the directions of the flow of ions and the direction of electron flow. Also indicate the positive and negative electrodes.

Analysis

Answering all these questions relies on identifying the anode and cathode from the equation for the cell reaction. By definition, the anode is the electrode at which oxidation occurs, and the cathode is where reduction occurs. The first step, therefore, is to determine which reactant is oxidised and which is reduced. One way to do this is to divide the cell reaction into half-reactions and balance them by adding electrons. Then, if electrons appear as a product, the half-reaction is oxidation; if the electrons appear as a reactant, the half-reaction is reduction.

Solution

The balanced half-equations are:

$$\begin{aligned} Zn(s) &\rightarrow Zn^{2+}(aq) + 2e^- \\ 2Ag^+(aq) + 2e^- &\rightarrow 2Ag(s) \end{aligned}$$

Zn(s) loses electrons and is oxidised, so it is the anode. The anodic half-cell is, therefore, a zinc electrode dipping into a solution that contains Zn^{2+} (e.g. from dissolved $Zn(NO_3)_2$or $ZnSO_4$). Within the cell diagram, the anodic half-cell is written on the left-hand side with the electrode material at the left of the vertical line and the oxidation product at the right:

$$Zn(s)\,|\,Zn^{2+}(aq)$$

Silver ions gain electrons and are reduced to metallic silver, so the cathodic half-cell consists of a silver electrode dipping into a solution containing Ag^+ (e.g. from dissolved $AgNO_3$). Within the cell diagram, the silver cathodic half-cell is written on the right-hand side, with the electrode material to the right of the vertical line and the substance reduced on the left:

$$Ag^+(aq)\,|\,Ag(s)$$

In the cell diagram, the zinc anodic half-cell (left) and the silver cathodic half-cell (right) are separated by double vertical dashed lines that represent the salt bridge.

$$\underset{\text{anode}}{Zn(s)\,|\,Zn^{2+}(aq)}\,||\,\underset{\text{cathode}}{Ag^+(aq)\,|\,Ag(s)}$$

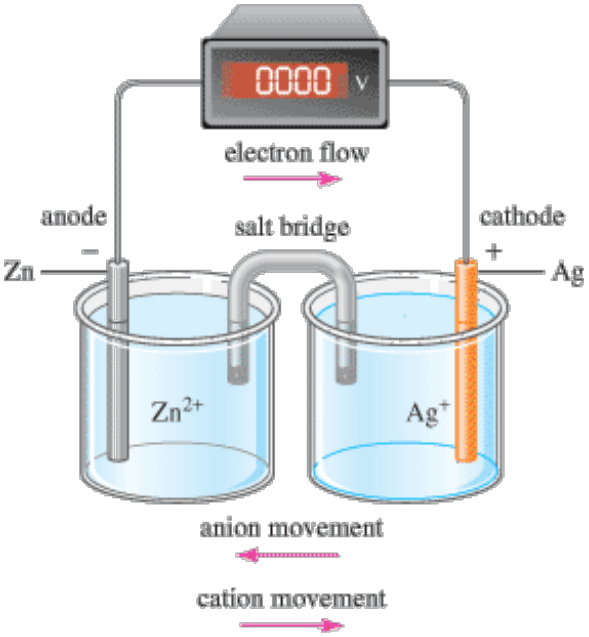
The cell may be sketched as shown on the right.

The anode always carries a negative charge in a galvanic cell, so the zinc electrode is negative and the silver electrode is positive. Electrons in the external circuit travel from the negative electrode to the positive electrode (i.e. from the Zn anode to the Ag cathode). The anions move towards the anode, and the cations move towards the cathode.

Is our answer reasonable?

All of the answers depend on determining which substance is oxidised and which is reduced, so that is what to check. Oxidation is electron loss, and Zn must lose electrons to become Zn^{2+}, so

zinc is oxidised and must be the anode. If zinc is the anode, then silver must be the cathode. All the rest follows by reasoning.



PRACTICE EXERCISE 12.7

Sketch and label a galvanic cell that makes use of the following spontaneous redox reaction:

$$Fe(s) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn(s)$$

Write the half-equations for the reactions that occur at the anode and cathode. Give the cell diagram. Sketch the cell and label the cathode and anode, the charges on each electrode, the directions of the flow of ions and the direction of electron flow.

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12.4 Reduction Potentials

Cell and Standard Cell Potentials

The voltage or potential of a galvanic cell varies with the amount of current flowing through the circuit. The *maximum* potential that a given cell can generate is called its **cell potential (E_{cell})**, or electrochemical potential, an expression introduced on p. 502. As mentioned previously, the convention in writing a cell diagram is to put the cathode (reduction process) on the right-hand side and the anode (oxidation process) on the left-hand side. The cell potential is then the potential difference between the cathodic and anodic half-cells, i.e. the right (R) and the left (L) half-cells, respectively.

$$E_{cell} = E_R - E_L$$

E_{cell} depends on the composition of the electrodes and the concentrations of the ions in the half-cells, as well as the temperature and pressure. To compare the potentials for different cells, we use the **standard cell potential** $\left(E^{\circ}_{cell}\right)$. This is the potential of the cell when all of the ion concentrations are 1 M and any gases involved in the cell reaction are at a pressure of 1×10^5 Pa. The temperature is generally assumed to be 298 K (25 °C), but should always be specified. The IUPAC convention for determining E°_{cell} is:

$$E^{\circ}_{cell} = E^{\circ}_R - E^{\circ}_L$$

A positive E°_{cell} cell means that reduction occurs at the right-hand electrode, whereas a negative E°_{cell} cell tells us that reduction occurs at the left-hand electrode. The cell diagram for the cell in figure 12.12 (p. 504) can be written as:

$$A(s)|A^{n+}(aq)||B^{n+}(aq)|B(s)$$

A positive E°_{cell} cell for any cell means that the defined cell reaction is spontaneous or, equivalently, the polarity of the right-hand electrode (cathode) is positive. Therefore, the cell reaction for the defined cell:

$$A(s) + B^{n+}(aq) \rightarrow A^{n+}(aq) + B(s)$$

will be spontaneous and the B^{n+} ions in the right-hand half-cell will be reduced to *B*. On the other hand, a negative E°_{cell} means that the defined cell reaction is not spontaneous, and the reverse reaction will be spontaneous. In a galvanic cell, the cell potential for the spontaneous reaction is always positive. If the calculated cell potential is negative, the reaction is spontaneous in the reverse direction. (This means that the cell diagram was written in the wrong direction.) We will be discussing the thermodynamics of spontaneous and non- spontaneous electrochemical processes in section 12.5.

Cell potentials are rarely larger than a few volts. As mentioned before, the standard cell potential for the galvanic cell constructed from silver and copper electrodes shown in figure 12.10b is only 0.46 V. One cell in a car battery produces only about 2 V. Batteries that generate higher voltages, such as a car battery, are assemblies of cells arranged in series so that their potentials add up to give the total battery potential. We will discuss the chemistry of important batteries in detail in section 12.8.

Reduction and Standard Reduction Potentials

It is useful to imagine that the measured overall cell potential arises from a competition, or 'tug of war', for electrons between the two half-cells. Thus, each half-cell has a certain natural tendency to acquire electrons and proceed as a *reduction*. The magnitude of this tendency is expressed by the **reduction potential (E_{red})** of the reaction (also known as redox potential or oxidation/reduction potential). When determined under standard conditions ($p = 1 \times 10^5$ Pa and concentrations of 1 M for all ions undergoing either oxidation or reduction), the reduction potential is called the **standard reduction potential**. These values are usually tabulated at 25 °C. To represent a standard reduction potential, we add a subscript to the symbol E° that identifies the substance undergoing reduction. Thus, the standard reduction potential for the half-reaction:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

is specified as $E^{\circ}_{Cu^{2+}/Cu}$

When two half-cells are connected, the one with the larger reduction potential (the greater tendency to undergo reduction) acquires electrons from the half-cell with the lower reduction potential, which is therefore forced to undergo oxidation.

The measured cell potential represents the magnitude and sign of the *difference* between the reduction potential of one half-cell and the reduction potential of the other. As we have discussed before, when E°_{cell} is positive, the cell reaction is spontaneous as written. We can see from $E^{\circ}_{cell} = E^{\circ}_R - E^{\circ}_L$ that, if E°_{cell} is positive, E°_R is greater than E°_L. An example of this is the copper–silver cell discussed previously:

$$Cu(s)|Cu^{2+}(aq)||Ag^{+}(aq)|Ag(s)$$

The two possible reduction processes in this cell are:

$$Ag^{+}(aq) + e^- \rightarrow Ag(s)$$
$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

As we have seen in figure 12.9, the spontaneous process in this cell is reduction of $Ag^{+}(aq)$ and oxidation of Cu(s) according to the equation:

$$2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

This means that the standard reduction potential of the Ag^+/Ag half-cell must be larger than the standard reduction potential of the Cu^{2+}/Cu half-cell. In other words, if we knew the values of $E^{\ominus}_{Ag^+/Ag}$ and $E^{\ominus}_{Cu^{2+}/Cu}$ and calculated $E^{\ominus}_{cell}$ by:

$$E^{\circ}_{cell} = E^{\ominus}_{Ag^+/Ag} - E^{\ominus}_{Cu^{2+}/Cu}$$

we would find that $E^{\ominus}_{cell}$ is positive.

A common error is to multiply the standard reduction potentials by the factors used to balance the two half-reactions. In this case, the temptation is to multiply $E^{\ominus}_{Ag^+/Ag}$ by a factor of 2. However, cell potentials are given in volts, energy per unit of charge. Thus, half-cell potentials are simply combined to give the cell potentials:

$$E^{\ominus}_{cell} = E^{\ominus}_{R} - E^{\ominus}_{L}$$

Determining Standard Reduction Potentials

Unfortunately, we have no way to measure the absolute standard reduction potential of an isolated half-cell. All that can be measured are potential differences when two half-cells are connected. Therefore, to assign values to the various standard reduction potentials, a reference electrode has been arbitrarily chosen and its standard reduction potential has been assigned a value of *exactly* 0 V. This reference electrode is called the **standard hydrogen electrode**, SHE (see figure 12.14). Gaseous hydrogen at a pressure of 1×10^5 Pa is bubbled over a platinum electrode coated with very finely divided platinum, which provides a large catalytic surface area on which the electrode reaction can occur. This electrode is surrounded by a solution in which the concentration of hydrogen ions, H^+, is 1 M. The reaction at the platinum surface, written as a reduction, is:

$$2H^+(aq, 1M) + 2e^- \rightleftharpoons H_2(g, 1 \times 10^5 Pa, 298 K) \quad E^{\ominus}_{H^+/H_2} = 0 V \text{ (by definition)}$$

where the double arrows indicate only that the reaction is reversible, not that there is true equilibrium. Whether the half-reaction occurs as a reduction or an oxidation depends on the reduction potential of the half-cell with which it is paired.

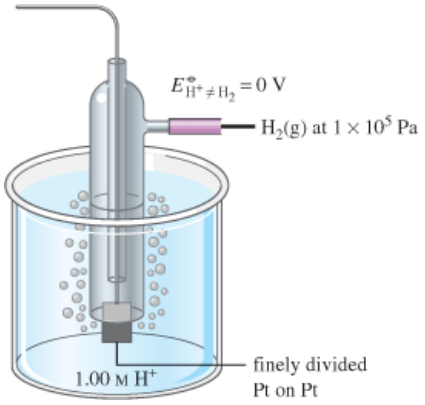


FIGURE 12.14 The standard hydrogen electrode (T = 298 K).

Figure 12.15a illustrates the hydrogen electrode connected to a copper half-cell to form a galvanic cell. When calculating a standard reduction potential, *the convention is to put the hydrogen half-cell on the left-hand side of the cell diagram*. Therefore, the cell diagram for this cell is:

$$Pt(s)\,|H_2(g)|\,H^+(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$$

Given $E^{\ominus}_{cell} = E^{\ominus}_{R} - E^{\ominus}_{L}$:

$$E^{\ominus}_{cell} = E^{\ominus}_{Cu^{2+}/Cu} - E^{\ominus}_{H^+/H_2}$$

We know that $E^{\ominus}_{H^+/H_2} = 0 V$, so:

$$E^{\ominus}_{cell} = E^{\ominus}_{Cu^{2+}/Cu} - 0$$
$$= E^{\ominus}_{Cu^{2+}/Cu}$$

We know from our measurement in figure 12.15a that $E^{\ominus}_{cell} = +0.34 V$ so $E^{\ominus}_{Cu^{2+}/Cu} = +0.34 V$. The positive value means that reduction is occurring at the right-hand electrode in the cell diagram so the spontaneous cell reaction is:

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$$

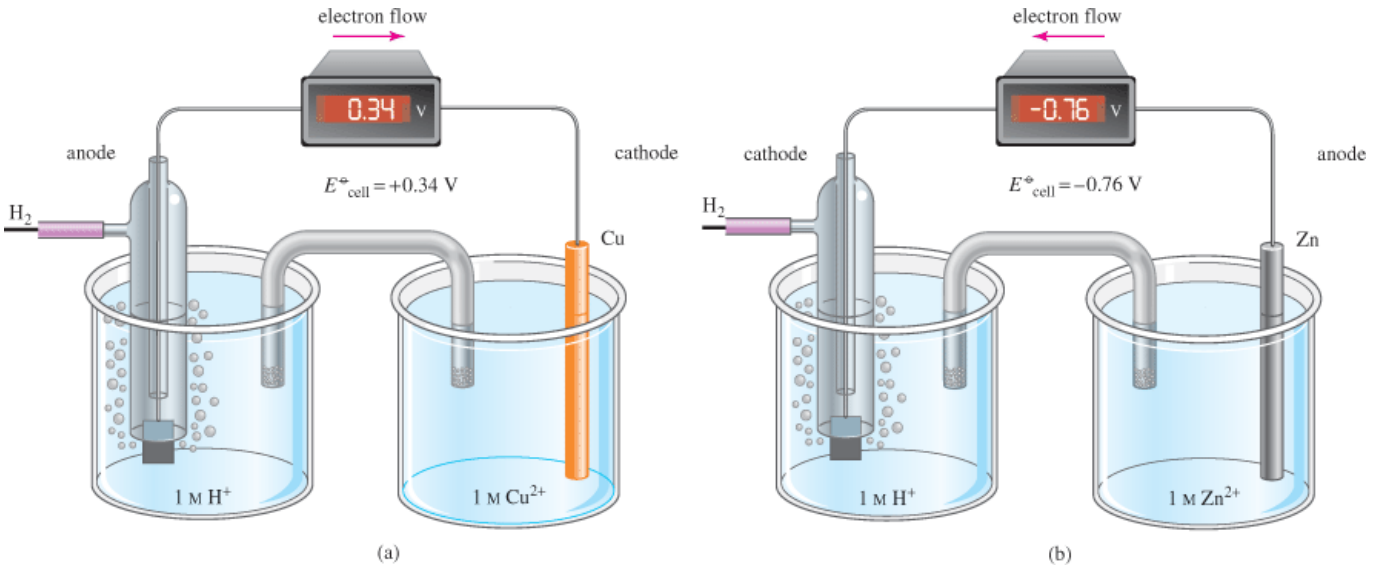


FIGURE 12.15 Galvanic cells composed of
(a) copper and hydrogen half-cells and
(b) zinc and hydrogen half-cells.

Now let's look at a galvanic cell set-up between a zinc electrode and a hydrogen electrode (see figure 12.15b). Remembering that the hydrogen electrode by definition appears on the left-hand side, the cell diagram is:

$$Pt(s)|H_2(g)|H^+(aq)||Zn^{2+}(aq)|Zn(s)$$

Given $E^{\ominus}_{cell} = E^{\ominus}_{R} - E^{\ominus}_{L}$:

$$E^{\ominus}_{cell} = E^{\ominus}_{Zn^{2+}/Zn} - E^{\ominus}_{H^+/H_2}$$

We know that $E^{\ominus}_{H^+/H_2} = 0\,V$, so:

$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{Zn^{2+}/Zn} - 0 \\ &= E^{\ominus}_{Zn^{2+}/Zn} \end{aligned}$$

We know from our measurement in figure 12.15b that $E^{\ominus}_{cell} = -0.76\,V$ so $E^{\ominus}_{Zn^{2+}/Zn} = -0.76\,V$. The negative value in this case means that reduction is in fact occurring at the left-hand electrode of the cell diagram so the spontaneous cell reaction is:

$$2H^+(aq) + Zn(s) \rightarrow H_2(g) + Zn^{2+}(aq)$$

We can visualise these results in a scaled graph of the reduction potentials, where a lower positioned species can donate electrons to a higher one (figure 12.16). From this, we can directly calculate the electrochemical potential in any galvanic cell. You can see from this figure that the values of $E^{\ominus}_{cell}$ are additive. We know that $E^{\ominus}_{cell}$ of the zinc-copper galvanic cell = 1.10 V and $E^{\ominus}_{cell}$ of the copper–silver cell = 0.46 V, so $E^{\ominus}_{cell}$ of the zinc-silver cell is the sum of both (1.10 V + 0.46 V = 1.56 V).

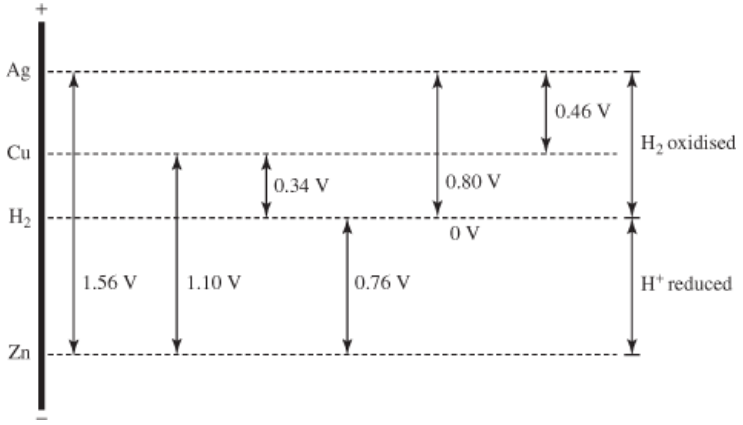


FIGURE 12.16 Choice of an arbitrary zero-point to determine standard reduction potentials $E^{\ominus}$ for a galvanic cell.

However, this set-up enables us to measure only potential *differences*. The *absolute* potentials of the respective electrodes are not known. But we don't need to know these because we are interested only in the $E^{\ominus}_{cell}$ of the galvanic cell itself, so it is sufficient to choose an arbitrary zero-point. (This is similar to defining zero on the celsius scale as the temperature of melting ice, or to measuring elevation relative to sea level rather than from the centre of the Earth.)

The standard reduction potentials of many half-reactions can be compared with that of the standard hydrogen electrode as described on the previous page. Table 12.1 lists values obtained for some typical half-reactions. They are arranged in decreasing order — the half-reactions at the top have the greatest tendency to occur as a reduction, while those at the bottom have the highest tendency to occur as an oxidation. Table 12.1 shows that:

- Substances located to the left of the double arrows are oxidising agents, because they become reduced when the reactions proceed in the forward direction.
- The strongest oxidising agents are those most easily reduced, and they are located at the top left of the table (e.g. F_2).
- Substances located to the right of the double arrows are reducing agents; they become oxidised when the reactions proceed from right to left.
- The strongest reducing agents are those found at the bottom right of the table (e.g. Li).

TABLE 12.1 Standard Reduction Potentials $E^\ominus$ 25 °C

	Half reaction			$E^\ominus$ (volts)	
Strongest oxidant ↑	$F_2(g) + 2e^-$	⇌	$2F^-(aq)$	+2.87	↓ Weakest reductant
	$S_2O_8^{2-}(aq) + 2e^-$	⇌	$2SO_4^{2-}(aq)$	+2.01	
	$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^-$	⇌	$PbSO_4(s) + 2H_2O(l)$	+1.69	
	$2HOCl(aq) + 2H^+(aq) + 2e^-$	⇌	$Cl_2(g) + 2H_2O(l)$	+1.63	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	⇌	$Mn^{2+}(aq) + 4H_2O(l)$	+1.51	
	$BrO_3^-(aq) + 6H^+(aq) + 6e^-$	⇌	$Br^-(aq) + 3H_2O(l)$	+1.47	
	$PbO_2(s) + 4H^+(aq) + 2e^-$	⇌	$Pb^{2+}(aq) + 2H_2O(l)$	+1.46	
	$ClO_3^-(aq) + 6H^+(aq) + 6e^-$	⇌	$Cl^-(aq) + 3H_2O(l)$	+1.45	
	$Au^{3+}(aq) + 3e^-$	⇌	$Au(s)$	+1.42	
	$ClO_4^-(aq) + 8H^+ + 8e^-$	⇌	$Cl^-(aq) + 4H_2O$	+1.38	
	$Cl_2(g) + 2e^-$	⇌	$2Cl^-(aq)$	+1.36	
	$O_2(g) + 4H^+(aq) + 4e^-$	⇌	$2H_2O(l)$	+1.23	
	$Br_2(aq) + 2e^-$	⇌	$2Br^-(aq)$	+1.07	
	$NO_3^-(aq) + 4H^+(aq) + 3e^-$	⇌	$NO(g) + 2H_2O(l)$	+0.96	
	$Ag^+(aq) + e^-$	⇌	$Ag(s)$	+0.80	
	$Fe^{3+}(aq) + e^-$	⇌	$Fe^{2+}(aq)$	+0.77	
	$I_2(s) + 2e^-$	⇌	$2I^-(aq)$	+0.54	
	$NiO_2(s) + 2H_2O(l) + 2e^-$	⇌	$Ni(OH)_2(s) + 2OH^-(aq)$	+0.49	
	$Cu^{2+}(aq) + 2e^-$	⇌	$Cu(s)$	+0.34	
	$Cl_2(aq) + 4OH^-(aq)$	⇌	$2OCl^-(aq) + 2H_2O(l) + 2e^-$	+0.32	
	$Hg_2Cl_2(s) + 2e^-$	⇌	$2Hg(l) + 2Cl^-(aq)$	+0.27	
	$AgCl(s) + e^-$	⇌	$Ag(s) + Cl^-(aq)$	+0.23	
	$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	⇌	$H_2SO_3(aq) + H_2O(l)$	+0.17	
	$Sn^{4+}(aq) + 2e^-$	⇌	$Sn^{2+}(aq)$	+0.15	
	$AgBr(s) + e^-$	⇌	$Ag(s) + Br^-(aq)$	+0.07	
	$2H^+(aq) + 2e^-$	⇌	$H_2(g)$	0	
	$Sn^{2+}(aq) + 2e^-$	⇌	$Sn(s)$	−0.14	
	$Ni^{2+}(aq) + 2e^-$	⇌	$Ni(s)$	−0.25	
	$Co^{2+}(aq) + 2e^-$	⇌	$Co(s)$	−0.28	
	$PbSO_4(s) + H^+(aq) + 2e^-$	⇌	$Pb(s) + HSO_4^-(aq)$	−0.36	
	$Cd^{2+}(aq) + 2e^-$	⇌	$Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2e^-$	⇌	$Fe(s)$	−0.44	
	$Cr^{3+}(aq) + 3e^-$	⇌	$Cr(s)$	−0.74	
	$Zn^{2+}(aq) + 2e^-$	⇌	$Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	⇌	$H_2(g) + 2OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3e^-$	⇌	$Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2e^-$	⇌	$Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	⇌	$Na(s)$	−2.71	
	$Ca^{2+}(aq) + 2e^-$	⇌	$Ca(s)$	−2.76	
	$K^+(aq) + e^-$	⇌	$K(s)$	−2.92	
Weakest oxidant	$Li^+(aq) + e^-$	⇌	$Li(s)$	−3.05	Strongest reductant ↓

WORKED EXAMPLE 12.6

Calculating Half-cell Potentials

The standard cell potential $E^\ominus_{cell}$ of the silver-copper galvanic cell has a value of 0.46 V. The cell reaction is:

$$2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

and $E^\ominus_{Cu^{2+}/Cu} = +0.34\,V$. What is $E^\ominus_{Ag^+/Ag}$?

Analysis

Because $E^{\ominus}_{cell}$ is positive, we know that reduction must be occurring at the right-hand electrode. We know from the equation that Ag^+ is reduced and therefore the Ag^+/Ag half-cell must be on the right-hand side. We then use the equation $E^{\ominus}_{cell} = E^{\ominus}_{R} \quad E^{\ominus}_{L}$ to calculate $E^{\ominus}_{Ag^+/Ag}$.

Solution

$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{R} - E^{\ominus}_{L} \\ &= E^{\ominus}_{Ag^+/Ag} - E^{\ominus}_{Cu^{2+}/Cu} \end{aligned}$$

Substituting values for $E^{\ominus}_{cell}$ and $E^{\ominus}_{Cu^{2+}/Cu}$:

$$+0.46\,V = E^{\ominus}_{Ag^+/Ag} - (+0.34\,V)$$

Then we solve for $E^{\ominus}_{Ag^+/Ag}$:

$$\begin{aligned} E^{\ominus}_{Ag^+/Ag} &= +0.46\,V + (+0.34\,V) \\ &= 0.80\,V \end{aligned}$$

Is our answer reasonable?

The half-cell with the larger $E^{\ominus}$ value will always undergo reduction. $E^{\ominus}_{Ag^+/Ag}$ is larger than $E^{\ominus}_{Cu^{2+}/Cu}$ so we predict that Ag^+ will be reduced, as is observed. Our calculated reduction potential appears to be correct.

PRACTICE EXERCISE 12.8

The galvanic cell described in practice exercise 12.7 has a standard cell potential of $E^{\ominus}_{cell} = 0.30\,V$. Given that $E^{\ominus}_{Fe^{2+}/Fe} = -0.44\,V$, calculate $E^{\ominus}_{Sn^{2+}/Sn}$. Check your answer by referring to table 12.1.

We can use the data in table 12.1 to show that we obtain the same spontaneous reaction regardless of how the cell diagram is written. For example, writing the silver-copper cell diagram with the silver half-cell on the right-hand side and the copper half-cell on the left:

$$Cu(s)\left|Cu^{2+}(aq)\right|\left|Ag^+(aq)\right|Ag(s)$$

gives:

$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{Ag^+/Ag} - E^{\ominus}_{Cu^{2+}/Cu} \\ &= +0.80\,V - (+0.34\,V) \\ &= +0.46\,V \end{aligned}$$

and the positive value predicts that $Ag^+(aq)$ will be reduced and Cu(s) will be oxidised. Conversely, if we write the cell diagram with the copper half-cell on the right-hand side and the silver half-cell on the left:

$$Ag(s)\left|Ag^+(aq)\right|\left|Cu^{2+}(aq)\right|Cu(s)$$

then:

$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{Cu^{2+}/Cu} - E^{\ominus}_{Ag^+/Ag} \\ &= +0.34\,V - (+0.80\,V) \\ &= -046\,V \end{aligned}$$

The negative value tells us that reduction does not occur at the right-hand electrode and that the reverse of the defined cell reaction is spontaneous. Therefore, Cu(s) is oxidised and $Ag^+(aq)$ is reduced.

The standard hydrogen electrode, SHE, is not the only reference electrode used. The **saturated calomel electrode** (SCE) is also common and consists of elemental mercury, mercury(I) chloride and Hg_2Cl_2 (calomel, Cl—Hg—Hg—Cl) in a saturated KCl solution. The reaction:

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$$

has a reduction potential of 0.244 V at 298 K versus SHE. Another popular reference electrode is the **silver/silver chloride electrode**, which contains an Ag rod coated with silver chloride and bathed in a saturated KCl solution. This has a reduction potential of 0.199 V at 298 K versus SHE for the reaction:

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$$

These electrodes are widely used because they are more stable and easier to use than the SHE.

Spontaneous and Nonspontaneous Reactions

One of the goals of chemistry is to predict reactions. This can be done for redox reactions — whether they occur in a galvanic cell or just in a container with all the chemicals combined in one reaction mixture — using the half-reactions and standard reduction potentials in table 12.1. We will illustrate this with some examples.

The reactants and products of *spontaneous* redox reactions are easy to spot when reduction potentials are listed in order of most positive to least positive (most negative), as in table 12.1. *For any pair of half-reactions, the one with the more positive reduction potential will occur as a reduction. The other half-reaction is reversed and occurs as an oxidation.* It is important to note that, when the direction of a reaction is reversed, the sign of the reduction potential is not changed when calculating $E^{\ominus}_{cell}$. The minus sign in the equation $E^{\ominus}_{cell} = E^{\ominus}_{R} - E^{\ominus}_{L}$ takes care of this, essentially reversing the reaction listed in table 12.1.

The IUPAC convention requires that you never:

- *change the sign of a reduction potential when calculating* E_{cell}
- *multiply by stoichiometric coefficients when balancing a cell equation.*

Worked examples 12.7 and 12.8 demonstrate this.

WORKED EXAMPLE 12.7

Predicting the Outcome of Redox Reactions

Predict the reaction that will occur when both Ni and Fe are added to a solution that contains both Ni^{2+} and Fe^{2+}, each at 1 M concentration.

Analysis

The first question would be, 'What *possible* reactions could occur?' The system involves a poss ible redox reaction that can be predicted using data in table 12.1. One way to do this is to note the relative positions of the half-reactions when arranged as they are in table 12.1.

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E^{\ominus}_{Ni^{2+}/Ni} = -0.25V$$
$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E^{\ominus}_{Fe^{2+}/Fe} = -0.44V$$

In table 12.1, the half-reaction with the more positive (in this case, less negative) reduction potential will occur as a reduction. Therefore $Ni^{2+}(aq)$ will be reduced and Fe(s) will be oxidised. The products are the substances on the opposite sides of each half-reaction, namely Ni(s) and $Fe^{2+}(aq)$.

Solution

We have done nearly all the work in our analysis of the problem. All that is left is to write the equation. The reactants are Ni^{2+} and Fe; the products are Ni and Fe^{2+}:

$$Ni^{2+}(aq) + Fe(s) \rightarrow Ni(s) + Fe^{2+}(aq)$$

The equation is balanced in terms of both atoms and charges, so this is the spontaneous reaction that will occur in the system specified in the problem.

Is our answer reasonable?

If our prediction of the spontaneous reaction is correct, $E^{\ominus}_{cell}$ should be positive.

$$E^{\ominus}_{cell} = E^{\ominus}_{R} - E^{\ominus}_{L}.$$

As Ni^{2+} is being reduced, Ni^{2+}/Ni will be the right-hand electrode (cathode):

$$E^{\ominus}_{cell} = E^{\ominus}_{Ni^{2+}/Ni} - E^{\ominus}_{Fe^{2+}/Fe}$$

From table 12.1:

$$E^{\ominus}_{cell} = -0.25\,V - (-0.44\,V)$$
$$= +0.19\,V$$

As $E^{\ominus}_{cell}$ is positive, our prediction is correct. Remember that, although the reaction $Fe^{2+} + 2e^- \rightarrow Fe$ is reversed, the sign of $E^{\ominus}_{Fe^{2+}/Fe}$ (-0.44 V) is not changed.

PRACTICE EXERCISE 12.9

What spontaneous reaction occurs if Cl_2 and Br_2 are added to a solution that contains both Cl^- and Br^-, each at 1 M concentration?

If you intend to use a particular spontaneous redox reaction in a galvanic cell, the reduction potentials can be used to predict what the standard cell potential will be, as illustrated in worked example 12.8

WORKED EXAMPLE 12.8

Predicting the Cell Reaction and Cell Potential of a Galvanic Cell

A typical cell of a lead storage battery of the type used to start cars is constructed using electrodes made of lead and lead(IV) oxide, PbO_2, and with sulfuric acid as the electrolyte. The half-reactions and their reduction potentials in this system are:

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(1) \quad E^\circ_{PbO_2/PbSO_4} = +1.69\ V$$

$$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq) \quad E^\circ_{PbSO_4/Pb} = -0.36\ V$$

What is the spontaneous cell reaction and what is the standard potential of this cell?

Analysis

In the spontaneous cell reaction, the half-reaction with the larger (more positive) reduction potential will take place as a reduction, while the other half-reaction will be reversed and occur as an oxidation. The cell potential is the difference between the two reduction potentials.

Solution

PbO_2 has a larger, more positive reduction potential than $PbSO_4$, so the first half-reaction will occur in the direction written. The second must be reversed to occur as an oxidation. In the cell, therefore, the half-reactions are:

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l) \quad \text{(reduction)}$$

$$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^- \quad \text{(oxidation)}$$

$$PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l) \quad \text{(cell reaction)}$$

(*Hint:* Use changes in oxidation numbers to check when balancing complex redox reactions.) The cell potential is obtained by:

$$E^\circ_{cell} = E^\circ_R - E^\circ_L$$

Because the first half-reaction occurs as a reduction, this becomes the right-hand electrode. Therefore:

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{PbO_2/PbSO_4} - E^\circ_{PbO_4/Pb} \\ &= (+1.69\,V) - (-0.36\,V) \\ &= +2.05\,V \end{aligned}$$

Again, even though we reversed the direction of the reaction:

$$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$$

we did not change the sign of the reduction potential when calculating E°_{cell}. The convention $E^\circ_{cell} = E^\circ_R - E^\circ_L$ took care of this.

PRACTICE EXERCISE 12.10

Determine the cell reaction and the standard cell potential of a galvanic cell employing the following half-reactions.

$$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s) \quad E^\circ_{Al^{3+}/Al} = -1.66\ V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^\circ_{Cu^{2+}/Cu} = +0.34\,V$$

Which electrode (Al or Cu) would be the anode?

Because the spontaneous redox reaction that takes place among a mixture of reactants can be predicted from the standard reduction potentials, it

should be possible to predict whether a particular reaction, *as written*, can occur spontaneously. We can do this by calculating the cell potential that corresponds to the reaction in question and seeing if the potential is *positive*.

Oxidising and Nonoxidising Acids

The standard reduction potentials in table 12.1 would predict that acids (represented by $H^+(aq)$ or H_3O^+) can oxidise certain metals, such as Fe, Zn, Sn and Mg (see figure 12.17), but not other metals, such as Ag, Cu and Au.



FIGURE 12.17 Zinc reacts with aqueous sulfuric acid. Bubbles of hydrogen are formed when a solution of sulfuric acid comes in contact with metallic zinc.

For example, when dilute aqueous sulfuric acid reacts with zinc, a zinc salt is formed and bubbles of gaseous hydrogen are released:

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

Dilute aqueous sulfuric acid ionises in water to give positively charged hydrogen ions (protons) and negatively charged sulfate ions. The proton can act as an oxidising agent by being reduced to H_2. Although the sulfate ion can be reduced (to SO_3^{2-}, for example), protons are much more easily reduced under these dilute conditions. Therefore, when a metal such as zinc is added to dilute aqueous sulfuric acid, it is H^+, rather than SO_4^{2-}, that removes the electrons from zinc.

A similar situation can be found with hydrochloric acid, which contains H^+ and Cl^- ions. H^+ is the oxidising agent, as the Cl^- ion shows no tendency to gain an electron under these (or any other) conditions.

Compared with many other chemicals, the solvated proton, $H^+(aq)$, is a rather poor oxidising agent, so hydrochloric acid and dilute aqueous sulfuric acid have only poor oxidising abilities. For this reason, they are often called **nonoxidising acids**, even though their protons can oxidise certain metals. Actually, when we call something a nonoxidising acid, we are saying that the *anion* of the acid is a weaker oxidising agent than H^+ (which is equivalent to saying that the anion of the acid is more difficult to reduce than H^+). Examples of nonoxidising acids are listed in table 12.2.

TABLE 12.2 Nonoxidising and Oxidising Acids

Nonoxidising acid	
HCl(aq)	
$H_2SO_4(aq)^{(a)}$	
$H_3PO_4(aq)$	
most carboxylic acids, e.g. CH_3COOH (acetic acid), HCOOH (formic acid)	
Oxidising acid	**Reduction reaction**
HNO_3	(conc.) $NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$
	(dilute) $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$
	(very dilute, with strong reducing agent) $NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow NH_4^+(aq) + 3H_2O(l)$
H_2SO_4	(hot, conc.) $SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow SO_2(g) + 2H_2O(l)$

	(hot, conc. with strong reducing agent) $SO_4^{2-}(aq) + 10H^+(aq) + 8e^- \rightarrow H_2S(g) + 4H_2O(l)$
$HClO_4$	$ClO_4^-(aq) + 8H^+(aq) + 8e^- \rightarrow Cl^-(aq) + 4H_2O$

(a) H_2SO_4 is a nonoxidising acid when cold and dilute.

Not all acids are like HCl and dilute aqueous H_2SO_4. **Oxidising acids** have anions that are stronger oxidising agents than H^+ (see table 12.2). An example is concentrated nitric acid, HNO_3. When dissolved in water, nitric acid ionises to give H^+ and NO_3^- ions. However, in this solution the nitrate ion is a more powerful oxidising agent than a proton. In the competition for electrons, therefore, the nitrate ion wins and, when nitric acid reacts with a metal, the nitrate ion is reduced.

Because the NO_3^- ion is a stronger oxidising agent than H^+, it can oxidise metals that H^+cannot. For example, if a copper coin is dropped into concentrated nitric acid, it reacts violently (figure 12.18). The reddish-brown gas is the highly toxic nitrogen dioxide, NO_2, which is formed by reduction of the NO_3^- ion.

$$\overset{0}{Cu}(s) + 4\overset{+5}{HNO_3}(aq) \rightarrow \overset{+2}{Cu}(NO_3)_2(aq) + 2\overset{+4}{NO_2}(g) + 2H_2O(l)$$

Notice that the oxidation number of nitrogen decreases; we identify the substance that contains this nitrogen, the NO_3^- ion, as the oxidising agent.



FIGURE 12.18 A copper coin in concentrated nitric acid showing the violent reaction, formation of the blue Cu^{2+} ion and the evolution of reddish-brown $NO_2(g)$.

When oxidising acids react with metals, it is often difficult to predict the products. The particular reaction that occurs depends very much on the concentration of the acid and experimental conditions (e.g. whether the reaction was performed with heating). Reduction of the nitrate ion, for example, can produce all sorts of compounds with different oxidation states of nitrogen, depending on the reducing power of the metal and the concentration of the acid. When concentrated nitric acid reacts with a metal, it often produces nitrogen dioxide, NO_2, as the reduction product. When dilute nitric acid is used to dissolve a metal, the product is often nitrogen monoxide (also called nitric oxide), NO, instead. Copper, for example, can display either behaviour towards nitric acid. The net ionic equations for the reactions are as follows.

Chemistry Research

Antioxidants and Free Radicals

Professor Carl H Schiesser, University of Melbourne and Director, Australian Research Council Centre of Excellence for Free Radical Chemistry and Biotechnology

One of the great paradoxes of life is this: while we need oxygen to live, oxygen can also be involved in our demise. If not burned for fuel, oxygen can cause free radical damage to cells. Free radicals are atoms or molecules that have one or more unpaired electrons. In biological systems, they form a major function in cell signalling, and Hund's rule (see chapter 4) requires that molecular oxygen, O_2, is itself a free radical. Superoxide, $O_2\bullet^-$, is formed during respiration through the reaction of O_2 with electrons that 'leak' from the electron-transport chain; when hydrogen peroxide, H_2O_2, formed by the reaction of $O_2\bullet^-$ with superoxide dismutase (SOD), reacts with iron, Fe^{2+}, hydroxyl radicals, •OH, are formed through a process known as the Fenton reaction. These reactive oxygen species (ROS) give rise to oxidative stress.

Mammals are protected from oxidative stress through a series of elaborate prevention, interception and repair defence mechanisms (figure 12.19). Glutathione peroxidase (GPx, figure 12.20) and catalase, for example, are enzymes whose principal function is to convert the products of oxidative stress (e.g. H_2O_2) into harmless species (e.g. H_2O, figure 12.21). Much of the selenium in our diet ends up as selenocysteine in enzymes such as glutathione peroxidase. Unlike sulfur, selenium has the correct reduction potential to reduce unwanted peroxides formed in our daily lives. Since the late 1990s, selenocysteine has been recognised as the twenty-first essential amino acid. Other important antioxidant molecules include vitamin C (ascorbic acid) and vitamin E (a mixture of tocopherols).

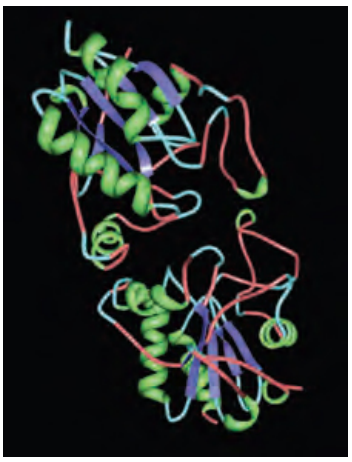


FIGURE 12.19 Ribbon diagram of selenoenzyme glutathione peroxidase at 0.2 nm resolution.

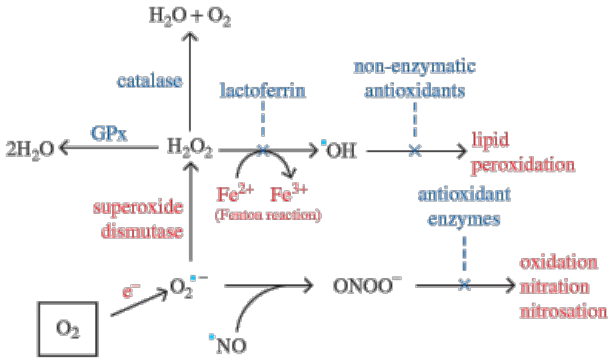


FIGURE 12.20 Antioxidant defences in the human body. Hydroxyl radicals can oxidise virtually all organic compounds, including DNA, proteins and fats. For this reason, it has been proposed that these and other free radicals are key damaging agents in some cancers, the ageing process and cardiac disease.

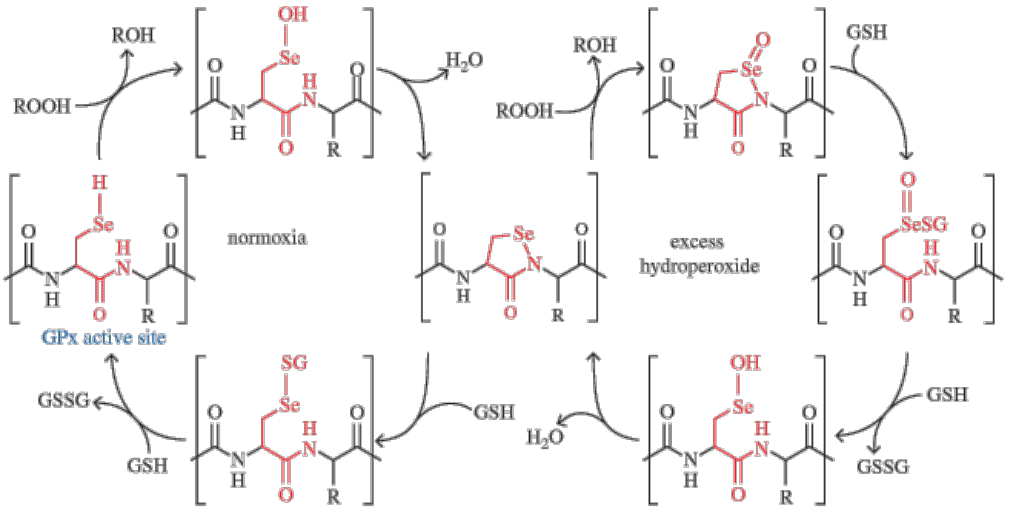


FIGURE 12.21 How glutathione peroxidase (GPx) works to remove reactive oxygen species under normal and hypoxic conditions. Note that glutathione (GSH) is a co-reductant.

Researchers at the Australian Research Council Centre of Excellence for Free Radical Chemistry and Biotechnology are adding antioxidant function to known pharmaceutical molecules, thereby creating dual-action drugs that will also protect against free radical damage associated with cardiac and hypertensive events. Such advances in free radical chemistry have the potential to improve the health of millions of people worldwide.

Concentrated HNO_3:

$$Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$$

Dilute HNO_3:

$$3Cu(s) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

If very dilute nitric acid reacts with a metal that is a particularly strong reducing agent, such as zinc, the nitrogen can be reduced all the way down to the -3 oxidation state that it has in NH_4^+ (or NH_3). The net ionic equation is:

$$4Zn(s) + 10H^+(aq) + NO_3^-(aq) \rightarrow 4Zn^{2+}(aq) + NH_4^+(aq) + 3H_2O(l)$$

The nitrate ion in the presence of protons makes nitric acid a powerful oxidising acid. All metals except the very unreactive ones, such as platinum and gold, are attacked by it. Nitric acid also does a good job of oxidising organic substances, so it is wise to be especially careful when working with this acid in the laboratory. Very serious accidents have occurred when concentrated nitric acid has been used around organic substances. It reacts very violently with most organic compounds, resulting in heat, gas or fire.

In a dilute solution, the sulfate ion of sulfuric acid has little tendency to serve as an oxidising agent. However, if the sulfuric acid is both concentrated and hot, it becomes a fairly potent oxidiser. For example, copper does not react with cool, dilute H_2SO_4, but it is attacked by hot, concentrated H_2SO_4 according to the equation:

$$Cu(s) + 2H_2SO_4(\text{hot, conc.}) \rightarrow CuSO_4(aq) + SO_2(g) + 2H_2O(l)$$

Because of this oxidising ability, hot, concentrated sulfuric acid can be very dangerous. The liquid is viscous and can stick to the skin, causing severe burns.

The mixture obtained by mixing concentrated nitric acid and concentrated hydrochloric acid (usually in a volumetric ratio of 1 : 3) is called aqua regia (figure 12.22). The name comes from the fact that the strong oxidising power of this acid mixture can dissolve even the so-called ‘royal’ (‘regal’ or ‘noble’) metals, gold and platinum.



FIGURE 12.22 Aqua regia, obtained by mixing concentrated nitric acid with concentrated hydrochloric acid.

Aqua regia is used to produce chloroauric acid, $HAuCl_4$, which is used as the electrolyte in the Wohlwill process for the production of gold with 99.999% purity. We will discuss electrolytic processes later in this chapter.

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12.5 Relationship Between Cell Potential, Concentration and Gibbs Energy

The fact that cell potentials can be used to predict the spontaneity of redox reactions is no co incidence. There is a relationship between the cell potential and the Gibbs energy change for a reaction. In chapter 8, we saw that ΔG for a reaction is a measure of the maximum useful work that can be obtained from a chemical reaction at constant temperature and pressure. Specifically, the relationship is:

$$\Delta G = \text{maximum non} - pV \text{ work}$$

The Gibbs Energy Change, ΔG

In an electrical system, work is supplied by the electric current that is pushed along by the potential of the cell. It can be calculated from the equation:

$$\text{maximum non} - pV \text{ work} = -zFE_{\text{cell}}$$

where z is the amount of electrons transferred, F is a constant called the **Faraday constant**, which is equal to the number of coulombs of charge equivalent to 1 mole of electrons ($1\ F = 96485\ \text{C mol}^{-1}$), and E_{cell} is the potential of the cell in volts. Analysis of the units in the equation shows that the answer will be in joules, the unit of energy. Recall that 1 volt = 1 J C^{-1}, so:

$$\begin{aligned} \text{maximum non} - pV \text{ work} &= [(\text{mol}) \times (\text{C mol}^{-1}) \times (\text{J C}^{-1})] = \text{joule} \\ &= -z \times F \times E_{\text{cell}} \end{aligned}$$

Combining our two equations gives:

$$\Delta G = -zFE_{\text{cell}}$$

What does this equation mean? It tells us that the change in Gibbs energy, ΔG, between the reactants and products of the reaction is directly related to the maximum potential of a cell, E_{cell}. When E_{cell} is positive, ΔG will be negative and the cell reaction will be spontaneous. On the other hand, when E_{cell} is negative, ΔG will be positive and the cell reaction will be spontaneous in the reverse direction. If the *standard* cell potential $E^{\ominus}_{\text{cell}}$ is used, the standard Gibbs energy change, $\Delta G^{\ominus}$, can be calculated:

$$\Delta G^{\ominus} = -zFE^{\ominus}_{\text{cell}}$$

WORKED EXAMPLE 12.9

Calculating the Standard Gibbs Energy Change

Calculate $\Delta G^{\ominus}$ for the following reaction, given that its standard cell potential is 0.32 V at 25 °C:

$$NiO_2(s) + 2Cl^-(aq) + 4H^+(aq) \rightarrow Cl_2(g) + Ni^{2+}(aq) + 2H_2O(l)$$

Analysis

This is a straightforward application of $\Delta G^{\ominus} = -zFE^{\ominus}_{cell}$. Because 2 moles of Cl^- are oxidised to Cl_2 and 2 moles of electrons are therefore transferred, the amount z = 2 mol. We will also use the Faraday constant, 1 F = 96 485 C mol^{-1}.

Solution

$$\begin{aligned}\Delta G^{\ominus} &= zFE^{\ominus}_{cell} \\ &= -(2\,\text{mol}) \times (96485\,\text{C mol}^{-1}) \times (0.32\,\text{J C}^{-1}) \\ &= -6.18 \times 10^4\,\text{J} \\ &= -61.8\,\text{KJ}\end{aligned}$$

PRACTICE EXERCISE 12.11

Calculate $\Delta G^{\ominus}$ for the reactions that take place in the galvanic cell described in practice exercise 12.10.

Equilibrium Constant, *K*

One useful application of electrochemistry is the determination of equilibrium constants. In Chapter 9 we saw that $\Delta G^{\ominus}$ is related to the equilibrium constant by the expression:

$$\Delta G^{\ominus} = -RT\ln K_c$$

Note that we use K_c for the equilibrium constant because the electrochemical reactions described here occur in solution: Combining:

$$\Delta G^{\ominus} = -zFE^{\ominus}_{cell}$$

with:

$$\Delta G^{\ominus} = -RT\ln K_c$$

we get:

$$-zFE^{\ominus}_{cell} = -RT\ln K_c$$

so:

$$E^{\ominus}_{cell} = \frac{RT}{zF}\ln K_c$$

This equation shows the relationship between $E^{\ominus}_{cell}$ and the equilibrium constant.

In this equation, the value of R = 8.314 J mol^{-1} K^{-1}, T is the temperature in kelvin, F = 96 485 C per mole of e^-, and z is the amount of electrons transferred in the reaction.

For historical reasons:

$$E^{\ominus}_{\text{cell}} = \frac{RT}{zF}\ln K_c$$

is sometimes expressed using the common logarithm, log (logarithm with base 10). Natural and common logarithms are related by the equation:

$$\ln x = 2.303 \log x$$

For reactions at 298 K (25 °C), all of the constants (*R*, *T* and *F*) can be combined with the factor 2.303 to give 0.0592 J C^{-1}. Because J C^{-1} = V, the equation reduces to:

$$E^{\ominus}_{\text{cell}} = \frac{0.0592\,\text{V}}{z}\log K_c$$

where *z* is the amount of electrons transferred in the cell reaction as it is written.

WORKED EXAMPLE 12.10

Calculating Equilibrium Constants from $E^{\ominus}_{\text{cell}}$

Calculate K_c for the reaction in worked example 12.9.

Analysis

The problem simply involves substituting values into:

$$E^{\ominus}_{\text{cell}} = \frac{RT}{zF}\ln K_c$$

and solving for the equilibrium constant.

Solution

The reaction in worked example 12.9 has $E^{\ominus}_{\text{cell}}$ and $z = 2$. The temperature is 25 °C (298 K).

We can solve:

$$E^{\ominus}_{\text{cell}} = \frac{RT}{zF}\ln K_c$$

for $\ln K_c$ and then substitute values:

$$\ln K_c = \frac{E^{\ominus}_{\text{cell}} zF}{RT}$$

Substituting values (1 V = 1 J C^{-1}):

$$\ln K_c = \frac{0.32\,\text{J C}^{-1} \times 2 \times 96\,485\,\text{C mol}^{-1}}{8.314\,\text{J mol}^{-1}\text{K}^{-1} \times 298\,\text{K}} = 24.9$$

Taking the antilogarithm:

$$K_c = e^{24.9} = 7 \times 10^{10}$$

Is our answer reasonable?

As a rough check, we can look at the magnitude of $E^{\ominus}_{\text{cell}}$ and apply some simple reasoning.

When $E^{\ominus}_{\text{cell}}$ is positive, $\Delta G^{\ominus}$ is negative. In chapter 9 we learned that, when $\Delta G^{\ominus}$ is negative,

the reaction proceeds far towards completion when equilibrium is reached. Therefore, we expect that K_c will be large, and that agrees with our answer.

PRACTICE EXERCISE 12.12

The calculated standard cell potential for the reaction:

$$Cu^{2+}(aq) + 2Ag(s) \rightleftharpoons Cu(s) + 2Ag^{+}(aq)$$

is $E^{\circ}_{cell} = -0.46\,v$. Calculate K_c for this reaction at 298 K.

The Nernst Equation

When all of the ion concentrations in a cell are 1 M, and the partial pressures of any gases involved in the cell reaction are at 1×10^5 Pa, the cell potential is equal to the standard potential. When the concentrations or pressures change, however, so does the cell potential. For example, in an operating cell or battery, the potential gradually drops as the reactants are used up and as the cell reaction approaches its natural equilibrium status. At equilibrium, the potential has dropped to 0 — the battery is dead.

The effect of concentration on the cell potential can be obtained from thermodynamics. In chapter 9, we learned that the Gibbs energy change is related to the reaction quotient (Q, see section 9.2) by the equation:

$$\Delta G = \Delta G^{\circ} + RT\ln Q$$

(Remember that the reaction quotient, Q, is used when the reactants are not in equilibrium; in other words, the equilibrium constant, K, is a special case of Q, used when the system is in equilibrium.) Substituting for ΔG and ΔG° from:

$$\Delta G = -zFE_{cell}$$

and:

$$\Delta G^{\circ} = -zFE^{\circ}_{cell}$$

gives:

$$-zFE_{cell} = -zFE^{\circ}_{cell} + RT\ln Q$$

Dividing both sides by $-zF$ gives:

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{zF}\ln Q$$

This equation is commonly known as the **Nernst equation**, named after Walter Nernst, a German chemist and physicist who was awarded the Nobel Prize in chemistry in 1920 in recognition of his work in thermochemistry. Using common logarithms instead of natural logarithms and calculating the constants for 298 K (25 °C) gives another form of the Nernst equation that is sometimes used:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592\ V}{z}\log Q$$

In writing the Nernst equation for a galvanic cell, we will construct the reaction quotient (Q) using molar concentrations for ions and partial pressures in pascals for gases. Thus, for a cell using a hydrogen electrode (with the partial pressure of H_2 not necessarily equal to 1×10^5 Pa) for which the cell reaction is:

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$$

the Nernst equation is:

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{zF} \ln \frac{\left[H^+\right]^2}{\left[Cu^{2+}\right]\frac{PH_2}{p^{\ominus}}}$$

(Remember that we do not include concentrations of pure solids or pure liquids in the reaction quotient, Q.)

Because of interionic attractions, ions do not always behave as though their concentrations are equal to their molarities. Strictly speaking, effective concentrations (called activities, see section 9.2) should be used in the expression for Q. Effective concentrations are difficult to calculate, so for simplicity we will use molarities and accept the fact that our calculations are not entirely accurate.

Alternatively, we could add a nonreacting background electrolyte at a much higher concentration than the reactants or products and report this concentration with our results. Often 1 M KCl or 1 M $LiClO_4$ is used as the background electrolyte. The reaction is then studied under conditions of constant ionic strength, and the reaction (and cell potentials) behaves simply according to molarities. In chapter 15, we will see that similar considerations are made when studying the kinetics of ionic reactions. For now, in worked examples, we will ignore ionic strength effects. In the laboratory, you should take care in your experimental set-ups to control these effects.

WORKED EXAMPLE 12.11

Calculating the Effect of Concentration on E_{cell}

Consider a galvanic cell involving the following half-reactions:

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E^{\ominus}_{Ni^{2+}/Ni} = -0.25\,V$$

$$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s) \quad E^{\ominus}_{Cr^{3+}/Cr} = -0.74\,V$$

Calculate the cell potential when $[Ni^{2+}] = 1.0 \times 10^{-4}$ M and $[Cr^{3+}] = 2.0 \times 10^{-3}$ M.

Analysis

Because the concentrations are not 1 M, we must use the Nernst equation. First, we need the cell reaction to determine z, the number of electrons transferred, and the correct form of the reaction quotient, Q. We must also note that the reacting system is heterogeneous; solid metals and a liquid solution of their dissolved ions are involved, so we have to remember that Q does not contain concentration terms for solids, such as Ni(s) and Cr(s).

Solution

The nickel half-cell has the more positive reduction potential, so its half-reaction will occur as a reduction. This means that Cr(s) will be oxidised. Making electron gain equal to electron loss, the cell reaction is:

$$\begin{array}{rl} 3\left[Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)\right] & \text{(reduction)} \\ 2[Cr(s)] \rightarrow Cr^{3+}(aq) + 3e^- & \text{(oxidation)} \\ \hline 3Ni^{2+}(aq) + 2Cr(s) \rightarrow 3Ni(s) + 2Cr^{3+}(aq) & \text{(cell reaction)} \end{array}$$

In this reaction, $6e^-$ are transferred ($z = 6$). The Nernst equation for the system is therefore:

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{6F}\ln\frac{\left[Cr^{3+}\right]^2}{\left[Ni^{2+}\right]^3}$$

Note that we calculate the reaction quotient using the concentrations of the ions raised to powers equal to their coefficients in the net cell reaction, and that we have not included concentration terms for the two solids. This is the procedure we followed for heterogeneous equilibria in chapter 9 (pp. 356-7).

$E^{\ominus}_{cell}$ is determined according to:

$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{Ni^{2+}/Ni} - E^{\ominus}_{Cr^{3+}/Cr} \\ &= (-0.25\,V) - (-0.74\,V) \\ &= 0.49\,V \end{aligned}$$

Now we can substitute this value for $E^{\ominus}_{cell}$ along with $R = 8.314$ J mol^{-1} K^{-1}, $T = 298$ K, $z = 6$, $F = 96\,485$ C mol^{-1}, $[Ni^{2+}] = 1.0 \times 10^{-4}$ M and $[Cr^{3+}] = 2.0 \times 10^{-3}$ M into the Nernst equation. Remembering that 1 V = 1 J C $^{-1}$, we obtain:

$$\begin{aligned} E_{cell} &= 0.49\,V - \frac{8.314\,J mol^{-1} K^{-1} \times 298\,K}{6 \times 96485\,C\,mol^{-1}}\ln\frac{(2.0\times10^{-3})^2}{(1.0\times10^{-4})^3} \\ &= 0.49\,V - (0.00428\,V)\ln(4.0\times10^6) \\ &= 0.49\,V - 0.0651\,V \\ &= 0.42\,V \end{aligned}$$

The potential of the cell is expected to be 0.42 V.

Is our answer reasonable?

There is no simple way to check the answer. However, there are certain critical points to look over. First, check that the half-reactions have been combined correctly to give the balanced cell reaction (check the oxidation numbers), because we need the coefficients of the equation to obtain the correct superscripts in the Nernst equation. Then, check that the temperature in kelvin has been used, that $R = 8.314$ J mol^{-1} K^{-1} has been used, and that the other substitutions have been made correctly.

PRACTICE EXERCISE 12.13

In a certain zinc-copper cell:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2}(aq) + Cu(s)$$

the concentrations of the ions are $[Cu^{2+}]$ = 0.0100 M and $[Zn^{2+}]$ = 1.0 M. Use the reduction potentials in table 12.1 to calculate the cell potential at 25 °C.

One of the principal uses of the relationship between concentration and cell potential is in the measurement of concentrations. Experimental determination of cell potentials, combined with modern developments in electronics, has provided a means of monitoring and analysing the concentrations of all sorts of substances in solution, even some that are not themselves ionic and that are not involved directly in electrochemical changes. Worked example 12.12 illustrates how the Nernst equation is applied in determining concentrations.

WORKED EXAMPLE 12.12

Using the Nernst Equation to Determine Concentrations

In a large number of samples of water, in which the copper ion concentration is expected to be quite small, $[Cu^{2+}]$ was measured using an electrochemical cell. This consisted of a silver electrode dipping into a 1.00 M solution of $AgNO_3$, which was connected by a salt bridge to a second half-cell containing a copper electrode. The copper half-cell was then filled with one water sample after another, and the cell potential was measured for each sample. In the analysis of one particular sample, the cell potential at 25 °C measured was 0.62 V, with the copper electrode being the anode. What was the concentration of Cu^{2+} in this sample?

Analysis

In this problem, we have been given the cell potential, E_{cell}, and we can calculate $E^{\ominus}_{cell}$ from the reduction potentials in table 12.1. The unknown quantity is one of the concentration terms in the Nernst equation.

Solution

The first step is to write the defined cell reaction, because we need it to calculate $E^{\ominus}_{cell}$ and to write the expression for Q for use in the Nernst equation. Because copper is the anode, it is being oxidised. This also means that Ag^{+} is being reduced. Therefore, the equation for the cell reaction is:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2}(aq) + 2Ag(s)$$

Because two electrons are transferred, $z = 2$ and the Nernst equation is therefore:

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{2F}\ln\frac{[Cu^{2+}]}{[Ag^{+}]^2}$$

The value of $E^{\ominus}_{cell}$ can be obtained using the data in table 12.1. Following our usual procedure and recognising that silver ions are reduced:

$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{Ag^+} - E^{\ominus}_{Cu^{2+}} \\ &= +0.08\,V - (+0.34\,V) \\ &= 0.46\,V \end{aligned}$$

Substitution of the values into the Nernst equation (remembering that 1 V = 1 J C^{-1}) gives:

$$0.62\,V = 0.46\,V - \frac{8.314\,J\,mol^{-1}K^{-1} \times 298\,K}{2 \times 96485\,C\,mol^{-1}}\ln\frac{[Cu^{2+}]}{[Ag^{+}]^2}$$

Solving for $\ln([Cu^{2+}]/[Ag^{+}]^2)$ gives:

$$\ln\frac{[Cu^{2+}]}{[Ag^{+}]^2} = -12$$

Taking the antilogarithm gives us the value of Q:

$$\frac{[Cu^{2+}]}{[Ag^{+}]^2} = 6 \times 10^{-6}$$

Because the concentration of Ag^+ is known (1.00 M):

$$\begin{aligned} \frac{[Cu^{2+}]}{(1.00)^2} &= 6 \times 10^{-6} \\ [Cu^{2+}] &= 6 \times 10^{-6}\,M \end{aligned}$$

Is our answer reasonable?

We should first check that we have written the correct chemical equation, which the rest of the solution to the problem relies on. We can then insert our calculated value of $[Cu^{2+}]$ back into the Nernst equation and ensure that we obtain E_{cell} = 0.62 V. This will show with certainty that our answer is correct.

As a final point, notice that the Cu^{2+} concentration is indeed very small and that it can be obtained very easily simply by measuring the potential generated by the electrochemical cell. Determining the concentrations in many samples is also very simple — just change the aqueous sample and measure the potential again.

PRACTICE EXERCISE 12.14

A galvanic cell was constructed by connecting a nickel electrode dipping into 1.20 M $NiSO_4$ solution to a chromium electrode dipping into a solution containing Cr^{3+} at an unknown concentration. The potential of the cell was measured to be 0.552 V, with the chromium serving as the anode. The standard cell potential for this system was determined to be 0.487 V. What was the concentration of Cr^{3+} in the solution of unknown concentration?

It should be noted that the ability of certain compounds to act as either oxidant or reductant can depend strongly on the pH of the reaction solution. For example, as can be seen from table 12.1, the standard reduction potential, $E^{\ominus}_{MnO_4^-,H^+/Mn^{2+}}$ is +1.51 V for the half-reaction:

$$MnO_4^-(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

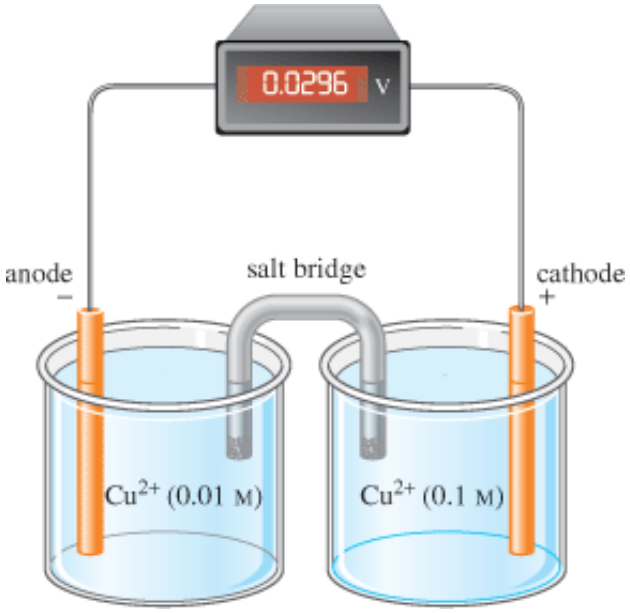
The Nernst equation for this system (z = 5 electrons exchanged) can also be applied to half-cell reactions so that we obtain:

$$E_{MnO_4^-,H^+/Mn^{2+}} = 1.51\,V - \frac{RT}{5F}\ln\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

Thus, the more acidic the solution becomes (i.e. the higher the $[H^+]$), the greater the reduction potential. In other words, MnO_4^- is a much stronger oxidant in acidic solutions than in neutral or even basic solutions.

Concentration Cells

Thus far, we have considered only cells with different chemical species at the right-hand and left-hand electrodes, and we have shown that a current invariably results from such an arrangement because one of the half-cells has a larger $E^{\ominus}$ than the other. We can also show that current will flow in an electrochemical cell when the chemical species at both electrodes are the same, providing that they are present at different concentrations. Such cells are called **concentration cells**.



Consider the cell on the right at 298 K. We can write the cell diagram for this cell as:

$$Cu(s)|Cu^{2+}(aq, 0.01M)||Cu^{2+}(aq, 0.1M)|Cu(s)$$

The two half reactions are:

$$\begin{aligned} Cu(s) &\rightarrow Cu^{2+}(aq, 0.01M) + 2e^- \\ Cu^{2+}(aq, 0.1M) + 2e^- &\rightarrow Cu(s) \end{aligned}$$

and the overall cell reaction is therefore:

$$Cu^{2+}(aq, 0.1M) \rightarrow Cu^{2+}(aq, 0.01M)$$

We can write the Nernst equation for this reaction as:

$$\begin{aligned} E &= E^{\ominus} - \frac{RT}{zF}\ln Q \\ &= E^{\ominus} - \frac{RT}{zF}\ln\frac{[0.01M]}{[0.1M]} \end{aligned}$$

Since the redox processes in the left and right half-cells are identical, we have:

$$E^{\ominus}_{cell} = E^{\ominus}_{R} - E^{\ominus}_{L} = 0V$$

Hence:

$$\begin{aligned} E_{cell} &= 0V - 0.0128\ln\frac{(0.01)}{(0.1)} \\ &= 0.0296V \end{aligned}$$

Therefore, there is a small, but measurable, potential difference between the electrodes that results solely from the different concentrations of the two Cu^{2+} solutions. As the reaction proceeds, the concentrations of the two solutions will eventually become the same and there will be no potential difference between the electrodes. This is similar to the spontaneous process of mixing that occurs when a 0.01 M solution of Cu^{2+} is poured into an equal volume of a 0.1 M solution of Cu^{2+} ions (and vice versa).

Interestingly, many biochemical processes are powered by concentration gradients. For example, adenosine-5'-triphosphate (ATP), which is the main energy-transfer molecule in cells, is synthesised from adenosine diphosphate (ADP) and inorganic phosphate in mitochondria; this process is powered by a proton gradient (see p. 495).

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12.6 Corrosion

The corrosion of iron and other metals is one of the most commonly encountered redox processes in our daily life, and it has plagued humanity ever since these metals were first discovered. At first glance, the rusting of a car or ship (see p. 489) does not seem to be a complicated process, since iron reacts with oxygen to give iron(II) oxide:

$$2Fe \rightarrow 2Fe^{2+} + 4e^- \quad \text{(oxidation)}$$
$$O_2 + 4e^- \rightarrow 2O^{2-} \quad \text{(reduction)}$$
$$2Fe + O_2 \rightarrow 2FeO \quad \text{(net reaction)}$$

The electrons released when the iron is oxidised travel through the metal to some other place where the iron is exposed to air. This is where reduction occurs. Is this process really that easy? Why does a car rust faster in moist air? Why doesn't it rust in pure water that is oxygen free? The corrosion process is apparently electrochemical in nature with the iron acting as the anode, as shown in figure 12.23.

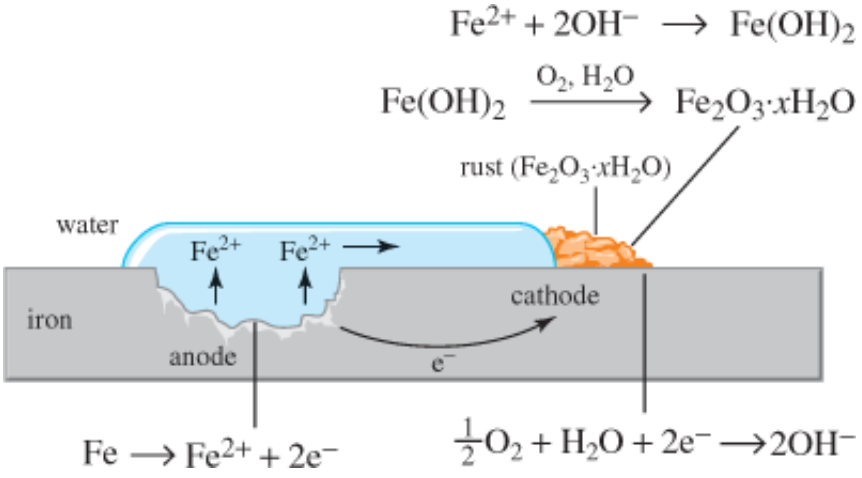


FIGURE 12.23 Corrosion of iron. Iron dissolves in anodic regions to give Fe^{2+}. Electrons travel through the metal to cathodic sites where oxygen is reduced, forming OH^-. The combination of the Fe^{2+} and OH^-, followed by oxidation in air, gives rust.

In aqueous solution, the reduction of oxygen proceeds differently from that shown in the equations above. Oxide anions, O^{2-}, are not very stable in aqueous solution. When they react with water, hydroxide anions are produced. The reduction process of oxygen in water is therefore:

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$$

The rusting of iron can now be written as:

$$2Fe \rightarrow 2Fe^{2+} + 4e^- \quad \text{(oxidation)}$$
$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \quad \text{(reduction)}$$
$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \quad \text{(net reaction)}$$

However, we are not finished yet. Rust contains not only iron(II) ions but also iron(III) ions. Thus, the iron(II) ions formed in the anodic regions gradually diffuse through the water and eventually contact the hydroxide ions. This causes a precipitate of iron(II) hydroxide, $Fe(OH)_2$, to form, which is further oxidised by oxygen to iron(III) hydroxide, $Fe(OH)_3$.

$$\begin{array}{rcll} 4Fe(OH)_2 & \rightarrow & 4Fe(OH)_2{}^+ + 4e^- & \text{(oxidation)} \\ O_2 + 4e^- + 2H_2O & \rightarrow & 4OH^- & \text{(reduction)} \\ \hline 4Fe(OH)_2 + O_2 + 2H_2O & \rightarrow & 4Fe(OH)_3 & \text{(net reaction)} \end{array}$$

We are still not finished. Rust does not consist of iron(III) hydroxide but of a remarkable mixed product with the formula FeO(OH), which can be called iron oxide hydroxide. FeO(OH) is formed by dehydration of $Fe(OH)_3$:

$$Fe(OH)_3 \rightarrow FeO(OH) + H_2O$$

This mechanism of rusting explains one of the more interesting aspects of this damaging process. Perhaps you have noticed that, when rusting occurs on the body of a car, the rust appears at and around a break or a scratch in the surface of the paint, but the damage extends under the surface for some distance. Apparently, the Fe^{2+} ions formed at the anode sites can diffuse rather long distances to the hole in the paint, where they finally react with air and water to form the rust.

Corrosion can be inhibited by several techniques. In a process called **galvanisation**, iron objects are coated with zinc. Since the reduction potential of Zn^{2+} is more negative than that of Fe^{2+}:

$$Zn^{2+} + 2e^- \rightarrow Zn \quad E^{\ominus}_{Zn^{2+}/Zn} = -0.76\,V$$

$$Fe^{2+} + 2e^- \rightarrow Fe \quad E^{\ominus}_{Fe^{2+}/Fe} = -0.44\,V$$

the oxidation of zinc is favoured. This leads to formation of a protective layer of a zinc oxide which lasts until all the zinc is corroded away. Tin plating as in 'tin' cans, in contrast, leads to a very rapid corrosion of the iron once its surface is scratched and the iron is exposed, because the Sn^{2+}/Sn reduction potential:

$$Sn^{2+} + 2e^- \rightarrow Sn \quad E^{\ominus}_{Sn^{2+}/Sn} = -0.14\,V$$

is greater than that of Fe^{2+}/Fe, and therefore Sn^{2+} oxidises Fe. Some oxides are stable in a sense because they adhere to the metal surface and form an impermeable layer over a fairly wide pH range. This is why aluminium reacts only very slowly in air even though its reduction potential is strongly negative ($Al(s) \rightarrow Al^{3+}(aq) + 3e^-, E^{\ominus}_{Al^{3+}/Al} = -1.66\,V$). Such a phenomenon is called **passivation**.

Another protecting method is to change the potential of the subject by pumping in electrons, which can be used to satisfy the demands of oxygen without involving oxidation of the metal. **Cathodic protection** is a concept used to protect large objects, such as ships, pipelines and buildings, from rusting (figure 12.24). The object is connected to a metal with a more negative electrode potential, such as magnesium ($Mg^{2+}(aq) + 2e^- \rightarrow Mg(s), E^{\ominus}_{Mg^{2+}/Mg} = -2.37\,V$). Magnesium acts as a *sacrificial anode* by supplying its electrons to the iron, while it is oxidised to Mg^{2+}. You can see from this that the occasional replacement of a piece of magnesium is much cheaper than replacing an entire ship.



FIGURE 12.24 Before launching, a shiny new zinc anode disk was attached to the bronze rudder of this boat to provide cathodic protection. Over time, the zinc has corroded, instead of the less reactive bronze.

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12.7 Electrolysis

The preceding sections have shown how spontaneous redox reactions can be used to generate electrical energy. We now turn our attention to the opposite process: the use of electrical energy to force nonspontaneous redox reactions to occur. In fact, these are precisely the kinds of reactions that take place when recharging batteries.

What is Electrolysis?

When electricity is passed through a molten (melted) ionic compound or through a solution of an electrolyte, a chemical reaction called **electrolysis** can occur. An example of an electrolysis apparatus, called an **electrolysis cell** or **electrolytic cell**, is shown in figure 12.25. This particular cell contains molten sodium chloride. (A substance undergoing electrolysis must be molten or in solution so its ions can move freely and conduction can occur.) Inert electrodes — electrodes that will not react with the molten NaCl — are dipped into the cell and then connected to a source of direct current (DC) electricity.

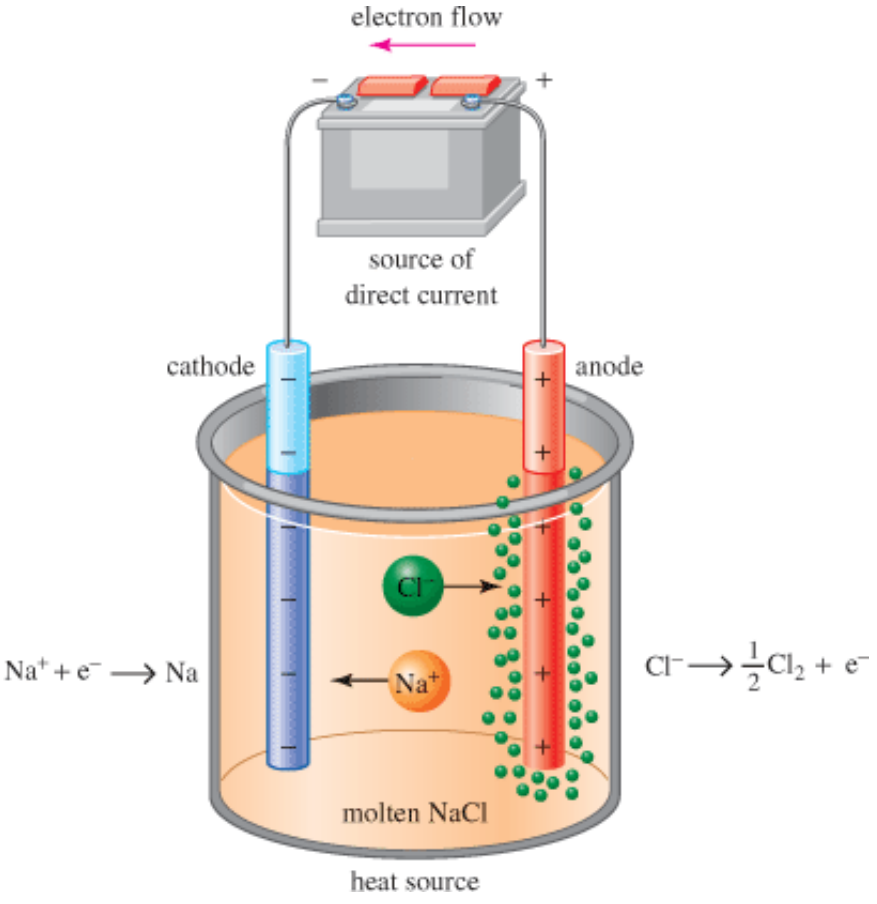


FIGURE 12.25 Electrolysis of molten sodium chloride. The passage of an electric current decomposes molten sodium chloride into metallic sodium and gaseous chlorine.

The DC source serves as an ‘electron pump’, pulling electrons away from one electrode and pushing them through the external wiring onto the other electrode. The electrode from which electrons are removed becomes positively charged, while the other electrode becomes negatively charged. In this example:

- At the positive electrode, oxidation occurs as electrons are pulled away from negatively charged chloride ions. Because of the nature of the chemical change in an electrolysis cell, the *positive electrode becomes the anode, to which the anions move*.
- The DC source pumps the electrons through the external electric circuit to the negative electrode.

Here, reduction takes place as the electrons are forced onto positively charged sodium ions, so the *negative electrode is the cathode, to which the cations move*.

The chemical changes that occur at the electrodes can be described by the following equations:

$$2Na^+(l) + 2e^- \rightarrow 2Na(l) \quad \text{(cathode)}$$
$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^- \quad \text{(anode)}$$
$$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g) \quad \text{(cell reaction)}$$

(At the melting point of NaCl, 801 °C, metallic sodium is a liquid.)

Comparison of Electrolytic and Galvanic Cells

- In a *galvanic cell*, the spontaneous cell reaction deposits electrons on the anode and removes them from the cathode. As a result, the anode carries a slight negative charge and the cathode a slight positive charge.
- In an *electrolytic cell*, the situation is reversed. Here, oxidation at the anode must be forced to occur, which requires that the anode is positive so it can remove electrons from the reactant at that electrode.

On the other hand, the cathode must be made negative so it can force the reactant at the electrode to accept electrons. By agreement among scientists, the names *anode* and *cathode* are always assigned according to the nature of the reaction taking place at the electrode:

- If the reaction is *oxidation*, the electrode is called the *anode*.
- If the reaction is *reduction*, the electrode is called the *cathode*.

It is important to remember:

- In an *electrolytic cell*, the cathode is negative (reduction) and the anode is positive (oxidation).
- In a *galvanic cell*, the cathode is positive (reduction) and the anode is negative (oxidation).

Electrolysis in Aqueous Solutions

When electrolysis is carried out in an aqueous solution, the electrode reactions can be more complicated; we must consider oxidation and reduction of the solute as well as oxidation and reduction of water. (It is important to note that the nature of the electrode material itself can also strongly influence the outcome of the electrolysis. We will not discuss this further here.) For example, electrolysis of a solution of potassium sulfate (figure 12.26) gives hydrogen and oxygen. At the cathode, water is reduced, not K^+:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad \text{(cathode)}$$

At the anode, water is oxidised, not the sulfate ion:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \quad \text{(anode)}$$

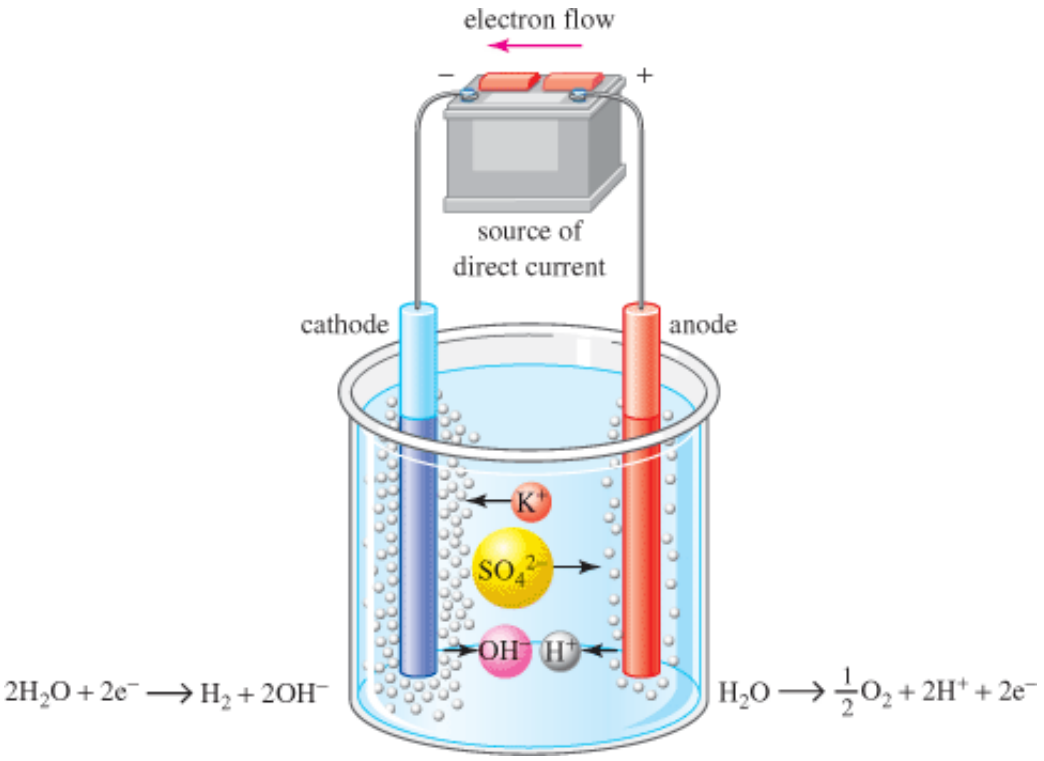


FIGURE 12.26 Electrolysis of an aqueous solution of potassium sulfate. The products of the electrolysis are the gases hydrogen and oxygen.

We can understand why these redox reactions occur if we examine reduction potential data from table 12.1. For example, at the cathode we have the following competing reactions:

$$K^+(aq) + e^- \rightarrow K(s) \qquad E^\ominus_{K^+/K} = -2.92\ V$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\ominus_{H_2O/H_2} = -0.83\ V$$

Water has a much less negative reduction potential than K^+, which means H_2O is much easier to reduce than K^+. During electrolysis, the more easily reduced substance is reduced and H_2 is formed at the cathode.

At the anode, the possible oxidation half-reactions are:

$$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^-$$

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$$

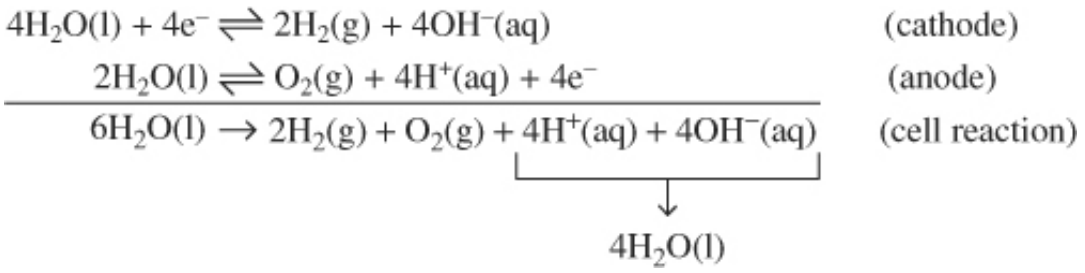
In table 12.1, we find them written in the opposite direction:

$$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq) \qquad E^\ominus_{S_2O_8^{2-}/SO_4^{2-}} = +2.01\ V$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \qquad E^\ominus_{O_2,H^+/H_2O} = +1.23\ V$$

The $E^\ominus$ values tell us that $S_2O_8^{2-}$ is more easily reduced than O_2. But if $S_2O_8^{2-}$ is *reduced*, then the product, SO_4^{2-}, must be *less easily oxidised*. Stated another way, *the half-reaction with the smaller (less positive) reduction potential occurs more easily as an oxidation*. As a result, during electrolysis, water is oxidised instead of SO_4^{2-}, and O_2 is formed at the anode.

The overall cell reaction for the electrolysis of the K_2SO_4 solution is:



The net change then is:

$$2H_2O(l) \xrightarrow{\text{electrolysis}} 2H_2(g) + O_2(g)$$

The word ‘electrolysis’ above the arrow in the equation shows that electricity is the driving force for this otherwise nonspontaneous reaction.

What is the role of potassium sulfate in this electrolysis, given that neither K^+ nor SO_4^{2-} ions are changed by the reaction? If the electrolysis is attempted with pure distilled water, nothing happens. There is no current flow, and no H_2 or O_2 forms. Apparently, the potassium sulfate must have some purpose.

The function of K_2SO_4 (or any other electrolyte) is to maintain electrical neutrality in the vicinity of the electrodes. If K_2SO_4 were not present and the electrolysis were to occur anyway, the solution around the anode would become positively charged. It would become filled with H^+ ions, with no negative ions to balance their charge. Similarly, the solution surrounding the cathode would become negatively charged as it is filled with OH^- ions, with no nearby positive ions. The formation of positively or negatively charged solutions requires too much energy so, in the absence of an electrolyte, the electrode reactions cannot take place.

When K_2SO_4 is in the solution, K^+ ions can move towards the cathode and mingle with the OH^- ions as they are formed. Similarly, the SO_4^{2-} ions can move towards the anode and mingle with the H^+ ions as they are produced there. In this way, at any moment, each small region of the solution can contain the same number of positive and negative charges and thereby remain neutral; in other words, the K^+ and SO_4^{2-} ions complete the electrical circuit.

Reduction potentials can be used to anticipate the products of an electrolysis. This is illustrated by worked example 12.13.

WORKED EXAMPLE 12.13

Predicting the Products in an Electrolysis Reaction

Electrolysis is planned for an aqueous solution that contains a mixture of 0.50 M $ZnSO_4$and 0.50 M $NiSO_4$. On the basis of reduction potentials, what products are expected to be observed at the electrodes? What is the expected net cell reaction?

Analysis

We need to consider the competing reactions at the cathode and the anode. At the cathode, the half-reaction with the *most positive* reduction potential will be the one expected to occur as a reduction. At the anode, the half-reaction with the *least positive* reduction potential is the one that should occur as an oxidation.

Solution

At the cathode, the competing reduction reactions involve the two cations and water. The reactions and their reduction potentials are:

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \qquad E^{\ominus}_{Ni^{2+}/Ni} = -0.25V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^{\ominus}_{Zn^{2+}/Zn} = -0.76V$$

$$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \qquad E^{\ominus}_{H_2O/H_2,OH^-} = -0.83V$$

The most positive reduction potential is that of Ni^{2+}, so we expect this ion to be reduced at the cathode and solid nickel to be formed.

At the anode, the competing oxidation reactions are for water and SO_4^{2-} ions. In table 12.1, oxidised substances are found on the right-hand side of the half-reactions. The two half-reactions with these as products are:

$$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq) \qquad E^{\ominus}_{S_2O_8^{2-}/SO_4^{2-}} = +2.01V$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \qquad E^{\ominus}_{O_2,H^+/H_2O} = +1.23V$$

The half-reaction with the less positive $E^{\ominus}$ occurs more easily as an oxidation, so we expect the oxidation half-reaction to be:

$$2H_2O(l) \rightleftharpoons O_2(g) + 4H^+(aq) + 4e^-$$

At the anode, we expect O_2 to be formed.

The predicted net cell reaction is obtained by combining the two expected electrode half-reactions, making the electron loss equal to the electron gain:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad \text{(anode)}$$

$$2Ni^{2+}(aq) + 4e^- \rightarrow 2Ni(s) \qquad \text{(cathode)}$$

$$2H_2O(l) + 2Ni^{2+}(aq) \rightarrow O_2(g) + 4H^+(aq) + 2Ni(s) \qquad \text{(cell reaction)}$$

Is our answer reasonable?

We can check the locations of the half-reactions in table 12.1 to confirm our conclusions. For the reduction step, the more positive the reduction potential, the greater its tendency to occur as a reduction. Among the competing half-reactions at the cathode, the reduction potential for Ni^{2+} is highest, so we expect that Ni^{2+} is the easiest to reduce and Ni(s) should be formed at the cathode.

For the oxidation step, the more negative the reduction potential, the easier it is to occur as an oxidation. On this basis, the oxidation of water is easier than the oxidation of SO_4^{2-}, so we

expect H_2O to be oxidised and O_2 to be formed at the anode.

PRACTICE EXERCISE 12.15

In the electrolysis of an aqueous solution containing both Cd^{2+} and Cr^{3+}, what product do we expect at the cathode?

Stoichiometry of Electrochemical Reactions

In about 1833, British scientist Michael Faraday discovered that the amount of chemical change that occurs during electrolysis is directly proportional to the amount of electric charge that is passed through an electrolytic cell. For example, the reduction of copper ions at a cathode is given by the equation:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Deposition of 1 mol of metallic copper requires 2 mol of electrons. Therefore, to deposit 2 mol of copper requires 4 mol of electrons, and that takes twice as much electricity. The half-reaction for an oxidation or reduction, therefore, relates the amount of chemical substance consumed or produced to the amount of electrons that the electric current must supply.

The SI unit of electric current is the **ampere (A)** and of charge is the coulomb (C). A coulomb is the amount of charge that passes by a given point in a wire when an electric current of 1 ampere flows for 1 second:

$$1\,\text{coulomb} = 1\,\text{ampere} \times 1\,\text{second}$$
$$1\,\text{C} = 1\,\text{A} \times 1\,\text{s}$$

For example, if a current of 4 A flows through a wire for 10 s, 40 C passes by a given point in the wire.

As we noted earlier, 1 mol of electrons carries a charge of 96 485 C. With this, laboratory measurements can be related to the amount of chemical change that occurs during an electrolysis. The amount of product formed can be calculated using **Faraday's law**:

$$\text{amount of product} = \frac{It}{zF}$$

where I = current (A), t = time (s), z = number of electrons transferred in the balanced equation and F = Faraday constant (C mol^{-1}). Worked example 12.14 demonstrates the use of this equation.

WORKED EXAMPLE 12.14

Calculations Related to Electrolysis

What mass of copper is deposited on the cathode of an electrolytic cell if an electric current of 2.00 A is run through a solution of $CuSO_4$ for a period of 20.0 min?

Analysis

We obtain the amount of copper by using Faraday's law. To determine the mass of copper, we multiply the amount of copper by the molar mass of copper.

Solution

First we convert minutes to seconds: 20.0 min = 1.20×10^3s. We then use Faraday's law to determine the amount of copper (remember that F = 96 485 C mol^{-1} or 9.6485×10^4 A s mol^{-1}):

$$\begin{aligned} \text{amount of product} &= \frac{It}{zF} \\ &= \frac{2.00\,\text{A} \times 1.20 \times 10^3\,\text{s}}{2 \times 9.6485 \times 10^4\,\text{A s mol}^{-1}} \\ &= 1.24 \times 10^{-2}\,\text{mol} \end{aligned}$$

We obtain the mass by multiplying by the molar mass of copper:

$$\text{mass of copper} = 1.24 \times 10^{-2}\,\text{mol} \times 63.55\,\text{g mol}^{-1}$$

The electrolysis will deposit 0.788 g of copper on the cathode.

Is our answer reasonable?

Check that you have inserted the correct numbers into the equation. It is important to remember to convert minutes to seconds in this type of problem.

PRACTICE EXERCISE 12.16

Electrolysis provides a useful way to deposit a thin metallic coating on an electrically conducting surface. The technique is called *electroplating*. How much time would it take in minutes to deposit 0.500 g of metallic nickel on a metal object using a current of 3.00 A? The nickel is reduced from the +2 oxidation state.

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12.8 Batteries

As mentioned earlier, the potential produced by one galvanic cell is not enough to power electronic instruments such as toys, torches, electronic calculators, laptop computers, heart pacemakers, video cameras or mobile phones, let alone a car. A **battery** (figure 12.27) contains a group of galvanic cells usually connected in series so that the potentials of the individual cells add up. These devices are classified as being either **primary cells** (cells not designed to be recharged; they are discarded after their energy is depleted) or **secondary cells** (cells designed for repeated use; they can be recharged). In this section, we will focus on the most important types of batteries, such as car batteries, dry cells and rechargeable batteries, as well as fuel cells.

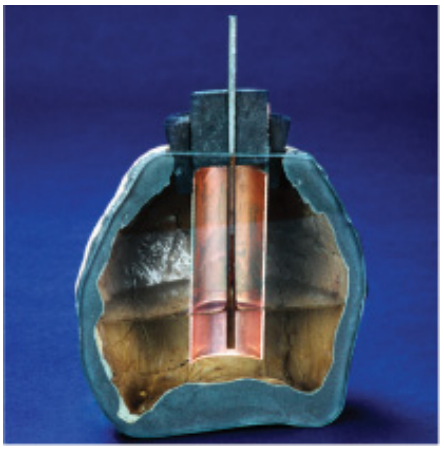


FIGURE 12.27 The oldest known electric battery in existence (dating from about 2200 years ago), discovered in 1938 in Baghdad, Iraq, consists of a copper tube surrounding an iron rod. If filled with an acidic liquid such as vinegar, the cell could produce a small electric current.

The Lead Storage Battery

The common **lead storage battery** (figure 12.28) used to start a car is composed of a number of secondary cells, each having a potential of about 2 V, that are connected in series so that their voltages are additive (see figure 12.29). Most car batteries contain six such cells and give about 12 V, but 6, 24 and 32 V batteries are also available.

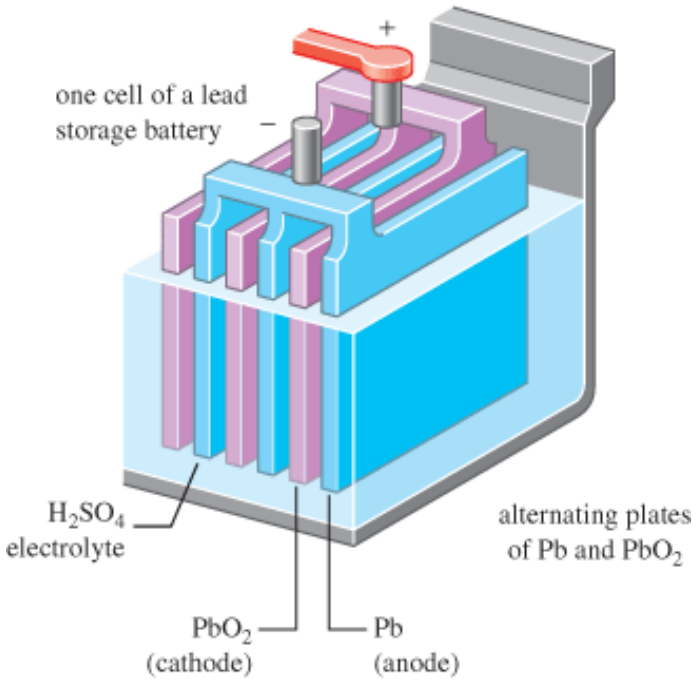


FIGURE 12.28 Lead storage battery. A 12-volt lead storage battery, such as those used in most cars, consists of six cells like the one shown here. Notice that the anode and cathode each consists of several plates connected together. This allows the cell to produce the large currents necessary to start a car.

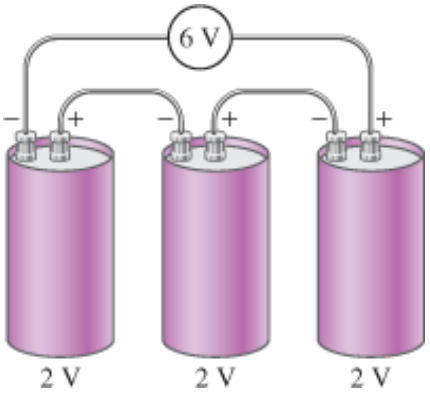


FIGURE 12.29 If three 2-volt cells are connected in series, their voltages are additive to provide a total of 6 volts. Cars generally use 12-volt batteries containing six cells.

The anode of each cell in a typical lead storage battery is composed of a set of lead plates, the cathode consists of another set of plates that hold a coating of PbO_2, and the electrolyte is sulfuric acid. When the battery is discharging, the electrode reactions are:

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l) \quad \text{(cathode)}$$

$$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^- \quad \text{(anode)}$$

The net cell reaction is therefore:

$$PbO_2(s) + Pb(s) + \underbrace{2H^+(aq) + 2HSO_4^-(aq)}_{2H_2SO_4(aq)} \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

The reaction occurring in a lead battery is an example of a **symproportionation** (or comproportionation) reaction, where a chemical reaction occurs between two reactants that contain the same element in different oxidation states. The product has an oxidation number intermediate to the two reactants. In this specific reaction, PbO_2 (oxidation state of Pb = +4) undergoes symproportionation with elemental Pb (oxidation state = 0) to give $PbSO_4$ (oxidation state of Pb = +2).

It should be noted that the reverse of a symproportionation reaction is a **disproportionation** reaction, where a species is simultaneously oxidised and reduced to form two different products. An example of a disproportionation reaction is that of chlorine gas (oxidation number = 0) with dilute sodium hydroxide, which gives sodium chloride, NaCl (oxidation state of Cl = -1), sodium chlorate, $NaClO_3$ (oxidation state of Cl = +5) and water. The relevant redox reaction is given by:

$$3Cl_2(aq) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O$$

As a lead battery discharges, the sulfuric acid concentration decreases, which provides a convenient means of checking the state of the battery. Because the density of a sulfuric acid solution decreases as its concentration drops, the concentration can be determined very simply by measuring the density with a **hydrometer**, which consists of a rubber bulb that is used to draw the battery fluid into a glass tube containing a float (see figure 12.30). The depth to which the float sinks is inversely proportional to the density of the liquid — the deeper the float sinks, the lower is the density of the acid and the weaker is the charge of the battery. The narrow neck of the float is usually marked to indicate the state of charge of the battery.



FIGURE 12.30 A battery hydrometer. Battery acid is drawn into the glass tube. The depth to which the float sinks is inversely proportional to the concentration of the acid and, therefore, to the state of charge of the battery.

The principal advantage of the lead storage battery is that the cell reactions that occur spontaneously during discharge can be reversed by the application of a voltage from an external source. In other words, the battery can be recharged by electrolysis. The reaction for battery recharge is:

$$2PbSO_4(s) + 2H_2O(l) \xrightarrow{\text{electrolysis}} PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq)$$

Disadvantages of the lead storage battery are that it is very heavy and that its corrosive sulfuric acid can spill. The most modern lead storage batteries use a lead-calcium alloy as the anode. This reduces the need to vent individual cells so the battery can be sealed, preventing spillage of the electrolyte.

Dry Cell Batteries

Electronic household instruments, such as remote controls, wristwatches, DVD and MP3 players, torches and radios, are powered by small, highly efficient **dry cell batteries**. They are manufactured in different sizes, named by the A-classification, where AAA and AA are the most common sizes used in remote controls, digital cameras and DVD players. The larger C size is most often used in portable stereos and many electrical toys, whereas size D is the standard battery used in baton-shaped torches.

The ordinary, relatively inexpensive 1.5 V dry cell is the **zinc–manganese dioxide cell**, or **Leclanché cell** (named after its inventor, George Leclanché, 1839-1882). Its outer shell is made of zinc, which serves as the anode (figure 12.31). The exposed outer surface at the bottom of the cell is the negative end of the battery. The cathode consists of a carbon (graphite) rod surrounded by a moist paste of graphite powder, manganese dioxide and ammonium chloride.

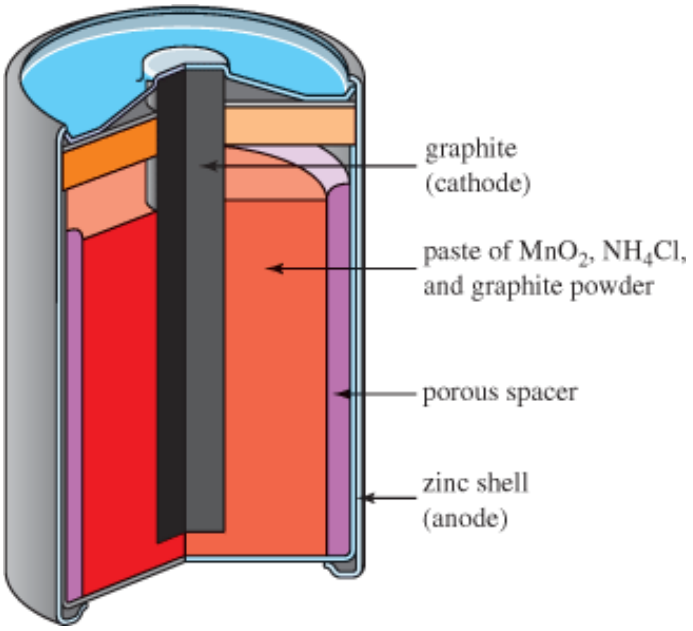


FIGURE 12.31 A cut-away view of a zinc–manganese dioxide dry cell (Leclanché cell).

The anode reaction is simply the oxidation of zinc:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad \text{(anode)}$$

The cathode reaction is complex, and a mixture of products is formed. One of the major reactions is:

$$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l) \quad \text{(cathode)}$$

The ammonia that forms at the cathode reacts with some of the Zn^{2+} produced from the anode to form a complex ion, $Zn(NH_3)_4^{2+}$. Because of the complexity of the cathode half-cell reaction, no simple overall cell reaction can be written.

A more popular version of the Leclanché battery uses a basic, or *alkaline*, electrolyte (generally potassium hydroxide) and is called an **alkaline battery** or **alkaline dry cell**. It, too, uses Zn and MnO_2 as reactants but under basic conditions (figure 12.32). The half-cell reactions are:

$$Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^- \quad \text{(anode)}$$
$$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq) \quad \text{(cathode)}$$

and the voltage is about 1.54 V. The alkaline dry cell has a longer shelf life and can deliver higher currents for longer than the less expensive Leclanché cell shown in figure 12.31. Over time, however, alkaline batteries are prone to corrosion and leaking. The released corrosive potassium hydroxide, which can also emerge from seams around the battery, forms a feathery crystalline structure on the outside of the battery (figure 12.33). The damage can spread further through the metal electrodes to circuit boards leading to oxidation of copper traces and other components, which can result in permanent damage to the circuitry and destruction of the equipment.

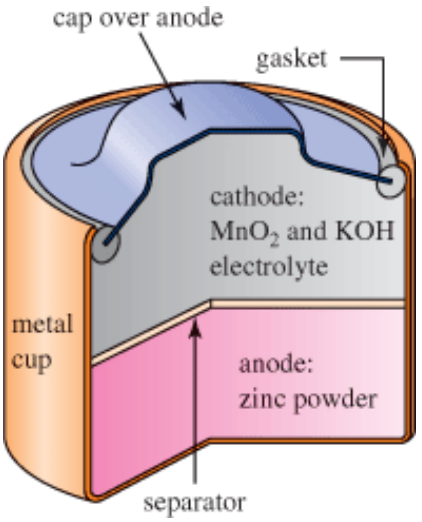


FIGURE 12.32 A simplified diagram of an alkaline zinc–manganese dioxide dry cell.



FIGURE 12.33 Alkaline dry cells are prone to leakage and corrosion.

The **nickel–cadmium storage cell**, or **nicad battery**, (commonly abbreviated to NiCd or nicad) is a secondary cell that produces a potential of about 1.3-1.4 V. The cathode in the NiCd cell is NiO(OH), a compound of nickel in the +3 oxidation state, and the electrolyte is a solution of KOH. The electrode reactions in the cell during discharge are:

$$\begin{aligned}
Cd(s) + 2OH^-(aq) &\rightarrow Cd(OH)_2(s) + 2e^- && \text{(anode)}\\
2NiO(OH)(s) + 2H_2O + 2e^- &\rightarrow 2Ni(OH)_2(s) + 2OH^-(aq) && \text{(cathode)}\\
\hline
Cd(s) + 2NiO(OH)(s) + 2H_2O &\rightarrow 2Ni(OH)_2(s) + Cd(OH)_2(s) \quad E^\circ_{cell} = 1.3 - 1.4V && \text{(cell reaction)}
\end{aligned}$$

The nickel-cadmium battery can be recharged by reversing the anode and cathode reactions above to remake the reactants. The battery can be sealed to prevent leakage, which is particularly important in electronic devices.

Nickel-cadmium batteries work especially well in applications such as portable power tools, DVD players

and even electric cars. They have a high *energy density* (available energy per unit volume), they can release energy quickly, and they can be recharged rapidly.

Modern High-performance Batteries

Nickel–Metal Hydride Battery

Nickel–metal hydride (NiMH) batteries are secondary cells and have been used extensively in recent years to power devices such as mobile phones, video cameras and even electric ve hicles. They are similar in many ways to the alkaline nickel-cadmium cells discussed earlier, except for the anode reactant, which is hydrogen. At first, this seems odd, because hydrogen is a gas at room temperature and atmospheric pressure. However, in the late 1960s, it was discovered that some metal alloys (such as $LaNi_5$, an alloy of lanthanum and nickel, and Mg_2Ni, an alloy of magnesium and nickel) can absorb and hold substantial amounts of hydrogen in its atomic form and that the hydrogen could be made to participate in reversible electrochemical reactions. (*Note:* The term 'metal hydride' has come to be used to describe the hydrogen-holding alloy in which hydrogen is contained in its atomic form. There are compounds of hydrogen with metals such as sodium that actually contain the *hydride ion*, H^-. The metal hydrides described here are not of that type.)

As in the NiCd cell, the cathode in NiMH batteries is NiO(OH) and the electrolyte is a solution of KOH. A diagram of a cylindrical cell is shown in figure 12.34. Using the symbol MH to stand for the metal hydride, the reactions in the cell during discharge are:

$$\begin{aligned} MH(s) + OH^-(aq) &\rightarrow MH(s) + H_2O(l) + e^- && \text{(anode)} \\ NiO(OH)(s) + 2H_2O + e^- &\rightarrow Ni(OH)_2(s) + OH^-(aq) && \text{(cathode)} \\ \hline MH(s) + 2NiO(OH)(s) &\rightarrow Ni(OH)_2(s) + M(s) \qquad E^\ominus_{cell} = 1.35\ V && \text{(cell reaction)} \end{aligned}$$

When the cell is recharged, these reactions are reversed. The principal advantage of the NiMH cell over the NiCd cell is that it can store about 50% more energy in the same volume.

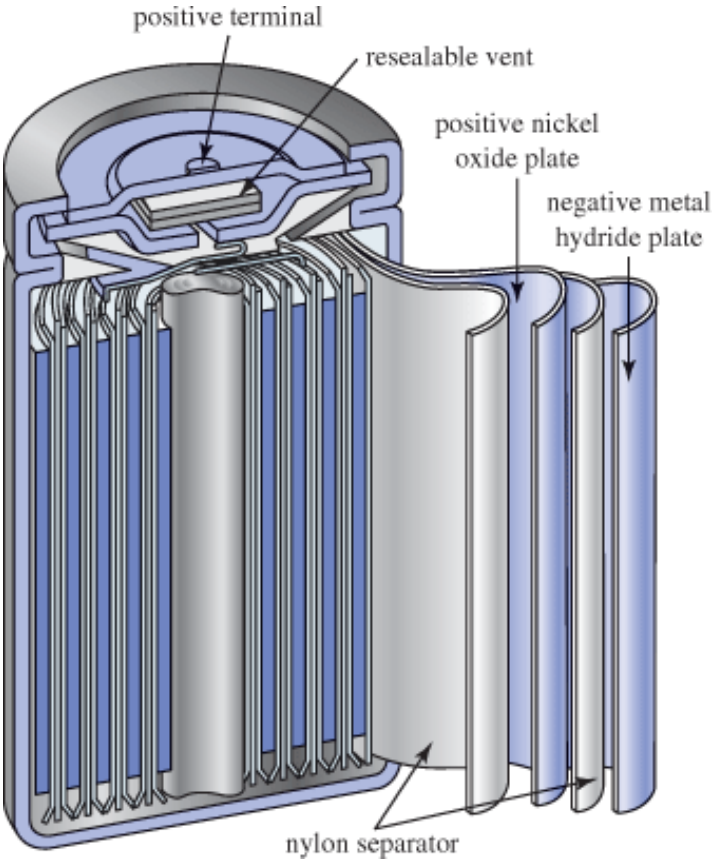


FIGURE 12.34 Cutaway view of a nickel–metal hydride cell. The electrode sandwich is rolled up; this yields a large effective electrode area and enables the cell to deliver large amounts of energy quickly.

Lithium Ion Cells

If you look at the location of lithium in the table of reduction potentials (table 12.1), you will see that it has the most negative reduction potential of any metal. This means that lithium is very easily oxidised electrochemically, and its large negative reduction potential suggests it has a lot of appeal as an anode material. Furthermore, lithium is a very lightweight metal, so a cell employing lithium as a reactant would also be lightweight.

Attempts to make rechargeable lithium batteries containing lithium metal electrodes have been plagued with safety problems. Success came with the development of the **lithium ion cell**, which uses lithium ions rather than metallic lithium. The transport of Li^+ ions through the electrolyte from one electrode to the other is accompanied by the transport of electrons through the external circuit to maintain charge balance. The following paragraphs describe how lithium ions are used in a rechargeable cell.

It was discovered that, because they are small, Li^+ ions can slip between layers of atoms in certain crystalline substances (a process called **intercalation**). Graphite is such a substance. As we saw in chapter 7, graphite consists of layers of fused hexagonal rings of carbon atoms. The other most commonly used compound able to intercalate Li^+ ions is $LiCoO_2$. These are the materials used to make the electrodes.

When the cell is constructed, it is in its 'uncharged' state with no Li^+ ions between the layers of carbon atoms in the graphite. When the cell is being charged (figure 12.35a), Li^+ ions leave $LiCoO_2$(with x being the amount of transferred Li^+) and travel through the electrolyte to the graphite:

$$LiCoO_2 + \text{graphite} \rightarrow Li_{1-x}CoO_2 + Li_x\text{graphite} \quad \text{(initial charging)}$$

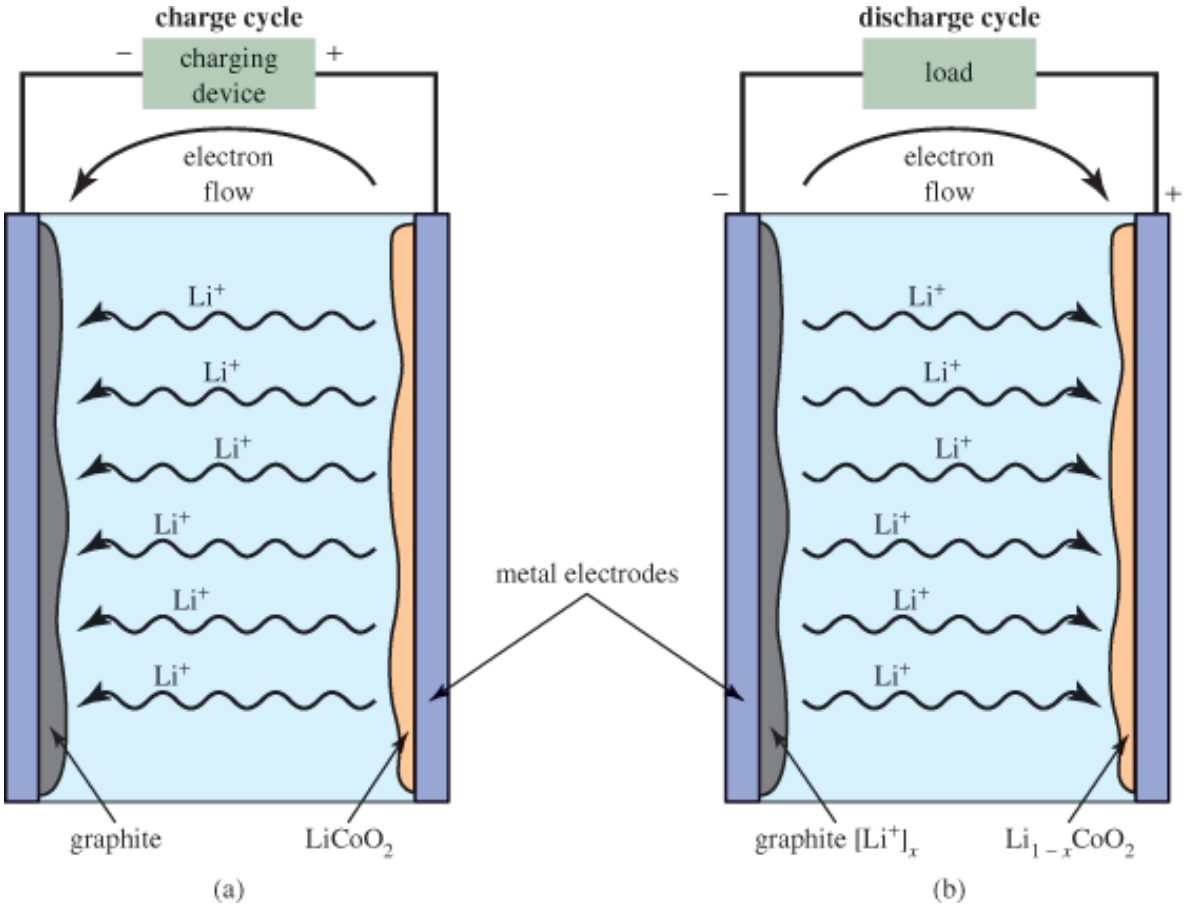


FIGURE 12.35 Lithium ion cell.

(a) During the charging cycle, an external voltage forces electrons through the external circuit and causes lithium ions to travel from the $LiCoO_2$ electrode to the graphite electrode.

(b) During discharge, the lithium ions spontaneously migrate back to the $LiCoO_2$ electrode, and electrons flow through the external circuit to balance the charge.

When the cell spontaneously discharges to provide electrical power (figure 12.35b), Li^+ ions move back through the electrolyte to the cobalt oxide, while electrons move through the external circuit from the graphite electrode (anode) to the cobalt oxide electrode (cathode). If we represent the amount of Li^+ transferring by *y*, the discharge 'reaction' is:

$$Li_{1-x}CoO_2 + Li_x\text{graphite} \rightarrow Li_{1-x+y} + Li_{x-y}\text{graphite} \quad \text{(discharging)}$$

Thus, the charging and discharging cycles simply sweep Li^+ ions back and forth between the two electrodes, with electrons flowing through the external circuit to keep the charge in balance.

Two types of lithium ion cells have been developed. The one most commonly used today in mobile phones and laptop computers employs a liquid electrolyte (usually containing $LiPF_6$, a compound with Li^+ and PF_6^- ions). The cell generates about 3.7 V, which means three NiCd cells connected in series would be required to form an equivalent battery pack. In addition, a lithium ion cell has about twice the energy density of a standard NiCd cell.

Fuel Cells

The galvanic cells discussed so far can produce power only for a limited time because the electrode

reactants are eventually degraded. Fuel cells are different; they are electrochemical cells in which the electrode reactants are supplied continuously and can operate without a theoretical limit as long as the supply of reactants is maintained. This makes fuel cells an attractive source of power where long-term generation of electrical energy is required.

Figure 12.36 illustrates an early design of a hydrogen–oxygen **fuel cell**. The electrolyte, a hot (˜200 °C), concentrated solution of potassium hydroxide in the centre compartment, is in contact with two porous electrodes that contain a catalyst (usually platinum) to facilitate the electrode reactions. Gaseous hydrogen and oxygen under pressure are circulated so as to come in contact with the electrodes. At the cathode, oxygen is reduced:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \quad \text{(cathode)}$$

At the anode, hydrogen is oxidised to water:

$$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^- \quad \text{(anode)}$$

Some of the water formed at the anode leaves as steam mixed with the circulating hydrogen gas. The net cell reaction, after making electron loss equal to electron gain, is:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \text{(cell reaction)}$$

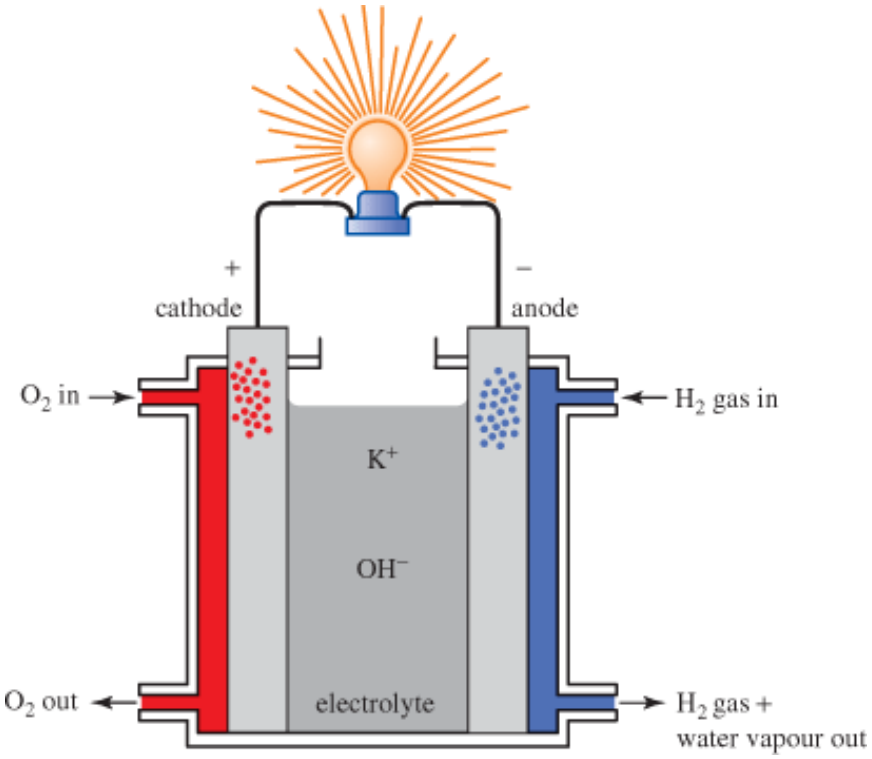


FIGURE 12.36 A hydrogen–oxygen fuel cell.

A major advantage of the fuel cell is that there is no electrode material to be replaced, as there is in an ordinary battery. The fuel can be fed in continuously to produce power. In fact, hydrogen–oxygen fuel cells were used in the Gemini and Apollo missions in the second half of the twentieth century and other space programs for just this reason.

One reason fuel cells are so appealing is their thermodynamic efficiency. In a fuel cell, the net reaction is equivalent to combustion. The production of usable energy by the direct combustion of fuels is an extremely inefficient process. Largely because of the constraints set by fundamental thermodynamic principles, modern electrical power plants are unable to harness more than about 35 to 40% of the potential energy in oil, coal or natural gas. A petrol or diesel engine has an efficiency of only about 25 to 30%. The rest of the energy is lost to the surroundings as heat, which is why a vehicle must have an effective cooling system.

Fuel cells ‘burn’ fuel under conditions that are much more thermodynamically reversible than simple combustion. They therefore achieve much greater efficiencies — 75% is quite feasible. In addition, hydrogen–oxygen fuel cells are essentially pollution free. The only product formed by the cell is water. However, hydrogen fuel is not necessarily produced by pollution-free processes.

Advances in fuel cell development have led to lower operating temperatures and the ability to use methanol, a liquid at room temperature, as a source of hydrogen. The hydrogen is generated from methanol vapour, $CH_3OH(g)$, by a catalytic process. The net reaction is:

$$CH_3OH(g) + H_2O(g) \rightarrow CO_2(g) + 3H_2(g)$$

DaimlerChrysler originally demonstrated the feasibility of such a system by driving its NECAR5 vehicle, powered by five fuel cells, 5000 kilometres across the United States in 16 days. An onboard fuel reformer extracted hydrogen from methanol to feed the fuel cells.

The development of efficient fuel cells is an active research area, especially for the transportation market.

Chemistry Research

Green Electrochemistry

Professor Alan M Bond is known worldwide for his extensive work in the area of electro-chemistry. He is R.L. Martin Distinguished Professor of Chemistry and Head of the Electrochemistry research group at Monash University in Victoria. His major research interest concerns the theory, instrumentation and application of modern electrochemical methods in the area of inorganic and analytical chemistry.

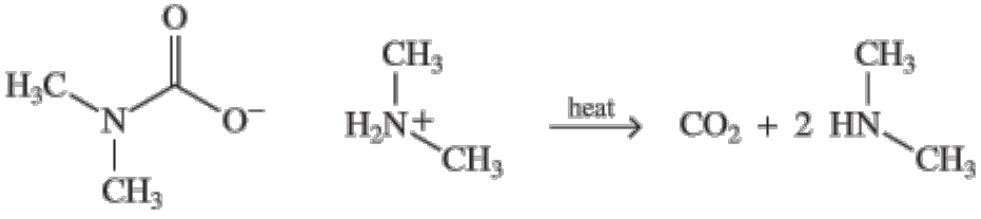
Electrochemistry is the study of the formation and separation of charge in matter, and the ways in which such charge moves in matter. It is central to many industrial processes used in mining and manufacturing, while its everyday importance is evident in the batteries used to power portable devices such as mobile phones and MP3 players. Despite its long history, the science of electrochemistry is still developing as chemists search for new and more powerful devices.

One area in which Professor Bond's group is focusing its research is green chemistry. Green chemistry uses so-called ‘green’ chemicals — ones that do not adversely affect the environment. Ionic liquids (figure 12.37) are increasingly being advocated as green solvents for electrochemical applications in metal deposition, battery electrolytes and electrosynthesis.



FIGURE 12.37 Ionic liquids display interesting miscibility characteristics. In this example, the ionic liquid (bottom layer) mixes with neither water (middle layer) nor an organic solvent (top layer).

Of particular interest are room-temperature ionic liquids because of their negligible vapour pressure, low toxicity, high chemical and thermal stability, high conductivity, significant electro-chemical stability and ability to dissolve a wide range of compounds. However, because of their low vapour pressure, room-temperature ionic liquids are nonvolatile and hence difficult to purify or recover. Professor Bond's group has recently investigated the electrochemical behaviour of the ‘distillable’ room-temperature ionic liquid DIMCARB. This ionic liquid is unusual because it can be readily prepared in large quantities and at low cost by mixing gaseous carbon dioxide, CO_2, with dimethylamine, $(CH_3)_2NH$, and it is easily recovered by decomposition back to its gaseous components.



DIMCARB

The Bond group has shown that this ionic liquid is a useful solvent in a number of unusual electrochemical processes. For example, both Ag^+ and Au^{3+} ions undergo spontaneous reduction in DIMCARB to form different types of nanostructures. Overall, Bond's studies have shown that certain green ionic liquids, such as DIMCARB, may be very suitable for the synthesis of chemicals that involve electrochemical transformations, and they may therefore find use as environmentally friendly replacements for the solvents usually used in these processes.

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SUMMARY

Oxidation and Reduction

Oxidation is the loss of electrons or an increase in oxidation number; reduction is the gain of electrons or a decrease in oxi dation number. Both always occur together in reduction-oxidation (or redox) reactions. The substance oxidised is the reducing agent; the substance reduced is the oxidising agent. Oxidation numbers are a bookkeeping device that we use to follow changes in redox reactions. The term ‘oxidation state’ is equivalent to oxidation number.

Balancing Net Ionic Equations for Redox Reactions

In a balanced redox equation, the number of electrons gained by one substance is always equal to the number lost by another substance. To balance a redox equation, the skeleton net ionic equation is divided into two half-equations, which are balanced separately before being recombined to give the final balanced net ionic equation. For reactions in basic solution, the equation is first balanced as if it occurred in an acidic solution, and then the balanced equation is converted to its proper form for a basic solution by adding an appropriate number of OH^- ions.

Galvanic Cells

A galvanic cell is composed of two half-cells, each containing an electrode in contact with an electrolyte reactant. A spontaneous redox reaction is thus divided into separate oxidation and reduction half-reactions, with the electron transfer occurring through an external electric circuit. Reduction occurs at the cathode; oxidation occurs at the anode. In a galvanic cell, the cathode is positively charged and the anode is negatively charged. The half-cells are usually connected by a salt bridge to complete the electric circuit; this permits electrical neutrality to be maintained by allowing cations to move towards the cathode and anions towards the anode.

Reduction Potentials

The potential (expressed in volts) produced by a cell is equal to the standard cell potential when all ion concentrations are 1 M and the partial pressure of any gas involved equals 1×10^5 Pa. The cell potential can be considered to be the difference between the reduction potentials of the half-cells. In the spontaneous reaction, the half-cell with the more positive reduction potential undergoes reduction and forces the other to undergo oxidation. The reduction potentials of isolated half-cells cannot be measured, but values are assigned by choosing the standard hydrogen electrode as a reference electrode; its reduction potential is assigned a value of exactly 0 V. Species more easily reduced than H^+ have positive reduction potentials; those less easily reduced have negative reduction potentials. Reduction potentials can be used to predict the cell reaction and to calculate $E^\ominus_{cell}$, as well as to predict whether a given reaction is spontaneous.

In solutions containing nonoxidising acids, the strongest oxidising agent is H^+. The reaction of a metal with a nonoxidising acid gives hydrogen gas and a salt of the acid. Only metals with more negative reduction potentials than hydrogen react this way. Oxidising acids, such as concentrated HNO_3 or concentrated H_2SO_4, contain an anion that is a stronger oxidising agent than H^+, and they can oxidise many metals that nonoxidising acids cannot.

Relationship Between Cell Potential, Concentration and Gibbs Energy

The values of $\Delta G^\ominus$ and K_c for a reaction can be calculated from $E^\ominus_{cell}$. They all involve the Faraday constant, F, which equals the number of coulombs (C) of charge per mole of electrons (1 F = 96 485 C

mol^{-1}). The Nernst equation relates the cell potential to the standard cell potential and the reaction quotient. It allows the cell potential to be calculated for ion concentrations other than 1 M.

Corrosion

Metals corrode because they oxidise easily. The corrosion of iron (formation of rust) is an electrochemical reaction that involves both oxygen and water. Some metals form insoluble oxides, which prevent them from further oxidation (passivation). Corrosion can be combatted by processes such as galvanisation and cathodic protection.

Electrolysis

In an electrolytic cell, a flow of electricity causes an otherwise nonspontaneous reaction to occur. A negatively charged cathode causes reduction of one reactant and a positively charged anode causes oxidation of another. The electrode reactions are determined by which species is most easily reduced and which is most easily oxidised; however, in aqueous solutions, complex surface effects at the electrodes can alter the natural order. In the electrolysis of water, an electrolyte must be present to maintain electrical neutrality at the electrodes. The Faraday constant, *F*, is equal to the charge carried by 1 mol of electrons, 96 485 C. The product of current (amperes) and time (seconds) gives coulombs. These relationships and the half-reactions that occur at the anode or cathode allow us to relate the amount of chemical change to measurements of current and time.

Batteries

The lead storage battery and the nickel-cadmium (nicad) battery are secondary cells and are rechargeable. The state of charge of a lead storage battery can be tested with a hydrometer, which measures the density of the sulfuric acid electrolyte. The zinc–manganese dioxide cell (the Leclanché cell or common dry cell) and the common alkaline battery (which uses essentially the same reactions as the less expensive dry cell) are primary cells and are not rechargeable. The rechargeable nickel–metal hydride battery (NiMH) uses hydrogen contained in a metal alloy as its anode reactant and has a higher energy density than the nicad battery. The rechargeable lithium ion cell produces a large cell potential and has a very large energy density. Lithium ion cells store and release energy by transferring lithium ions between electrodes where the Li^+ ions are intercalated between layers of atoms in the electrode materials. Fuel cells, which have high thermodynamic efficiencies, can provide continuous power because they consume fuel that can be fed continuously.

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KEY CONCEPTS AND EQUATIONS

Rules for assigning oxidation numbers *(section 12.1)*

Use these rules to assign oxidation numbers to the atoms in a chemical formula. Use changes in oxidation numbers to identify oxidation and reduction.

1. The oxidation number of any free element (an element not combined chemically with a different element) is 0. For example, Ar, Fe, O in O_2, P in P_4 and S in S_8 all have oxidation numbers of 0.
2. The oxidation number of any simple, monatomic ion (e.g. Na^+ and Cl^-) is equal to the charge on the ion.
3. The sum of all the oxidation numbers of the atoms in a neutral molecule must equal 0. The sum of all the oxidation numbers in a polyatomic ion must equal the charge on the ion.
4. In all of its compounds, fluorine has an oxidation number of -1.
5. In most of its compounds, hydrogen has an oxidation number of +1.
6. In most of its compounds, oxygen has an oxidation number of -2.

Balancing redox equations *(section 12.2)*

The following steps are used to balance an equation for a redox reaction in an acidic solution.

1. Identify reactants and products for each half-equation.
2. Balance atoms other than H and O.
3. Balance oxygen by adding H_2O.
4. Balance hydrogen by adding H^+.
5. Balance net charge by adding e^-.
6. Make e^- gain equal e^- loss.
7. Add the balanced half-equations.
8. Cancel any species that is the same on both sides.
9. Check that there are the same number and type of atoms and the same charge on each side of the reaction.

The following additional steps are used to balance an equation for a redox reaction in a basic solution.

10. Take note of the number of H^+ in the balanced equation and add the same number of OH^- to *each* side.
11. Combine each pair of H^+ and OH^- to form one H_2O.
12. Cancel any H_2O that occur on both sides.
13. Check that there are the same number and type of atoms and the same charge on each side of the reaction.

Standard reduction potentials *(section 12.4)*

In a galvanic cell, the difference between two standard reduction potentials equals the standard cell potential. Comparing reduction potentials lets us predict the electrode reactions in electrolysis.

Standard cell potentials *(section 12.4)*

By calculating E°_{cell}, we can predict the spontaneity of a redox reaction. We can use E°_{cell} to calculate ΔG° and equilibrium constants. They are also needed in the Nernst equation to relate concentrations of species in galvanic cells to the cell potential.

$\Delta G^{\ominus} = -zFE^{\ominus}_{cell}$ *(section 12.5)*

This equation is used to calculate standard Gibbs energy changes from standard cell potentials, and vice versa.

$E^{\ominus}_{cell} = \frac{RT}{zF}\ln K_c$ *(section 12.5)*

This equation is used to calculate equilibrium constants from standard cell potentials.

Nernst equation $E_{cell} = E^{\ominus}_{cell} = \frac{RT}{zF}\ln Q$ *(section 12.5)*

This equation is used to calculate the cell potential from $E^{\ominus}_{cell}$ and concentration data; we can also calculate the concentration of a species in solution from $E^{\ominus}_{cell}$ and a measured value of $E^{\ominus}_{cell}$.

Faraday constant, F = 96 485 C mol^{-1} *(section 12.5)*

Besides being a constant in the equations above, the Faraday constant relates coulombs (obtained from the product of current and time) to moles of chemical change in electrochemical reactions.

Faraday's law *(section 12.7)*

$$\text{amount of product} = \frac{It}{zF}$$

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REVIEW QUESTIONS

Oxidation and Reduction

12.1 Define ‘oxidation’ and ‘reduction’ in terms of (a) electron transfer and (b) oxidation numbers.

12.2 In the reaction $2Mg + O_2 \rightarrow 2MgO$, which substance is the oxidising agent and which is the reducing agent? Which substance is oxidised and which is reduced?

12.3 Why must both oxidation and reduction occur simultaneously during a redox reaction? What is an oxidising agent? What happens to it in a redox reaction? What is a reducing agent? What happens to it in a redox reaction?

12.4 Are the following reactions redox reactions? Explain.

(a) $2NO_2 \rightarrow N_2O_4$

(b) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

12.5 If the oxidation number of phosphorus in a certain molecule changes from +3 to -2 during a reaction, is phosphorus oxidised or reduced? How many electrons are gained (or lost) by each phosphorus atom?

12.6 Bromine gas is used to make fire-retardant chemicals used on children's pyjamas. However, to dispose of excess bromine, it is passed through a solution of sodium hydroxide. The products are NaBr and NaOBr. What is being reduced and what is being oxidised? Write a balanced equation for the reaction.

Balancing Net Ionic Equations for Redox Reactions

12.7 The following equations are not balanced. Why? Balance them.

(a) $Ag + Fe^{2+} \rightarrow Ag^+ + Fe$

(b) $Cr^{3+} + Zn \rightarrow Cr + Zn^{2+}$

(c) $Ag + Au^{3+} \rightarrow Ag^+ + Au$

(d) $Ca + Al^{3+} \rightarrow Ca^{2+} + Al$

12.8 What are the net charges on the left and right sides of the following equations? Add electrons as necessary to make each of them a balanced half-reaction.

(a) $NO_3^- + 10H^+ \rightarrow NH_4^+ + 3H_2O$

(b) $Cl_2 + 4H_2O \rightarrow 2ClO_2^- + 8H^+$

12.9 In question 12.8, which half-reaction represents oxidation? Which represents reduction?

12.10 At first glance, the following equation may appear to be balanced:

$$MnO_4^- + Sn^{2+} \rightarrow SnO_2 + MnO_2$$

What is wrong with it?

Galvanic Cells

12.11 What is a galvanic cell? What is a half-cell?

12.12 What is the function of a salt bridge?

12.13 In the copper–silver cell, why must the Cu^{2+} and Ag^+ solutions be kept in separate containers?

12.14 Which redox processes take place at the anode and cathode in a galvanic cell? What electric charges do the anode and cathode carry in a galvanic cell?

12.15 How do electrolytic conduction and metallic conduction differ?

12.16 Why is the movement of the ions relative to the electrodes the same in both galvanic and

electrolytic cells? Explain.

12.17 When magnesium metal is placed into a solution of copper sulfate, the magnesium dissolves to give Mg^{2+}, and copper metal is formed. Write a net ionic equation for this reaction. Describe how you could use the reaction in a galvanic cell. Which metal, copper or magnesium, is the cathode?

12.18 Aluminium will displace tin from solution according to the equation:

$$2Al(s) + 3Sn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Sn(s)$$

What would be the individual half-cell reactions if this were the cell reaction in a galvanic cell? Which metal would be the anode and which the cathode?

12.19 Sketch a galvanic cell for which the cell diagram is:

$$Sn(s)|Sn^{2+}(aq)||Al^{+}(aq)|Ag(s)$$

(a) Label the anode and the cathode.

(b) Indicate the charge on each electrode.

(c) Indicate the direction of electron flow in the external circuit.

(d) Write the equation for the net cell reaction.

12.20 Sketch a galvanic cell in which inert platinum electrodes are used in the half-cells for the system:

$$Pt(s)|Fe^{2+}(aq), Fe^{3+}(aq)||Br_2(aq), Br^{-}(aq)|Pt(s)$$

Label the diagram to indicate the composition of the electrolytes in the two cell compartments. Show the signs of the electrodes and label the anode and cathode. Write the equation for the net cell reaction.

Reduction Potentials

12.21 For a galvanic cell, what is the meaning of the term 'potential'? What are its units?

12.22 What is the difference between a cell potential and a standard cell potential?

12.23 How are standard reduction potentials combined to give the standard cell potential for a spontaneous reaction?

12.24 What ratio of units gives volts? What are the units of amperes × volts × seconds?

12.25 Is it possible to measure the potential of an isolated half-cell? Explain your answer.

12.26 Describe the hydrogen electrode. What is the value of its standard reduction potential?

12.27 What do the positive and negative signs of reduction potentials tell us?

12.28 If $E^{\ominus}_{Ag^{+}/Ag}$ had been chosen as the standard reference electrode and had been assigned a potential of 0 V, what would the reduction potential of the hydrogen electrode be relative to it?

12.29 If you set up a galvanic cell using metals not found in table 12.1, what experimental information will tell you which is the anode and which is the cathode in the cell?

12.30 What is a nonoxidising acid? Give two examples. What is the oxidising agent in a nonoxidising acid?

12.31 What is the strongest oxidising agent in a dilute aqueous solution of sulfuric acid?

12.32 If a metal can react with a solution of HCl, is its reduction potential more negative or more positive than hydrogen?

12.33 Where in table 12.1 do we find the best reducing agents? Where do we find the best oxidising agents?

12.34 Which metals in table 12.1 will react with water? Write chemical equations for each of these reactions.

Relationship Between Cell Potential, Concentration and Gibbs Energy

12.35 Write the equation that relates the standard cell potential to the standard Gibbs energy change for a reaction.

12.36 What is the equation that relates the equilibrium constant to the standard cell potential?

12.37 Show how the equation that relates the equilibrium constant to the standard cell potential can be derived from the Nernst equation.

12.38 You have learned that the principles of thermodynamics allow the following equation to be derived:

$$\Delta G = \Delta G^{\ominus} + RT\ln Q$$

where Q is the reaction quotient. Without referring to the text, use this equation and the relationship between ΔG and the cell potential to derive the Nernst equation.

12.39 The cell reaction during the discharge of a lead storage battery is:

$$Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

The standard cell potential is 2.05 V. What is the correct form of the Nernst equation for this reaction at 25 °C?

Corrosion

12.40 Explain the chemical processes involved in the rusting of iron.

12.41 Explain how galvanisation works.

12.42 Define ‘passivation’.

12.43 What is cathodic protection?

Electrolysis

12.44 What electric charges do the anode and the cathode carry in an electrolytic cell? What does the term ‘inert electrode’ mean?

12.45 In a galvanic cell, do electrons travel from anode to cathode, or from cathode to anode? Explain.

12.46 Why must NaCl be melted before it is electrolysed to give Na and Cl_2? Write the anode, cathode and overall cell reactions for the electrolysis of molten NaCl.

12.47 Write half-reactions for the oxidation and the reduction of water.

12.48 What happens to the pH of the aqueous solution near the cathode and anode during the electrolysis of K_2SO_4? What function does K_2SO_4 serve in the electrolysis of a K_2SO_4 solution?

12.49 What is described by the Faraday constant, F? What relationships relate F to current and time measurements?

12.50 Using the same current, which will require more time: depositing 0.10 mol Cu from a Cu^{2+} solution or depositing 0.10 mol of Au from a Au^{3+} solution? Explain your reasoning.

12.51 An electric current is passed through two electrolysis cells connected in series (so the same amount of current passes through each of them). One cell contains Cu^{2+} and the other contains Fe^{2+}. In which cell will the greater mass of metal be deposited? Explain your answer.

Batteries

12.52 What are the anode and cathode reactions during discharge of a lead storage battery? How can a battery produce a potential of 12 V if the cell reaction has a standard potential of only 2 V?

12.53 What is a symproportionation reaction?

12.54 What are the anode and cathode reactions during the charging of a lead storage battery?

12.55 What reactions occur at the electrodes in the ordinary dry cell?

12.56 What chemical reactions take place at the electrodes in an alkaline dry cell?

12.57 Give the half-cell reactions and the cell reaction that take place in a nicad battery during discharge. What are the reactions that take place during charging of the cell?

12.58 How is hydrogen held as a reactant in a nickel–metal hydride battery? Write the chemical formula for a typical alloy used in this battery. What is the electrolyte?

12.59 What are the anode, cathode and net cell reactions that take place in a nickel–metal hydride battery during discharge? What are the reactions while the battery is being charged?

12.60 What are the electrode materials in a typical lithium ion cell? Explain what happens when the cell is charged. Explain what happens when the cell is discharged.

12.61 Write the cathode, anode and net cell reaction in a hydrogen–oxygen fuel cell.

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12.62 For the following reactions, identify the substance oxidised, the substance reduced, the oxidising agent and the reducing agent.

(a) $2HNO_3 + 3H_3AsO_3 \rightarrow 2NO + 3H_3AsO_4 + H_2O$

(b) $NaI + 3HOCl \rightarrow NaIO_3 + 3HCl$

(c) $2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$

(d) $6H_2SO_4 + 2Al \rightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$

(e) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

(f) $3SO_2 + 2HNO_3 + 2H_2O \rightarrow 3H_2SO_4 + 2NO$

(g) $5H_2SO_4 + 4Zn \rightarrow 4ZnSO_4 + H_2S + 4H_2O$

(h) $I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(i) $HCl + NaCl + 2NaClO_4 \rightarrow 2ClO_2 + 2NaCl + NaOH$

12.63 Assign oxidation numbers to the atoms indicated by boldface type.

(a) $\mathbf{S}^{2-}$

(b) $\mathbf{S}O_2$

(c) $\mathbf{P}_4$

(d) $\mathbf{P}H_3$

(e) $\mathbf{Cl}O_4^-$

(f) $\mathbf{Cr}Cl_3$

(g) $\mathbf{Sn}S_2$

(h) $\mathbf{Au}(NO_3)_3$

(i) $\mathbf{C}O_2$

12.64 Assign oxidation numbers to all of the atoms in the following compounds and ions:

(a) Na_2HPO_4

(b) MnO_4

(c) $Na_2S_4O_6$

(d) ClF_3

(e) OCl^-

(f) ClO_2^-

(g) ClO_3^-

(h) ClO_4^-

(i) $Ca(VO_3)_2$

(j) $SnCl_4$

(k) MnO_4^{2-}

(l) MnO_2

(m) PbS

(n) $TiCl_4$

(o) $Sr(IO_3)_2$

(p) Cr_2S_3

(q) F_2O

(r) HOF

(s) ClO_2

(t) F_2O_2

(u) $Bi(NO_3)_3$

12.65 Assign oxidation numbers to nitrogen in the following.

(a) NO

(b) N_2O_5

(c) NH_2OH

(d) NO_2

(e) N_2H_4

(f) NH_3

(g) N_2O_3

(h) N_2

(i) NaN_3

(j) HNO_2

(k) N_2H_2

12.66 When chlorine is added to drinking water to kill bacteria, some of the chlorine is converted to chloride ions by the following equilibrium:

$$Cl_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq)$$

In the forward reaction (the reaction going from left to right), which substance is oxidised and which is reduced? In the reverse reaction, which is the oxidising agent and which is the reducing agent?

12.67 Nitrogen dioxide, NO_2, is a pollutant in smog. The gas has a reddish-brown colour and is responsible for the red-brown colour associated with this type of air pollution. Nitrogen dioxide is also a contributor to acid rain because, when rain passes through air contaminated with NO_2, it dissolves and undergoes the following reaction:

$$3NO_2(g) + H_2O(l) \rightarrow NO(g) + 2H^+(aq) + 2NO_3^-(aq)$$

In this reaction, which element is reduced and which is oxidised?

12.68 Chlorine dioxide, ClO_2, is used to kill bacteria in the dairy, meat and other food and beverage industries. It is unstable, but can be made by the following reaction:

$$Cl_2 + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl$$

Identify the substances oxidised and reduced as well as the oxidising and reducing agents in the reaction.

12.69 Balance the following half-equations occurring in an acidic solution. Indicate whether each is an oxidation or a reduction.

(a) $BiO_3^- \rightarrow Bi^{3+}$

(b) $Pb^{2+} \rightarrow PbO_2$

(c) $NO_3^- \rightarrow NH_4^+$

(d) $Cl_2 \rightarrow ClO_3^-$

12.70 In each of the following reactions, indicate the element that has been oxidised and the element that has been reduced. Label the oxidation state of each before and after the reaction.

(a) $2Na + FeCl_2 \rightarrow 2NaCl + Fe$

(b) $2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$

(c) $2PbS + 3O_2 \rightarrow 2SO_2 + 2PbO$

(d) $H_2 + Cl_2 \rightarrow 2HCl$

(e) $Zn + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2$

(f) $2AgNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2Ag$

12.71 Balance the following half-equations occurring in a basic solution. Indicate whether each is an oxidation or a reduction.

(a) $Fe \rightarrow Fe(OH)_2$

(b) $SO_2Cl_2 \rightarrow SO_3^{2-} + Cl^-$

(c) $Mn(OH)_2 \rightarrow MnO_4^{2-}$

(d) $H_4IO_6^- \rightarrow I_2$

12.72 Balance the following equations for reactions occurring in an acidic aqueous solution.

(a) $S_2O_3^{2-} + OCl^- \rightarrow Cl^- + S_4O_6^{2-}$

(b) $NO_3^- + Cu \rightarrow NO_2 + Cu^{2+}$

(c) $IO_3^- + AsO_3^{3-} \rightarrow I^- + AsO_4^{3-}$

(d) $SO_4^{2-} + Zn \rightarrow Zn^{2+} + SO_2$

(e) $NO_3^- + Zn \rightarrow NH_4^+ + Zn^{2+}$

(f) $Cr^{3+} + BiO_3^- \rightarrow Cr_2O_7^{2-} + Bi^{3+}$

(g) $I_2 + OCl^- \rightarrow IO_3^- + Cl^-$

(h) $Mn^{2+} + BiO_3^- \rightarrow MnO_4^- + Bi^{3+}$

(i) $H_3AsO_3 + Cr_2O_7^{2-} \rightarrow H_3AsO_4 + Cr^{3+}$

(j) $I^- + HSO_4^- \rightarrow I_2 + SO_2$

(k) $Sn + NO_3^- \rightarrow SnO_2 + NO$

(l) $PbO_2 + Cl^- \rightarrow PbCl_2 + Cl_2$

(m) $Ag + NO_3^- \rightarrow NO_2 + Ag^+$

(n) $Fe^{3+} + NH_3OH^+ \rightarrow Fe^{2+} + N_2O$

(o) $HNO_2 + I^- \rightarrow I_2 + NO$

(p) $C_2O_4^{2-} + HNO_2 \rightarrow CO_2 + NO$

(q) $HNO_2 + MnO_4^- \rightarrow Mn^{2+} + NO_3^-$

(r) $H_3PO_2 + Cr_2O_7^{2-} \rightarrow H_3PO_4 + Cr^{3+}$

(s) $VO_2^+ + Sn^{2+} \rightarrow VO^{2+} + Sn^{4+}$

(t) $XeF_2 + Cl^- \rightarrow Xe + F^- + Cl_2$

(u) $OCl^- + S_2O_3^{2-} \rightarrow Cl^- + SO_4^{2-}$

12.73 Balance equations for the following reactions occurring in a basic aqueous solution:

(a) $CrO_4^{2-} + S^{2-} \rightarrow S + CrO_2^-$

(b) $MnO_4^- + C_2O_4^{2-} \rightarrow CO_2 + MnO_2$

(c) $ClO_3^- + N_2H_4 \rightarrow NO + Cl^-$

(d) $NiO_2 + Mn(OH)_2 \rightarrow Mn_2O_3 + Ni(OH)_2$

(e) $SO_3^{2-} + MnO_4^- \rightarrow SO_4^{2-} + MnO_2$

(f) $CrO_2^- + S_2O_8^{2-} \rightarrow CrO_4^{2-} + SO_4^{2-}$

(g) $SO_3^{2-} + CrO_4^{2-} \rightarrow SO_4^{2-} + CrO_2$

(h) $O_2 + N_2H_4 \rightarrow H_2O_2 + N_2$

(i) $Fe(OH)_2 + O_2 \rightarrow Fe(OH)_3 + OH^-$

(j) $Au + CN^- + O_2 \rightarrow [Au(CN)_4]^- + OH^-$

12.74 Ozone, O_3, is a very powerful oxidising agent, and can be used to treat water to kill bacteria and make it safe to drink. One of the problems with this method of purifying water is that any bromide ions (Br^-) in the water are oxidised to bromate ions, BrO_3^-, which have shown evidence of causing cancer in test animals. Assuming that ozone is reduced to water, write a balanced chemical equation for the reaction. (Assume an acidic solution.)

12.75 On the basis of the discussions in this chapter, suggest chemical equations for the oxidation of metallic silver to Ag^+ ions with (a) dilute HNO_3 and (b)concentrated HNO_3.

12.76 When hot and concentrated, sulfuric acid is a fairly strong oxidising agent. Write a balanced chemical equation for the oxidation of metallic copper to copper(II) ion by hot, concentrated H_2SO_4, in which the sulfur is reduced to SO_2.

12.77 Use table 12.1 to predict the outcome of the following reactions in aqueous solution. If no reaction occurs, write NR. If a reaction occurs, write a balanced chemical equation for it.

(a) $Fe + Mg^{2+} \rightarrow$

(b) $Cr + Pb^{2+} \rightarrow$

(c) $Ag^+ + Fe \rightarrow$

(d) $Ag + Au^{3+} \rightarrow$

(e) $Mn + Fe^{2+} \rightarrow$

(f) $Cd + Zn^{2+} \rightarrow$

(g) $Mg + Co^{2+} \rightarrow$

(h) $Cr + Sn^{2+} \rightarrow$

(i) $Zn + Sn^{2+} \rightarrow$

(j) $Cr + H^+ \rightarrow$

(k) $Pb + Cd^{2+} \rightarrow$

(l) $Mn + Pb^{2+} \rightarrow$

(m) $Zn + Co^{2+} \rightarrow$

(n) $Cu^{2+} + Au \rightarrow$

12.78 The following reactions occur spontaneously:

$$Pu + 3Tl^+ \rightarrow Pu^{3+} + 3Tl$$
$$Ru + Pt^{2+} \rightarrow Ru^{2+} + Pt$$
$$2Tl + Ru^{2+} \rightarrow 2Tl^+ + Ru$$

List the metals Pu, Pt and Tl in order of increasing ease of oxidation.

12.79 The following reactions occur spontaneously:

$$2Ga + 3Ni^{2+} \rightarrow 3Ni + 2Ga^{3+}$$
$$3Be^{2+} + 2Pu \rightarrow 2Pu^{3+} + 3Be$$
$$2Ga^{3+} + 3Be \rightarrow 2Ga + 3Be^{2+}$$

List the metals Be, Ga and Pu in order of increasing ease of oxidation.

12.80 It is found that the following reaction occurs spontaneously:

$$Ru^{2+}(aq) + Cd(s) \rightarrow Ru(s) + Cd^{2}(aq)$$

What reaction will occur if a mixture is prepared containing Cd(s), $Cd(NO_3)_2(aq)$, Pt(s) and $PtCl_2(aq)$? (Refer to the information in question 12.78.)

12.81 Write the half-equations and the balanced cell reaction for each of the following galvanic cells.

(a) $Cd(s)|\ Cd^{2+}(aq)||Au^{3+}(aq)|\ Au(s)$

(b) $Pb(s),\ PbSO_4(s)|\ HSO_4^-(aq)||H^+(aq),\ HSO_4^-(aq)|PbO_2(s),\ PbSO_4(s)$

(c) $Cr(s)|\ Cr^{3+}(aq)||\ Cu^{2+}(aq)|Cu(s)$

(d) $Zn(s)|\ Zn^{2+}(aq)||Cr^{3+}(aq)|\ Cr(s)$

(e) $Fe(s)|\ Fe^{2+}(aq)||\ Br_2(aq),\ Br^-(aq)|\ Pt(s)$

(f) $Mg(s)|\ Mg^{2+}(aq)||Sn^{2+}(aq)|\ Sn(s)$

12.82 Write the cell diagrams for the following galvanic cells. For half-reactions in which all the reactants are in solution or are gases, assume the use of inert platinum electrodes.

(a) $Cd^{2+}(aq) + Fe(s) \rightarrow Cd(s) + Fe^{2+}(aq)$

(b) $Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$

(c) $Au^{3+}(aq) + 3Ag(s) \rightarrow Au(s) + 3Ag^+(aq)$

(d) $NO_3^-(aq) + 4H^+(aq) + 3Fe^{2+}(aq) \rightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O(l)$

(e) $NiO_2(s) + 4H^+(aq) + 2Ag(s) \rightarrow Ni^{2+}(aq) + 2H_2O(l) + 2Ag^+(aq)$

(f) $Mg(s) + Cd^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cd(s)$

12.83 Use the data in table 12.1 to calculate the standard cell potential for each of the following reactions at 25 °C.

(a) $Cd^{2+}(aq) + Fe(s) \rightarrow Cd(s) + Fe^{2+}(aq)$

(b) $Br_2(aq) + 2Cl^-(aq) \rightarrow Cl_2(g) + 2Br^-(aq)$

(c) $Au^{3+}(aq) + 3Ag(s) \rightarrow Au(s) + 3Ag^+(aq)$

(d) $NO_3^-(aq) + 4H^+(aq) + 3Fe^{2+}(aq) \rightarrow 3Fe^{3+}(aq) + NO(g) + 2H_2O(l)$

(e) $NiO_2(s) + 4H^+(aq) + 2Ag(s) \rightarrow Ni^{2+}(aq) + 2H_2O(l) + 2Ag^+(aq)$

(f) $Mg(s) + Cd^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cd(s)$

(g) $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

(h) $2Ag^+(aq) + Fe(s) \rightarrow 2Ag(s) + Fe^{2+}(aq)$

12.84 Use the data in table 12.1 to determine which of the following reactions should occur spontaneously under standard conditions in aqueous solution at 25 °C.

(a) $2Au^{3+} + 6I^- \rightarrow 3I_2 + 2Au$

(b) $3Fe^{2+} + 2NO + 4H_2O \rightarrow 3Fe + 2NO_3^- + 8H^+$

(c) $3Ca + 2Cr^{3+} \rightarrow 2Cr + 3Ca^{2+}$

(d) $Br_2 + 2Cl^- \rightarrow Cl_2 + 2Br^-$

(e) $Ni^{2+} + Fe \rightarrow Fe^{2+} + Ni$

(f) $H_2SO_3 + H_2O + Br_2 \rightarrow 4H^+ + SO_4^{2-} + 2Br^-$

(g) $SO_4^{2-} + 4H^+ 2I^- \rightarrow H_2SO_3 + I_2 + H_2O$

12.85 Write cell diagrams using the following pairs of half-reactions. For half-reactions in which all the reactants are in solution, assume the use of inert platinum electrodes. Calculate their standard cell potentials. For each pair, identify the anode and cathode.

(a) $Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$

$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$

(b) $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$

$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s)$

(c) $Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$

$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$

(d) $BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightleftharpoons Br^-(aq) + 3H_2O(l)$

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

(e) $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$

(f) $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$

12.86 From the half-equations below, determine the cell reaction and standard cell potential.

(a)

$$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O \qquad E^\ominus_{BrO_3^-/Br^-} = +1.44\,V$$
$$I_2 + 2e^- \rightleftharpoons 2I^- \qquad E^\ominus_{I_2/I^-} = +0.54\,V$$

(b)
$$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O \qquad E^\ominus_{MnO_2/Mn^{2+}} = +1.23\,V$$
$$PbCl_2 + 2e^- \rightleftharpoons Pb + 2Cl^- \qquad E^\ominus_{PbCl_2/Pb} = -0.27\,V$$

12.87 Determine the spontaneous reaction between H_2SO_3, $S_2O_3^{2-}$, HOCl and Cl_2. The half-equations involved are:

$$2H_2SO_3 + 2H^+ + 4e^- \rightleftharpoons S_2O_3^{2-} + 3H_2O \qquad E^\ominus_{H_2SO_3/S_2O_3} = +0.40\,V$$
$$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O \qquad E^\ominus_{HOCl/Cl_2} = +1.63\,V$$

12.88 Determine the spontaneous reaction between Br_2, I_2, Br^- and I^- at 25 °C. Use the data in table 12.1.

12.89 Calculate $\Delta G^\ominus$ for the reaction:

$$2MnO_4^- + 6H^+ + 5HCOOH \rightarrow 2Mn^{2+} + 8H_2O + 5CO_2$$

for which $E^\ominus_{cell} = +1.69\,V$.

12.90 Given the following half-equations and their standard reduction potentials:

$$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O \qquad E^\ominus_{ClO_3^-/Cl_2} = +1.47\,V$$
$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-} \qquad E^\ominus_{S_2O_8^{2-}/SO_4^{2-}} = +2.01\,V$$

calculate (a) $E^\ominus_{cell}$, (b) $\Delta G^\ominus$ for the cell reaction and (c) K_c for the cell reaction.

12.91 Calculate K_c for the following reactions, using the data in table 12.1. Assume T = 298 K.

(a) $Ni^{2+} + Co \rightleftharpoons Ni + Co^{2+}$

(b) $2H_2O + 2Cl_2 \rightleftharpoons 4H^+ + 4Cl^- + O_2$

12.92 The system $2AgI + Sn \rightleftharpoons Sn^{2+} + 2Ag + 2I^-$ has a calculated $E^\ominus_{cell} = -0.015\,V$. What is the value of K_c for this system?

12.93 The cell reaction:

$$NiO_2(s) + 4H^+(aq) + Ag(s) \rightarrow Ni^{2+}(aq) + 2H_2O(l) + 2Ag^+(aq)$$

has $E^\ominus_{cell} = -+2.48\,V$. What will the cell potential be at a pH of 5.00 when the concentrations of Ni^{2+} and Ag^+ are each 0.010 M?

12.94 $E^\ominus_{cell} = -+1.35\,V$ for the reaction:

$$3I_2(s) + 5Cr_2O_7^{2-}(aq) + 34H^+(aq) \rightarrow 6IO_3^-(aq) + 10Cr^{3+}(aq) + 17H_2O(1)$$

What is E_{cell}, if $[Cr_2O_7^{2-}]$ = 0.010 M, $[H^+]$ = 0.10 M, $[IO_3^-]$ = 0.000 10 M and $[Cr^{3+}]$ = 0.0010 M?

12.95 A cell having the following cell-reaction was set up:

$$Mg(s) + Cd^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cd(s) \quad E^{\ominus}_{cell} = +1.97\,V$$

The magnesium electrode was dipped into a 1.00 M solution of $MgSO_4$ and the cadmium electrode was dipped into a solution of unknown Cd^{2+} concentration. The potential of the cell was measured to be +1.54 V. What was the unknown Cd^{2+} concentration?

12.96 A silver wire coated with AgCl is sensitive to the presence of chloride ions because of the half-cell reaction:

$$AgCl(S) + e^- \rightleftharpoons Ag(s) + Cl^-$$

A student, wishing to measure the chloride ion concentration in a number of water samples, constructed a galvanic cell using the AgCl electrode as one half-cell and a copper wire dipped into a 1.00 M $CuSO_4$ solution as the other half-cell. In one analysis, the potential of the cell was measured to be +0.0925 V, with the copper half-cell serving as the cathode. What was the chloride ion concentration in the water, assuming a temperature of 25 °C? Use the data in table 12.1.

12.97 Suppose a galvanic cell was constructed at 25 °C using a Cu^{2+}/Cu half-cell (in which the molar concentration of Cu^{2+}/Cu was 1.00 M) and a hydrogen electrode having a partial pressure of H_2 equal to 1.0×10^5 Pa. The hydrogen electrode dipped into a solution of unknown hydrogen ion concentration, and the two half-cells were connected by a salt bridge. Use the data in table 12.1.

(a) Derive an equation for the pH of the solution with the unknown hydrogen ion concentration, expressed in terms of E_{cell} and $E^{\ominus}_{cell}$. You will need to use the equation:

$$\ln x = 2.303 \log x$$

to answer this question.

(b) If the pH of the solution was 5.15, what would be the observed potential of the cell?

(c) If the potential of the cell was 0.645 V, what would be the pH of the solution?

12.98 How many coulombs are passed through an electrolysis cell by (a)a current of 4.00 A for 600 s, (b)a current of 10.0 A for 20.0 min and (c) a current of 1.50 A for 6.00 h? What amount of electrons corresponds to the answers to each part of this question?

12.99 State the amount of electrons required to:

(a) reduce 0.20 mol Fe^{2+} to Fe

(b) oxidise 0.70 mol Cl^- to Cl_2

(c) reduce 1.50 mol Cr^{3+} to Cr

(d) oxidise 1.0×10^{-2} mol Mn^{2+} to MnO_4^-

(e) produce 5.00 g Mg from molten $MgCl_2$

(f) form 41.0 g Cu from a $CuSO_4$ solution.

12.100 What amount of Cr^{3+} would be reduced to Cr by the same amount of electricity that produces 12.0 g Ag from a solution of $AgNO_3$? If a current of 4.00 A was used, how many minutes would the electrolysis take?

12.101 What mass of $Fe(OH)_2$ is produced at an iron anode when a basic solution undergoes electrolysis at a current of 8.00 A for 12.0 min?

12.102 What mass of Cl_2 would be produced in the electrolysis of molten NaCl by a current of 4.25 A for 35.0 min?

12.103 How long would it take to produce 75.0 g of metallic chromium by the electrolytic reduction of

Cr^{3+} with a current of 2.25 A?

12.104 How long would it take to generate 35.0 g of lead from $PbSO_4$ during the charging of a lead storage battery using a current of 1.50 A? The half-reaction is:

$$PbSO_4 + H^+ + 2e^- \rightarrow Pb + HSO_4^-$$

12.105 How many amperes would be needed to produce 60.0 g of magnesium during the electrolysis of molten $MgCl_2$ in 2.00 hours?

12.106 The electrolysis of 250 mL of a brine solution (NaCl) was carried out for a period of 20.00 min with a current of 2.00 A. The resulting solution was titrated with 0.620 M HCl. What volume of the HCl solution was required for the titration?

12.107 A solution of NaCl in water was electrolysed with a current of 2.50 A for 15.0 min. What volume of Cl_2 gas would be formed if it was collected over water at 25 °C and a total pressure of 1.0×10^5 Pa?

12.108 What volume of dry gaseous H_2, measured at 20 °C and 1.0×10^5 Pa, would be produced at the cathode in the electrolysis of dilute H_2SO_4 with a current of 0.750 A for 15.00 min?

12.109 Write the anode reaction for the electrolysis of an aqueous solution that contains

(a) SO_4^{2-},

(b) Br^- and

(c) SO_4^{2-} and Br^-

12.110 Write the cathode reaction for the electrolysis of an aqueous solution that contains

(a) K^+,

(b) Cu^{2+} and

(c) K^+ and Cu^{2+}.

12.111 What products would we expect at the electrodes if a solution containing

(a) both KBr and $CuSO_4$ and

(b) both $BaCl_2$and CuI_2 were electrolysed? Write the equations for the respective net cell reactions.

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12.112 The following chemical reactions are observed to occur in aqueous solution:

$$2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$$
$$2Al + 3Fe^{2+} \rightarrow 3Fe + 2Al^{3+}$$
$$Pb^{2+} + Fe \rightarrow Pb + Fe^{2+}$$
$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$$
$$2Al + 3Pb^{2+} \rightarrow 3Pb + 2Al^{3+}$$
$$Pb + Cu^{2+} \rightarrow Pb^{2+} + Cu$$

Arrange the metals Al, Pb, Fe and Cu in order of increasing ease of oxidation. Were all the experiments described actually necessary to establish the order?

12.113 What is the oxidation number of sulfur in the tetrathionate ion, $S_4O_6^{2-}$?

12.114 In each pair below, choose the metal that would most likely react more rapidly with a nonoxidising acid such as HCl:

(a) aluminium or iron,

(b) zinc or cobalt,

(c) cadmium or magnesium.

12.115 Balance the following equations in aqueous solution under the specified conditions.

(a) $NBr_3 \rightarrow N_2 + Br^- + HOBr$ (basic solution)

(b) $Cl_2 \rightarrow Cl^- + ClO_3^-$ (basic solution)

(c) $H_2SeO_3 + H_2S \rightarrow S + Se$ (acidic solution)

(d) $MnO_2 + SO_3^{2-} \rightarrow Mn^{2+} + S_2O_6^{2-}$ (acidic solution)

(e) $XeO_3 + I^- \rightarrow Xe + I_2$ (acidic solution)

(f) $(CN)_2 \rightarrow CN^- + OCN^-$(basic solution)

(g) $KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$ (neutral)

12.116 Lead(IV) oxide reacts with hydrochloric acid to give chlorine. The equation for the reaction is:

$$PbO_2 + 4Cl^- + 4H^+ \rightarrow PbCl_2 + 2H_2O + Cl_2$$

What mass of PbO_2 must react to give 15.0 g of Cl_2?

12.117 Biodiesel is formed from the reaction of oils with methanol or ethanol. One of the products is methyl octanoate, $C_9H_{18}O_2$, which burns completely in a diesel engine. Give a balanced equation for this reaction. If the density of methyl octanoate is 0.877 g mL^{-1}, what mass of CO_2 will be formed from the burning of 1 litre of methyl octanoate?

12.118 Suppose that a galvanic cell was set up having the net cell reaction:

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$

The Ag^+ and Zn^{2+} concentrations in their respective half-cells are initially 1.00 M, and each half-cell contains 100 mL of electrolyte solution. If this cell delivers current at a constant rate of 0.10 A, what will the cell potential be after 15.00 h?

12.119 To determine the reduction potential of the Pt^{2+} ion, a galvanic cell was set up in which one

half-cell consisted of a Pt electrode dipped into a 0.0100 M solution of $Pt(NO_3)_2$ and the other of a silver wire coated with AgCl dipped into a 0.100 M solution of HCl. The potential of the cell was measured to be 0.778 V, and it was found that the Pt electrode carried a positive charge. Given the following half-reaction and its reduction potential:

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq) \quad E^\ominus_{AgCl/Ag} = +0.23\,V$$

calculate the standard reduction potential for the half-reaction:

$$Pt^{2+}(aq) + 2e^- \rightleftharpoons Pt(s)$$

12.120 A student set up an electrolysis apparatus and passed a current of 1.22 A through a 3 M H_2SO_4 solution for 30.0 min. The H_2 formed at the cathode was collected and found to have a volume, over water at 27 °C, of 288 mL at a total pressure of 1.0×10^5 Pa. Use these data to calculate the charge on the electron, expressed in coulombs.

12.121 A hydrogen electrode is immersed in a 0.10 M solution of acetic acid at 25 °C. This electrode is connected to another consisting of an iron nail dipped into 0.10 M $FeCl_2$. What will be the measured potential of this cell? Assume $p_{H2} = 1.0 \times 10^5$ Pa.

12.122 Consider the following half-reactions at 25 °C.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
$$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$$

(a) Use the data in table 12.1 to determine the value of:

i. $E^\ominus_{cell}$

ii. $\Delta G^\ominus$ for this reaction

iii. K_c for this reaction at 25 °C.

(b) Write the Nernst equation for this reaction.

(c) What is the potential of the cell when $[MnO_4^-] = 0.20$ M, $[Mn^{2+}] = 0.050$ M, $[Cl^-] = 0.0030$ M, $[ClO_3^-] = 0.110$ M and the pH of the solution is 4.25?

12.123 A solution of NaCl is neutral, with a pH of 7 at 25 °C. If electrolysis is carried out on 500 mL of an NaCl solution with a current of 0.500 A, how long would it take for the pH of the solution to rise to a value of 9.00?

12.124 Consider the following galvanic cell:

$$Ag(s)\left|Ag^+\left(3.0\times10^{-4}M\right)\right\|Fe^{3+}\left(1.1\times10^{-3}M\right), Fe^{2+}(0.040M)\left|Pt(s)\right.$$

Calculate the cell potential. Determine the sign of the electrodes in the cell. Write the equation for the spontaneous cell reaction.

12.125 Balance the following equations for reactions occurring in acidic aqueous solution.

(a) $MnO_4^- + S_2O_3^{2-} \rightarrow Mn^{2+} + S_4O_6^{2-}$

(b) $ClO_3^- + Cl^- \rightarrow Cl_2 + ClO_2$

(c) $MnO_4^- + S^{2-} \rightarrow MnS + S$

(d) $Cu^{2+} + P \rightarrow Cu + H_2PO_4^-$

(e) $PH_3 + I_2 \rightarrow I^- + H_3PO_2^-$

(f) $NO_2 \rightarrow NO_3^- + NO$

(g) $MnO_2 + Cl^- \rightarrow MnCl_2 + Cl_2$

(h) $Ni^{2+} + IO_4^- \rightarrow Ni^{2+} + I^-$

(i) $O_2 + Br^- \rightarrow H_2O + Br_2$

(j) $Ca + Cr_2O_7^{2-} \rightarrow Ca^{2+} + Cr^{3+}$

12.126 Balance the following equations for reactions occurring in basic aqueous solution.

(a) $ClO_2 \rightarrow ClO_3^- + ClO_2^-$

(b) $Cu(NH_3)_4^{2+} + S_4O_6^{2-} \rightarrow SO_3^{2-} + Cu + NH_3$

(c) $Zn + NO_3M \rightarrow Zn(OH)_4^{2+} + NH_3$

(d) $Al + OH^- \rightarrow AlO_2^- + H_2$

(e) $Cr + CrO_4^{2-} \rightarrow Cr(OH)_3$

(f) $CN^- + MnO_4^- \rightarrow CNO^- + MnO_2$

(g) $SO_2 + I_2 \rightarrow IM + SO_3$

(h) $K + H_2O \rightarrow K^+ + H_2$

12.127 Use the following half-reactions and accompanying standard reduction potentials to determine the best reducing agent under standard conditions: Ga^{3+}, Ga, Be^{2+}, Be, Pd^{2+} or Pd.

$$Ga^{3+} + 3e^- \rightarrow Ga \qquad E^{\ominus}_{Ga^{3+}/Ga} = -0.560\,V$$
$$Be^{2+} + 2e^- \rightarrow Be \qquad E^{\ominus}_{Be^{2+}/Be} = -1.70\,V$$
$$Pd^{2+} + 2e^- \rightarrow Pd \qquad E^{\ominus}_{Pd^{2+}/Pd} = -0.560\,V$$

12.128 Answer the following questions for the cell:

$$Al|Al^{3+}||Pb^{2+}|Pb$$

(a) Identify the anode and the cathode.

(b) Write the balanced overall reaction.

(c) What is the potential of this cell under standard conditions (refer to table 12.1)?

12.129 Consider a galvanic cell involving chromium(III) and gold(III) and the corresponding Cr and Au electrodes. (Use the data in table 12.1.)

(a) Sketch this cell.

(b) Identify the anode and the cathode.

(c) Write the balanced overall reaction.

(d) Which electrode will lose mass?

(e) Indicate the direction of the electron flow.

(f) Indicate the flow of the anions and cations.

(g) What is the potential of this cell under standard conditions?

(h) Write the shorthand notation.

(i) Calculate $\Delta G^{\ominus}$ for this reaction.

12.130 Label each of the following reactions (in the direction it is written) as spontaneous or

nonspontaneous (use the data given in table 12.1).

(a) $2Cr^{3+} + 3Ni \rightarrow 2Cr + 3Ni^{2+}$

(b) $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

(c) $Cl_2 + Sn \rightarrow 2Cl^- + Sn^{2+}$

(d) $Al + Au^{3+} \rightarrow Al^{3+} + Au$

12.131 The silvery look of 'white gold' results from plating with rhodium (Rh). How many coulombs of electricity must be pumped through an rhodium(III) solution to plate 1 gram of solid rhodium?

12.132 Calculate the quantity of electricity (coulombs) necessary to deposit 100.00 g of copper from a $CuSO_4$ solution.

12.133 How many minutes will it take to plate out 30.00 g of Ni from a solution of $NiSO_4$ using a current of 3.45 ampere?

12.134 A constant electric current deposits 0.3650 g of silver metal in 12 960 seconds from a solution of silver nitrate. Calculate the current. What is the half-equation for the deposition of silver?

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KEY TERMS

alkaline battery
alkaline dry cell
ampere (A)
anode
battery
cathode
Cathodic protection
cell diagram
cell potential (E_{cell})
cell reaction
concentration cell
coulomb (C)
disproportionation
dry cell battery
electrochemical changes
electrochemical potential
electrochemistry
electrolysis
electrolysis cell
electrolytic cell
electrolytic conduction
electronic conduction
Faraday constant
Faraday's law
fuel cell
galvanic cell
galvanisation
half-cell
half-equation
hydrometer
intercalation
joules (J)
lead storage battery
Leclanché cell
lithium ion cell
Nernst equation
nicad battery
nickel–cadmium storage cell
nonoxidising acid
oxidation
oxidation number
oxidation state
oxidising acid
oxidising agent
passivation
potential difference
primary cell
redox reaction
reducing agent
Reduction
reduction potential (E_{red})
reduction–oxidation reaction
salt bridge
saturated calomel electrode
secondary cell
silver/silver chloride electrode
standard cell notation
standard cell potential $\left(E^{\ominus}_{cell}\right)$
standard hydrogen electrode (Eored)
symproportionation
volt (V)
voltmeter
zinc–manganese dioxide cell

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CHAPTER

13 Transition Metal Chemistry

Australia is one of the world's main sources of rubies and sapphires. These precious gemstones are prized for their beautiful colours; rubies are always red, whereas sapphires can exhibit a range of colours. Remarkably, both rubies and sapphires are composed primarily of colourless aluminium oxide, Al_2O_3, and their colours are due to the presence of small amounts of transition metal ions — chromium in rubies, and titanium, nickel and iron in sapphires. The colours that these transition metals impart result from both the energies of the *d* orbitals of the transition metal ions and how the *d* electrons are arranged in these orbitals. In this chapter, we will investigate what makes transition metals unique among the elements of the periodic table with respect to the colours and magnetic behaviours of their compounds.



KEY TOPICS

13.1 Metals in the periodic table

13.2 Transition metals

13.3 Ligands

13.4 Transition metal complexes

13.5 Transition metal ions in biological systems
13.6 Isolation and purification of transition metals
13.7 Applications of transition metals

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13.1 Metals in the Periodic Table

In chapter 1, we learned that the chemical elements can be divided into three groups: metals, metalloids and nonmetals. Of the 118 known elements, 91 or 92 are metals (polonium is variously described as either a metal or metalloid). Metals can be classified into different types on the periodic table, generally according to the nature of their valence orbitals (figure 13.1)

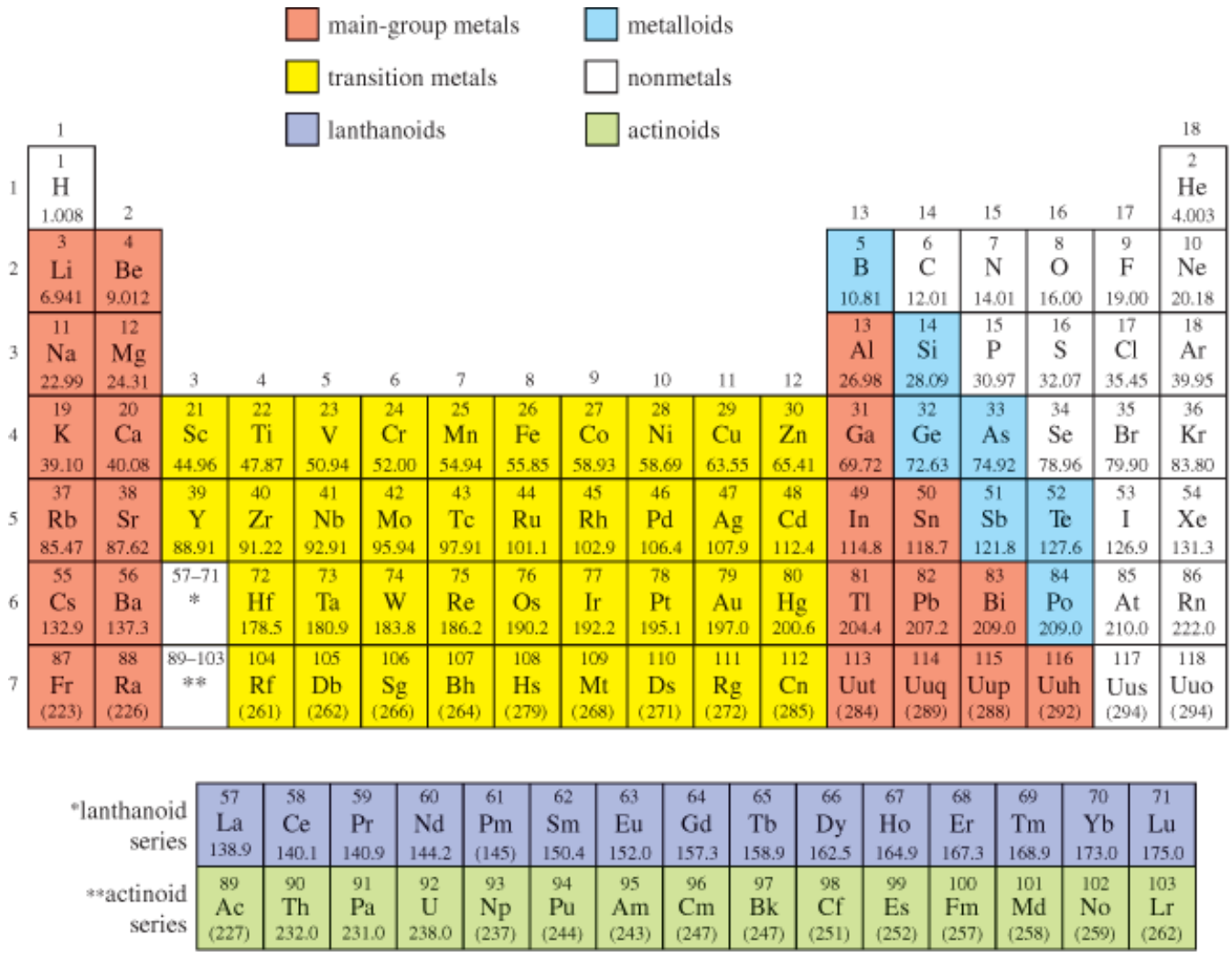


FIGURE 13.1 The metals in the periodic table of the elements. The transition metals are shown in yellow and occupy groups 3 to 12 of the periodic table.

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The metals in groups 1 and 2 have *s* valence orbitals, whereas those in groups 13 to 16 have *p* valence orbitals. (The former are sometimes called pre-transition metals and the latter post-transition metals.) Collectively, these metals are known as **main-group metals**. The lanthanoid and actinoid metals are characterised by partially filled *f* orbitals. The lanthanoids, with the exception of promethium, Pm, occur naturally; the majority of the actinoid elements must be prepared by nuclear reactions (see section 27.3).

The metals in groups 3 to 12 of the periodic table are collectively called the **transition metals**, and their chemistry contrasts significantly with other metals in the periodic table. For example, if we dissolve any group 1 or 2 metal (carefully!) in nitric acid, we obtain a colourless solution in all cases. However, repeating the experiment using metallic cobalt, nickel or copper produces purple, green and blue solutions, respectively. In fact, we obtain coloured solutions for many of the transition metals; there are some exceptions (silver, zinc, cadmium and mercury), and gold does not dissolve in nitric acid. If we reduce the solutions containing cobalt, nickel or copper to dryness, we find that the resulting solids are **paramagnetic**, meaning that they are attracted into a magnetic field, and, indeed, this is the case for many (but not all) of the transition metals. The corresponding solids obtained from the group 1 and 2 metals

exhibit **diamagnetic** behaviour, being very slightly repelled from a magnetic field.

Colour and magnetic behaviour are two of the defining characteristics of compounds containing transition metals. As we saw in chapter 1, transition metal elements are sometimes called the *d*-block elements, because the valence orbitals of these elements are *d* orbitals, and we will see that many of the spectral and magnetic properties of transition metal compounds can be related to the energies of the five *d* orbitals of the transition metal ion.

Transition metals are distinguished by their ability to form **complexes**. In these chemical species, transition metal ions (usually positively charged) are surrounded by one or more ions (usually negatively charged) or neutral molecules, which are called **ligands**. When writing the formula of a transition metal complex, we enclose the metal and the bound ligands in square brackets (the metal ion first, followed by the ligands in alphabetical order), with the overall charge (if any) superscripted outside the brackets.

The $[Co(OH_2)_6]^{2+}$ ion is a simple example of a transition metal complex, in which a single cobalt ion is bonded to six water molecules. The structure of this pink complex, which results from the dissolution of metallic cobalt in nitric acid as described on the previous page, is shown in figure 13.2a. In this complex, the cobalt ion has a formal charge of +2, and is surrounded by six H_2O ligands to give an octahedral geometry about the metal ion.

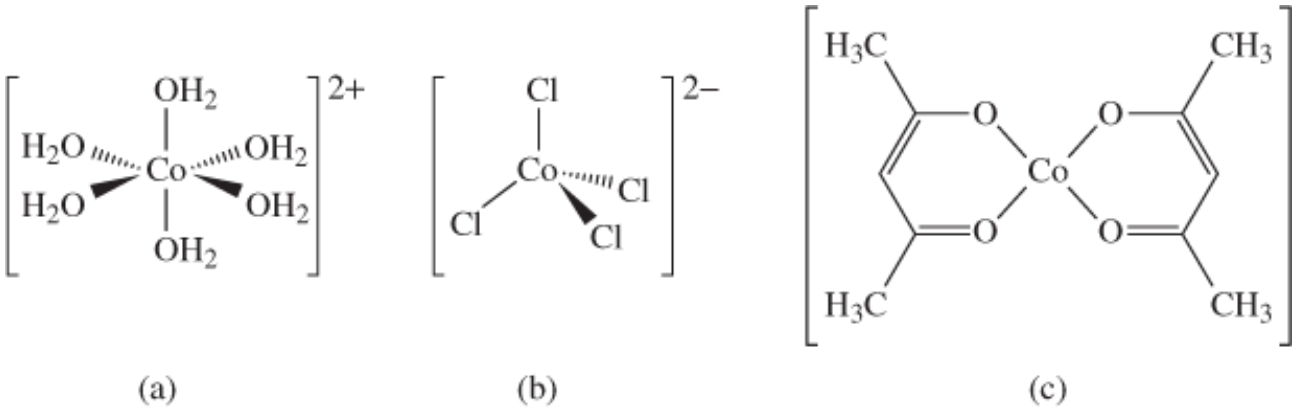


FIGURE 13.2 The structures of three transition metal complexes in which the cobalt ion has a formal charge of +2:

(a) the $[Co(OH_2)_6]^{2+}$ complex cation,

(b) the $[CoCl_4]^{2-}$ complex anion and

(c) the neutral complex $[Co(acac)_2]$.

If we dissolve metallic cobalt in hydrochloric acid, rather than nitric acid, we obtain a deep blue solution, due to the formation of the $[CoCl_4]^{2-}$ complex anion. The cobalt ion again has a formal charge of +2, but in this case is surrounded by four chloride ions in a tetrahedral arrangement (figure 13.2b).

Finally, if we react a suitable cobalt salt with the acetylacetonate (acac) ligand, we obtain the neutral complex $[Co(acac)_2]$. As for $[Co(OH_2)_6]^{2+}$ and $[CoCl_4]^{2-}$, the cobalt ion has a formal charge of +2, but here it is bonded to four oxygen atoms of two acac ligands (figure 13.2c). The geometry around the cobalt ion is square planar, and the complex is green.

The examples above give some idea of the wide range of structures, charges and colours of transition metal complexes. Most importantly, you can see that:

- transition metal complexes can be positively or negatively charged, or neutral
- the number of ligands around the central metal ion can vary
- there are a number of different possible geometries of the ligands around the central metal ion.

In addition, as we will see, there is usually a variety of oxidation states available to the transition metal ion, and transition metal complexes can often contain more than one metal ion.

Transition metal complexes are essential to many biological processes; for example, oxygen is transported around our bodies in a complex containing iron, a zinc complex ensures that we can process potentially toxic CO_2, and a manganese complex in green plants facilitates the conversion of water to oxygen. Transition metal complexes find extensive use in industrial processes, often being used as catalysts for the formation of plastics, bulk chemicals and pharmaceuticals. They are also used increasingly as drugs in chemotherapy and photodynamic therapy.

Transition metal complexes are formed by a Lewis acid–Lewis base interaction between a transition metal cation and one or more ligands, with each ligand formally donating one or more electron pairs to the metal ion. Therefore, we will investigate the two component parts of a complex, the transition metal and the ligand, before we consider transition metal complexes in detail. Note that transition metals are not unique in their ability to form complexes, and other Lewis acidic metal ions and main-group elements in the periodic table can also be surrounded by one or more ligands to form complexes. However, we concentrate on transition metal complexes in this chapter because of their extremely unusual properties mentioned previously. Any use of the term ‘complex’ in this chapter refers to a transition metal complex.

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13.2 Transition Metals

As we saw in chapter 4, the transition metals are characterised by *d* valence orbitals, so the neutral atoms generally have valence electron configurations of $(n + 1)s^2nd^{(x - 2)}$, where *x* is the group number of the metal in the periodic table, and *n* is the principal quantum number. The group 4 element titanium, for example, has the valence configuration $4s^23d^2$. Recall from chapter 4, however, that there are exceptions to this general rule, most notably for the first-row (3*d*) elements Cr($4s^13d^5$) and Cu($4s^13d^{10}$). More important for transition metal complexes are the electron configurations of the ions. As we learned in chapter 4, the *nd* orbital is always of lower energy than the $(n + 1)s$ orbital in transition metal cations, which therefore always have vacant $(n + 1)s$ orbitals. Knowledge of the electron configuration of transition metal ions is important as another of the defining characteristics of transition metals is their ability, in contrast to most other metals in the periodic table, to exist in a variety of oxidation states, the values of which, for transition metal ions, we denote using Roman numerals. For example, the oxidation state of iron in the majority of its complexes is either Fe(II) or Fe(III), while complexes containing manganese in every oxidation state from Mn(0) to Mn(VII) are known. Table 13.1 shows the common oxidation states encountered for the first-row transition metal ions, along with their corresponding electron configurations.

TABLE 13.1 Common oxidation states and electron configurations for the first-row transition metal ions. The most important oxidation states of each metal are highlighted

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni		
Group	3	4	5	6	7	8	9	10		
Oxidation state	Valence configuration									
I			d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	
II		d^2	d^3	**d^4**	**d^5**	**d^6**	**d^7**	**d^8**	**d^9**	**d^{10}**
III	**d^0**	d^1	d^2	**d^3**	**d^4**	**d^5**	**d^6**	d^7	d^8	
IV		**d^0**	d^1	d^2	**d^3**	d^4	d^5	d^6		
V			**d^0**	d^1	d^2	d^3	d^4			
VI				**d^0**	d^1	d^2				
VII					**d^0**					

WORKED EXAMPLE 13.1

Determining *d*-electron configurations

What are the *d*-electron configurations of the transition metal ions Mn^{2+}, Cu^{2+}, Co^{3+}, Ti^{3+} and Cr^{2+}?

Analysis

Although the required *d*-electron configurations can be obtained from table 13.1, you should determine the answers by first calculating the number of electrons in each ion and then using these

to fill the orbitals in each ion.

Solution

Each transition metal is in the first row, so they share a common [Ar] core electron configuration for their first 18 electrons. Recall also that the 4*s* orbitals are of higher energy than the 3*d* orbitals in transition metal ions, so we start filling the 3*d* orbitals first. The numbers of electrons in the neutral atoms are obtained from the atomic numbers, and we remove the appropriate number depending on the charge on the ion. Given that the first 18 electrons are core electrons, any electrons in excess of 18 go directly into the 3*d* orbitals.

- Mn: $Z = 25$, so there are 25 electrons in the neutral atom. Hence, Mn^{2+} has 23 electrons. Mn^{2+} has five *d* electrons (23 - 18), so its electron configuration is [Ar]$3d^5$.
- Cu: $Z = 29$, so there are 29 electrons in the neutral atom. Hence, Cu^{2+} has 27 electrons. Cu^{2+} has nine *d* electrons (27 - 18), so its electron configuration is [Ar]$3d^9$.
- Co: $Z = 27$, so there are 27 electrons in the neutral atom. Hence, Co^{3+} has 24 electrons. Co^{3+} has six *d* electrons (24 - 18), so its electron configuration is [Ar]$3d^6$.
- Ti: $Z = 22$, so there are 22 electrons in the neutral atom. Hence, Ti^{3+} has 19 electrons. Ti^{3+} has one *d* electron (19 - 18), so its electron configuration is [Ar]$3d^1$.
- Cr: $Z = 24$, so there are 24 electrons in the neutral atom. Hence, Cr^{2+} has 22 electrons. Cr^{2+} has four *d* electrons (22 - 18), so its electron configuration is [Ar]$3d^4$.

Is our answer reasonable?

All the answers indicate that the 3*d* orbitals are partially filled, as we would expect for a tran sition metal ion. Our answers are therefore likely to be correct, barring arithmetical errors.

One quick way of determining *d* electron configurations is to subtract the charge on the ion from the group number of the transition metal. For example, Co is in group 9 of the periodic table, so the Co^{3+} ion has (9 - 3) = 6 *d* electrons. Using this method, we can confirm that our answers are correct. This method is particularly useful in determining the *d* electron configurations of row-3 transition metal ions, as the lanthanoid elements lie between the main-group metals and these transition metals, thereby complicating the core electron count. You should also be aware that the *d* electron configuration of transition metal ions belonging to the same group is the same. For example, Co^{3+}, Rh^{3+} and Ir^{3+} all have a d^6 electron configuration.

PRACTICE EXERCISE 13.1

What are the *d*-electron configurations of the transition metal ions Fe^{3+}, Ni^{2+}, Pt^{2+}, Ir^{+} and Re^{+}?

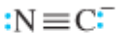
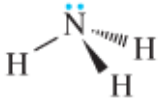
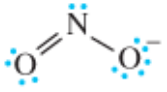
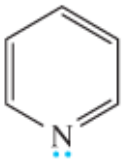
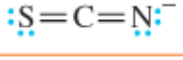
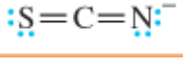
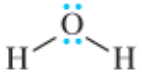
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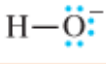
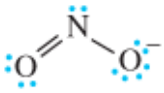
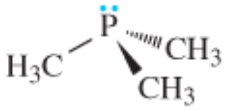
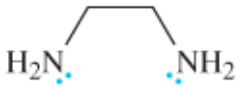
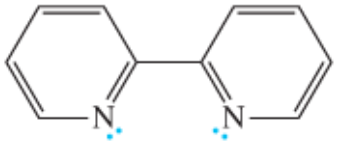
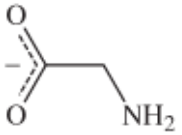
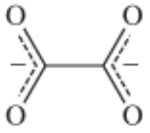
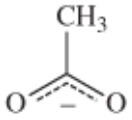
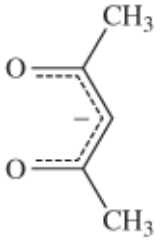
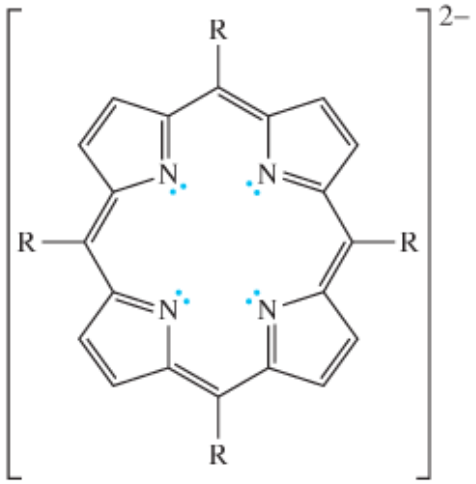
13.3 Ligands

Transition metal ions are Lewis acids (see chapter 11), and therefore act as electron pair acceptors towards one or more ligands when forming metal complexes. The word 'ligand' is derived from the Latin *ligare* meaning 'to bind'. Ligands are Lewis bases and can donate an electron pair to a Lewis acidic transition metal ion. The electron pair is usually a lone pair located on an atom or ion. The atom on which the lone pair is located is called the **donor atom**. Ligands can have one or more donor atoms. The necessity for a lone pair of electrons means that relatively few elements in the periodic table can act as donor atoms; the most common are F, Cl, Br, I, O, S, N and P.

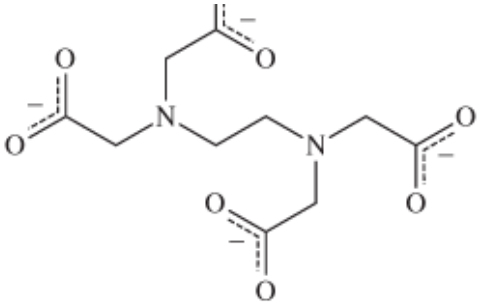
As stated earlier, ligands can be either ions or molecules, and they can be negatively charged, neutral or, in very rare cases, positively charged. Anions that serve as ligands include many simple monatomic ions, such as the halide ions (F^-, Cl^-, Br^-, I^-) and the sulfide ion (S^{2-}), each of which contains four lone pairs of electrons. Common polyatomic anions that are ligands are the nitrite ion (NO_2^-), cyanide ion (CN^-), hydroxide ion (OH^-), thiocyanate ion (SCN^-) and acetate ion (CH_3COO^-) (table 13.2). The most common neutral molecule that serves as a ligand is water, which contains two lone pairs of electrons on the O atom.

TABLE 13.2 Common ligands found in transition metal complexes. Rules for naming ligands are found in section 13.4

Type of ligand	Ligand name[a]	Formula or abbreviation	Structure	Donor atom(s)
monodentate	bromido	Br^-		Br
	chlorido	Cl^-		Cl
	fluorido	F^-		F
	iodido	I^-		I
	cyanido	CN^-		C
	carbonyl	CO		C
	ammine[b]	NH_3		N
	nitrito-κN	NO_2^-		N
	pyridine	C_5H_5N		N
	thiocyanato-κN	NCS^-		N
	thiocyanato-κS	NCS^-		S
	aqua	H_2O		O
	oxido	O^{2-}		O

	hydroxido	OH^-		O
	nitrito-κO	NO_2^-		O
	hydrido	H^-		H
	trimethylphosphane[c]	$P(CH_3)_3$		P
bidentate	ethylenediamine	en		N, N
	bipyridine	bipy		N, N
bidentate	glycinato[d]	gly		N, O
	oxalato	ox		O, O
	acetato	OAc		O, O
	acetylacetonato	acac		O, O
tetradentate	porphyrin-21, 23-diido			N, N, N, N



hexadentate	ethylenediaminetetraacetato	EDTA		N, N, O, O, O, O

(a) Note that ligands are named according to the rules given on pp. 558–60.
(b) Amines (derivatives of NH_3), such as methylamine, CH_3NH_2, also are common ligands.
(c) This is the simplest of a group of ligands called *phosphanes*, which have three organic groups bonded to phosphorus.
(d) The anionic forms of all common amino acids act as bidentate ligands.

Most of the reactions of transition metal ions in aqueous solutions are actually reactions of complex ions in which the metal is attached to a number of water molecules, depending on the identity of the metal ion. Therefore, the notation $M^{n+}(aq)$ actually refers to a complex ion with the formula $[M(OH_2)_x]^{n+}$ ·$Cu^{2+}(aq)$, for example, is believed to exist as the complex ion $[Cu(OH_2)_5]^{2+}$ in aqueous solution, but $Co^{2+}(aq)$ forms $[Co(OH_2)_6]^{2+}$ under the same conditions. Another common neutral ligand is ammonia, NH_3, which has one lone pair of electrons on the nitrogen atom. If ammonia is added to an aqueous solution containing the $[Ni(OH_2)_6]^{2+}$ ion, for example, the colour changes almost instantaneously from green to blue as ammonia molecules bind preferentially to the metal ion, displacing water molecules (figure 13.3) according to the equation:



FIGURE 13.3 Complex ions of nickel. Addition of ammonia to a solution of green $[Ni(OH_2)_6]^{2+}$ ions (left) leads to the formation of blue $[Ni(NH_3)_6]^{2+}$ ions (right).

$$[Ni(OH_2)_6]^{2+}(aq) + 6NH_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

Ligands that use only one atom to bond to a metal ion are called **monodentate** (literally 'one-toothed') ligands. There are also many ligands that have two or more donor atoms. Collectively they are referred to as **polydentate** ligands. Ligands with two donor atoms are called **bidentate** ligands, and, when they form complexes, both donor atoms can become bound to the same metal ion. The best known example of a bidentate ligand is ethylenediamine, $NH_2CH_2CH_2NH_2$, which is usually abbreviated en (this is a historical name but is used almost exclusively in preference to its IUPAC name, ethane-1,2-diamine). Oxalate ion, $C_2O_4^{2-}$ (ox), is another common bidentate ligand, and the structures of both are shown in figure 13.4.

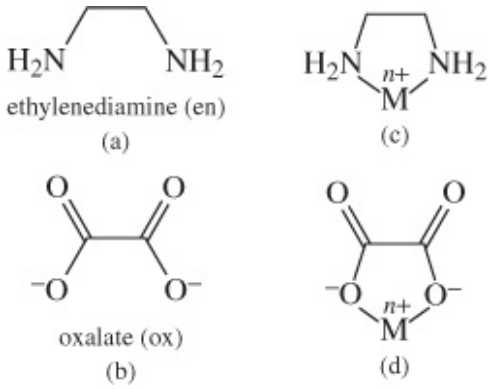


FIGURE 13.4 The structures of the bidentate ligands
(a) ethylenediamine (en) and
(b) oxalate (ox), and
(c) and
(d) the five-membered chelate rings formed on binding to a metal ion, M.

When bidentate ligands bind to a metal ion, they form **chelate rings** (figure 13.4). Complexes containing chelate rings are often called **chelate complexes** (the word 'chelate' is derived from the Greek word for 'claw'). Ligands containing three or more donor atoms can potentially form more than one chelate ring with the same metal ion and such ligands often have particularly high affinities for transition metal ions. An excellent example of this is the polydentate ligand ethylenediaminetetraacetic acid, abbreviated H_4EDTA (figure 13.5).

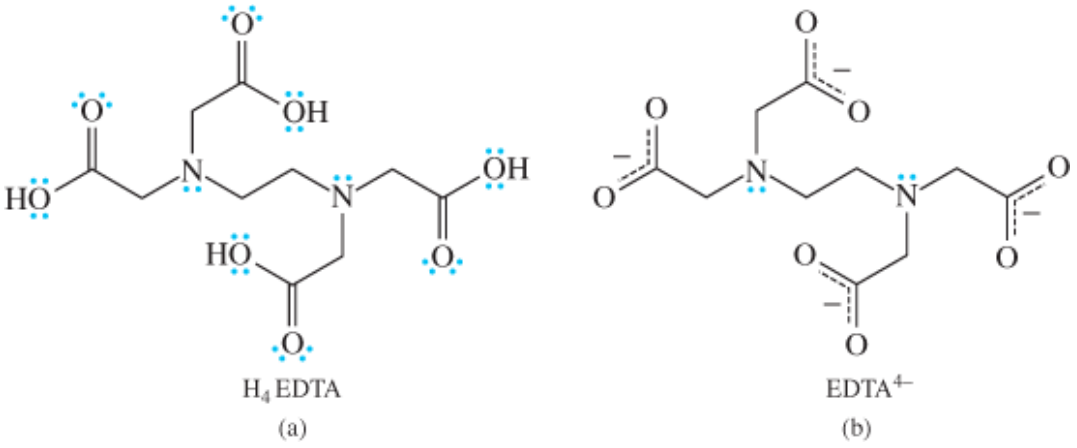


FIGURE 13.5 Representations of the structures of
(a) H_4EDTA and
(b) the tetraanion $EDTA^{4-}$.

The neutral H_4EDTA molecule loses four protons to become the $EDTA^{4-}$ tetraanion, which is a hexadentate ligand that binds strongly through four O atoms and the two N atoms to a large number of metal ions. $EDTA^{4-}$ is a particularly useful and important ligand. It is relatively nontoxic, which allows it to be used in small amounts in foods to retard spoilage. Many shampoos contain the tetra sodium salt, Na_4EDTA, to soften water; the $EDTA^{4-}$ binds to Ca^{2+}, Mg^{2+} and Fe^{3+} ions, which removes them from the water and prevents them from interfering with the action of soaps in the shampoo. Sometimes, $EDTA^{4}$ is added in small amounts to whole blood to prevent clotting; it works by binding calcium ions, which the clotting process requires. $EDTA^{4-}$ has even been used as a treatment in

cases of poisoning because it can help remove poisonous heavy metal ions such as Pb^{2+} from the body when they have been accidentally ingested. Figure 13.6 shows how the $EDTA^{4-}$ ligand wraps around the metal in a transition metal complex.

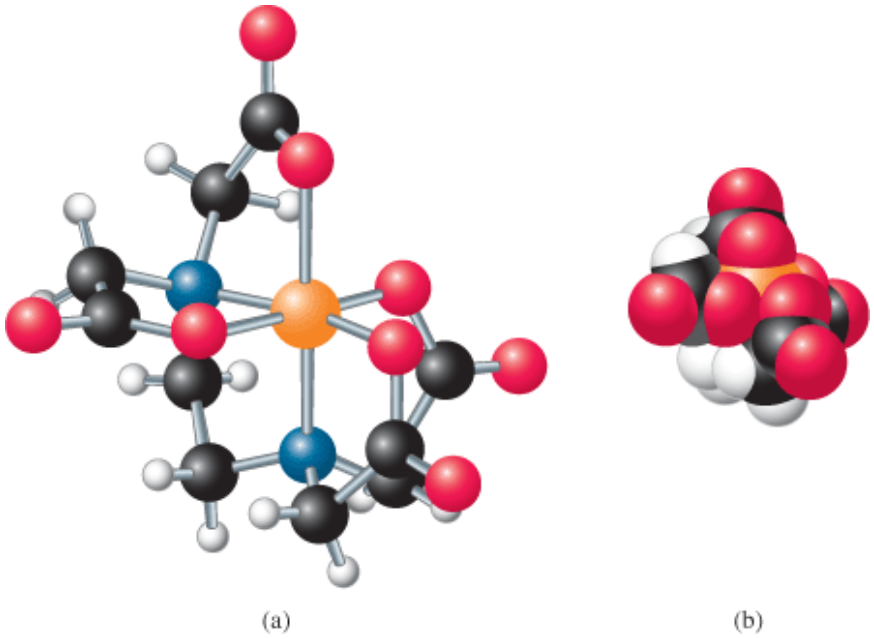


FIGURE 13.6 Two representations of the transition metal complex $[Co(EDTA)]^-$:
(a) ball-and-stick model and
(b) space-filling model (the Co(III) ion is orange). Note the almost complete encapsulation of the metal ion in the space-filling model.

Ligands containing two or more donor atoms can potentially act as bridges between two or more metal ions, provided the donor atoms are oriented correctly. An example of this is provided by the copper acetate complex, $[Cu_2(OH_2)_2(OOCCH_3)_4]$, in which the four acetate ligands bridge the two Cu(II) ions, as shown in figure 13.7.

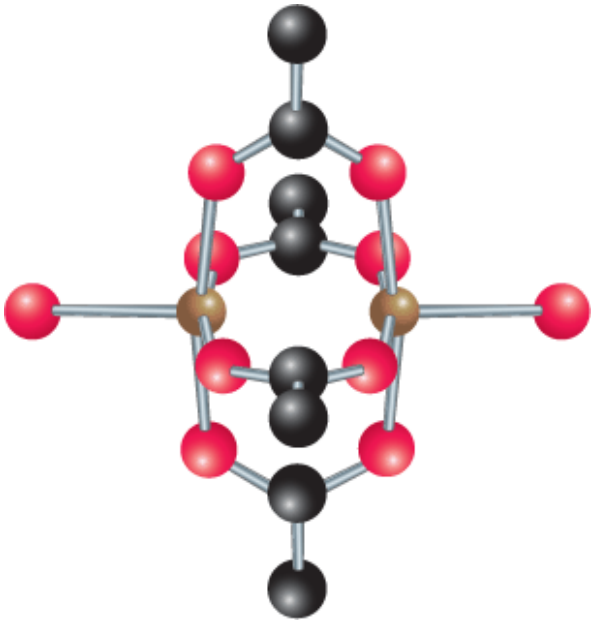


FIGURE 13.7 Ball-and-stick model of $[Cu_2(OH_2)_2\ (OOCCH_3)_4]$ (the Cu ions are brown). Hydrogen atoms have been omitted for clarity.

There are a vast number of known ligands, and table 13.2 summarises some of the more common and important of those used in the synthesis of transition metal complexes.

WORKED EXAMPLE 13.2

Identifying ligands

Which of the following species would be unlikely to function as a ligand in a transition metal complex?

(a) NH_4^+

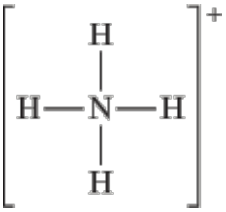
(b) $B(CH_3)_3$

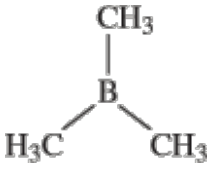
(c) HS^-

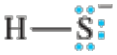
Analysis

We learned on p. 547 that, in order to function as a ligand, a molecule or ion must have an available electron pair to donate to a transition metal ion. Therefore, we will proceed by drawing the Lewis structures of (a), (b) and (c) and looking for the presence of electron pairs.

The Lewis structures of (a), (b) and (c) are as follows.







From these, it can be seen that only HS^- has electron pairs available for donation to a transition metal ion and could thus potentially act as a ligand.

PRACTICE EXERCISE 13.2

By drawing Lewis structures, determine which of the following species could act as a ligand towards a transition metal ion by donating a lone pair of electrons: BH_3, BH_4^-, CH_4, CH_3^-.

Many Australian and New Zealand chemists have been instrumental in the development of novel ligands, and two in particular deserve special mention. New Zealand chemist Neil Curtis and coworkers at Victoria University in the early 1960s reported the first metal complex containing a macrocyclic ligand, shown in figure 13.8. Macrocyclic ligands are simply large cyclic ligands that contain three or more donor atoms. The work of Curtis has led to the development of macrocyclic chemistry as an important subdiscipline of inorganic chemistry, and literally thousands of complexes containing macrocyclic ligands have been prepared in the years since his pioneering research.

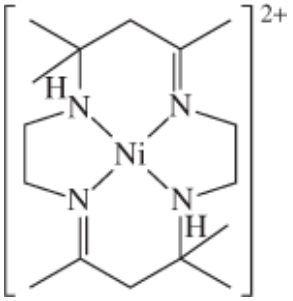


FIGURE 13.8 The first transition metal complex containing a macrocyclic ligand, prepared by New Zealand chemists in the early 1960s.

In 1977, Australian chemist Alan Sargeson and coworkers at the Australian National University prepared the first examples of groups of ligands called sepulchrates (from 'sepulchre' meaning 'tomb') and sarcophagines (from 'sarcophagus' meaning 'coffin'), examples of which are shown in figure 13.9.

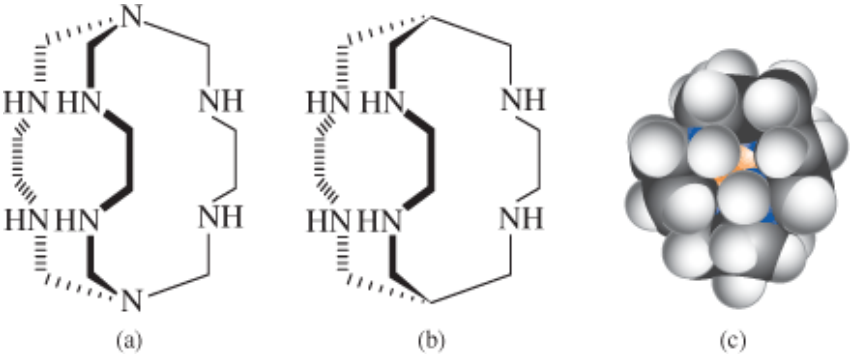


FIGURE 13.9
(a) A sepulchrate ligand,
(b) a sarcophagine ligand and
(c) a space-filling model of a Co(III) complex of a sarcophagine ligand. Note that the orange Co(III) ion is completely enclosed inside the ligand.

These hexadentate ligands, which are trivially called 'cage' ligands, completely encapsulate a transition metal ion, and, once inserted inside the ligand cavity, the metal ion is extremely difficult to remove. Complexes of cage ligands show extremely interesting properties, particularly in biological systems. Such complexes have effective antiviral action against viruses, such as hepatitis and herpes, and work by inhibiting their replication. Cage compounds can also kill tapeworms, both in vitro (in a test tube) and in vivo (in a live organism), and destroy giardia in vitro at micromolar concentrations of the complex.

All of the ligands described thus far contain a donor atom with at least one lone pair of electrons. There is also a variety of organic molecules, that can function as ligands in transition metal complexes, in which one or more carbon atoms are bound to the transition metal ion. Neutral unsaturated organic molecules, including alkenes, alkynes and aromatic species such as benzene, can bind to metal ions using electrons from their π orbitals (chapter 16); alkenes and alkynes generally donate two electrons, while benzene usually donates six. Negatively charged organic ligands can be generated by deprotonation, thus allowing coordination of, for example, the anions of alkanes, while the cyclopentadienide anion, $C_5H_5^-$ has also found extensive use as a ligand. Compounds which contain organic ligands bound to a metal ion through one or more carbon atoms are called **organometallic compounds** (figure 13.10).

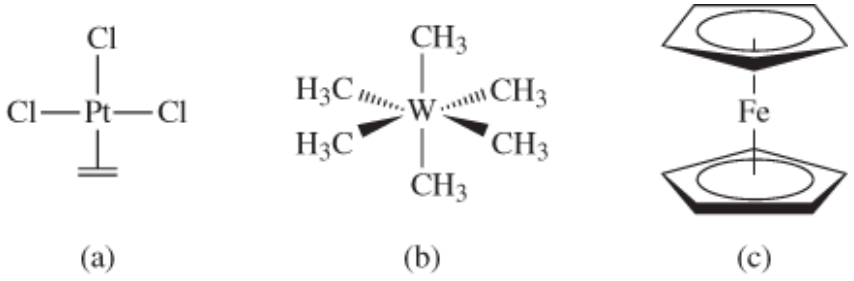


FIGURE 13.10 Representations of the structures of some organometallic complexes:
(a)

$[Pt(C_2H_4)Cl_3]^-$, the anion of Zeise's salt, contains a molecule of ethene bound to the Pt ion.

(b) $[W(CH_3)_6]$ contains six CH_3^- ligands, which are formally derived from deprotonation of CH_4.

(c) In $[Fe(C_5H_5)_2]$, commonly known as ferrocene, each $C_5H_5^-$ ligand donates six electrons to the Fe ion.

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13.4 Transition Metal Complexes

The interaction between a transition metal ion and a ligand can be understood in terms of a Lewis acid–Lewis base interaction, in which the ligand formally donates an electron pair to the metal ion to form a covalent bond. We usually think of a covalent single bond as resulting from the sharing of an electron pair between two atoms, where each atom donates one electron to the bond (chapter 5). In transition metal complexes, as well as all Lewis acid–Lewis base adducts, *both* of the electrons in the covalent bond are formally contributed by the ligand (Lewis base). Although metal-ligand covalent bonds in metal complexes and single covalent bonds in organic compounds both involve sharing a pair of electrons, the former are sometimes called **coordinate bonds**, **donor covalent bonds** or **dative bonds**, and we often say that a ligand is 'coordinated to' rather than 'bound to' a transition metal ion. Transition metal complexes in general are often called **coordination compounds**, while the discipline of the study of transition metal complexes is called **coordination chemistry**. Coordinate bonds are sometimes drawn with an arrow on one end to show the direction of electron donation, but it is more common to depict such bonds in the same way as all other covalent bonds (figure 13.11).

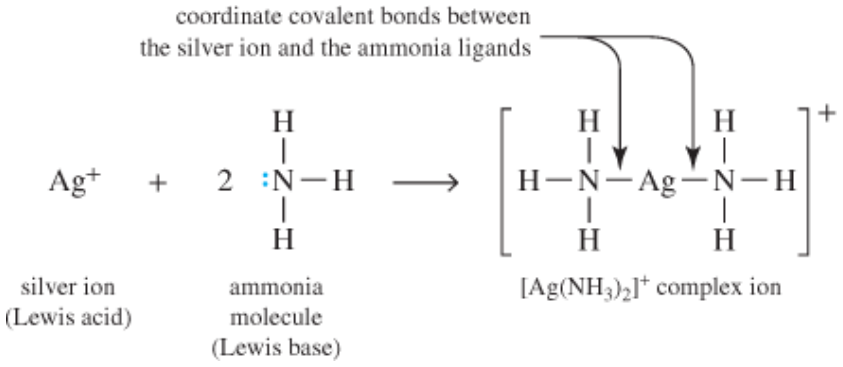


FIGURE 13.11 Formation of a coordinate bond between Ag^+ and NH_3. Note that the overall charge on the complex is the same as the sum of the charges on the metal ion and the ligands.

When assigning formal charges to the coordinated ligand atoms in a transition metal complex, we assume that both electrons in the donated electron pair 'belong' to the ligand donor atom. This is illustrated in the example above, where, in $[Ag(NH_3)_2]^+$, the N atoms are regarded as having five electrons, with both electrons in each Ag—N bond assigned to the N atom. Therefore, both N atoms are formally neutral, rather than positively charged.

When writing the formula of a transition metal complex, we always enclose the metal-containing section in square brackets, with the overall charge on the complex (if any) superscripted outside the brackets. For example, we would write the formula of the complex containing an Fe(III) ion surrounded by six Cl^- ligands as $[FeCl_6]^{3-}$. The sodium salt of this complex anion would be written as $Na_3[FeCl_6]$ with the charges omitted, as is usual for ionic compounds. Ions outside the square brackets are termed **counterions** and may be either cations or anions, depending on the charge on the complex ion. It is important that you can determine the oxidation state of the metal ion in a transition metal complex from the formula of the complex, and this can usually be done using the equation:

oxidation state of transition metal ion = charge on the complex–sum of charges on the ligands

WORKED EXAMPLE 13.3

Determining the oxidation state of a transition metal ion in a complex

What is the oxidation state of the transition metal ion in each of the following complexes?

(a) $Na_3[FeCl_6]$

(b) $[CoCl(NH_3)_5]Cl_2$

(c) $[Re(CO)_5Cl]$

Analysis

We will use the equation:

$$\text{oxidation state of transition metal ion} = \text{charge on the complex} - \text{sum of charges on the ligands}$$

to determine the oxidation state of the transition metal ion. (Remember that we denote oxidation state using Roman numerals.) We calculate the charge on the complex by removing the counterion(s) (if any), and we can use table 13.2 to obtain the charges of the ligands.

(a) Removing three Na^+ ions means that the charge on the complex is 3- i.e. $[FeCl_6]^{3-}$. Each of the Cl^- ligands has a 1- charge, so the total charge on the ligands is 6-. Therefore:

$$\begin{aligned}\text{oxidation state of the transition metal ion} &= (3-) - (6-) \\ &= \text{III}\end{aligned}$$

(b) Removing the two Cl^- counterions leaves a charge on the complex of 2+; i.e. $[CoCl(NH_3)_5]^{2+}$. There are five NH_3 ligands, which are neutral, and one Cl^- ligand with a 1- charge. This gives a total charge on the ligands of 1-. Therefore:

$$\begin{aligned}\text{oxidation state of the transition metal ion} &= (2+) - (1-) \\ &= \text{III}\end{aligned}$$

(c) There are no counterions to remove, so the charge on the complex must be 0. There are five CO ligands, which are neutral, and one Cl^- ligand with a 1- charge. This gives a total charge on the ligands of 1-. Therefore:

$$\begin{aligned}\text{oxidation state of the transition metal ion} &= 0 - (1-) \\ &= \text{I}\end{aligned}$$

PRACTICE EXERCISE 13.3

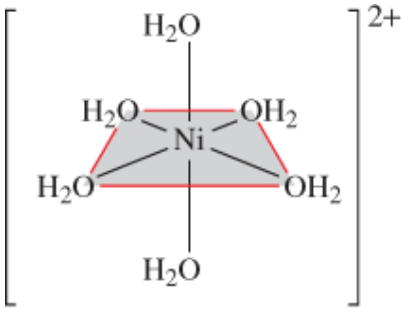
Determine the oxidation states of the transition metal ions in the following complexes: $[Co(NH_3)_6]Cl_3$, $Na_2[MnCl_5]$, $[RhCl_2(en)_2]Cl$, $K_3[Cr(ox)_3]$, $[CoCl(en)(NCS)(NH_3)_2]NO_3$.

When writing the formulae of transition metal complexes, it is usual to write ligands with their donor atom(s) first. For example, we would write $[Fe(OH_2)_6]^{2+}$ instead of $[Fe(H_2O)_6]^{2+}$. In the case of potentially bidentate ligands such as CO_3^{2-} and $C_2O_4^{2-}$, we write the two donor atoms first, followed by the rest of the atoms. Therefore, the formulae $[Co(O_2CO)_3]^{3-}$ and $[Fe(O_2C_2O_2)_3]^{3-}$ imply that the carbonate and oxalate ligands are chelated to the Co(III) and Fe(III) centres respectively. Such notation allows us to easily distinguish between complexes in which the ligands act as chelates and, for example, the monodentate carbonate ligand found in $[Co(NH_3)_5OCO_2]^+$.

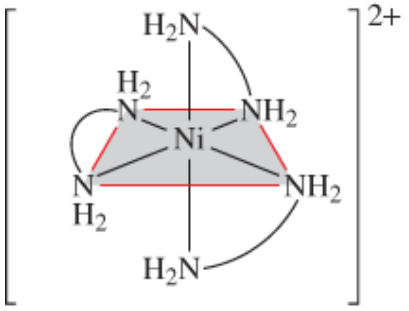
Structures of transition metal complexes

Transition metal complexes exhibit a huge variety of structures, as is to be expected when the central metal ion can be surrounded by anything from one to nine monodentate ligands. Central to the structure adopted by any transition metal complex is the **coordination number** of the metal ion. This is defined as the number of donor atoms directly attached to the metal ion. For example, the complex $[CuCl_4]^{2-}$ has four chloride ligands bound to a Cu(II) ion, so the coordination number of the metal ion in this complex is 4; we also say that the metal ion is 4-coordinate. Similarly, the complex $[Co(NH_3)_6]^{3+}$ contains a 6-coordinate Co(III) ion bonded to the N atoms of the six surrounding NH_3 ligands. The coordination number of a metal ion may not be so obvious when the metal complex contains polyden-tate

ligands. For example, the Ni(II) ion in $[Ni(en)_3]^{2+}$ (figure 13.12) is 6-coordinate, not 3-coordinate, as each en ligand contains two donor atoms, meaning that the Ni(II) ion is bound to six N atoms. A similar argument can be used to show that the Co(III) ion in $[Co(EDTA)]^-$ (figure 13.6) is also 6-coordinate. The most common coordination number among transition metal complexes is 6, while 4-coordinate complexes are the next most common. Certain geometries are associated with each coordination number, and these are outlined on the following pages.



$[Ni(OH_2)_6]^{2+}$ complex with monodentate ligands



$[Ni(en)_3]^{2+}$ complex with bidentate ligands

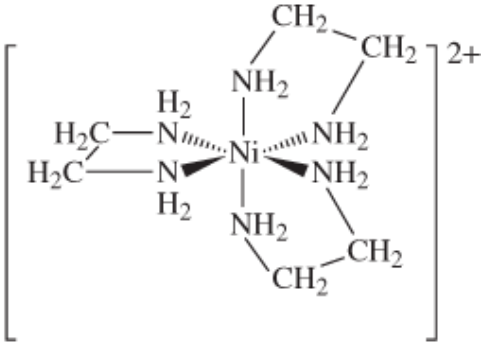


FIGURE 13.12 Octahedral complexes. Complexes with this geometry can be formed with either monodentate ligands, such as water, or polydentate ligands, such as ethylenediamine (en). To simplify drawing the ethylenediamine complex, the two methylene groups joining the donor nitrogen atoms in the ligand, $—CH_2—CH_2—$, are represented as the curved line between the N atoms. Also notice that the nitrogen atoms of the bidentate ligand span adjacent positions within the octahedron, as the methylene chain is not long enough to allow them to span opposite positions.

Coordination number 6

Most 6-coordinate complexes adopt an **octahedral** geometry, in which the six ligand donor atoms are positioned at the vertices of an octahedron (figure 13.13). The octahedron is so named because it contains eight faces. The two ligands in the plane of the page are called the **axial** ligands, while the remaining four are called the **equatorial** ligands.

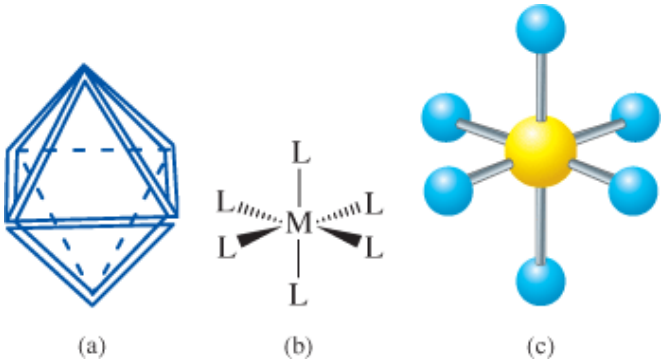


FIGURE 13.13

(a) An octahedron,

(b) a structural diagram and

(c) a ball-and-stick representation of an octahedral ML_6 complex. Note that each ligand is situated at one of the six vertices of the octahedron.

Such an arrangement minimises ligand-ligand repulsions by placing the ligands as far away as possible from each other, and this geometry is in fact that predicted by VSEPR theory (chapter 5, pp. 176-82). The octahedral geometry can accommodate both monodentate and polydentate ligands, as shown in figure 13.12.

Coordination number 4

VSEPR predicts that a tetrahedral geometry is favoured for a coordination number of 4, but both **tetrahedral** and **square planar** geometries are found for 4-coordinate complexes, and these are illustrated in figures 13.14 and 13.15.

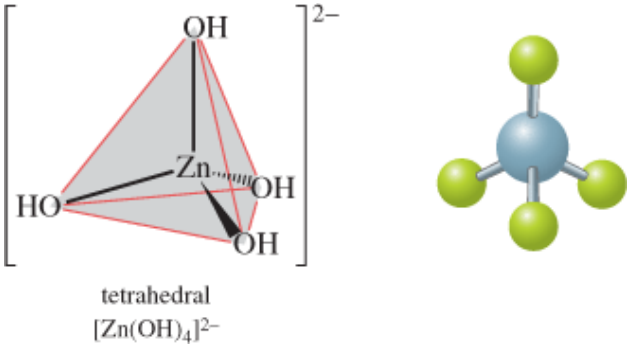


FIGURE 13.14 Tetrahedral geometry. $[Zn(OH)_4]^{2-}$ adopts a tetrahedral structure.

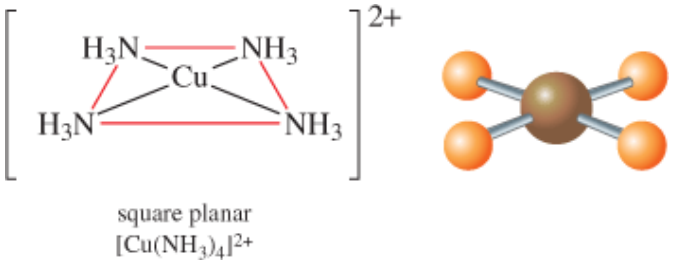


FIGURE 13.15 Square planar geometry. $[Cu(NH_3)_4]^{2+}$ adopts a square planar structure.

Tetrahedral geometries are often observed for complexes of d^{10} metal ions such as Cu(III) and Zn(II), while square planar complexes are often formed by Ni(II), Pt(II) and Au(III) metal ions with d^8 electron configurations. In fact, a

perfect tetrahedral or square planar geometry is rarely observed, and many 4-coordinate complexes adopt a geometry intermediate between the two.

Coordination number 5

This is probably the most important coordination number following 6 and 4. There are two possible geometries for 5-coordinate complexes: **trigonal bipyramidal** and **square pyramidal**, which are illustrated in figure 13.16.

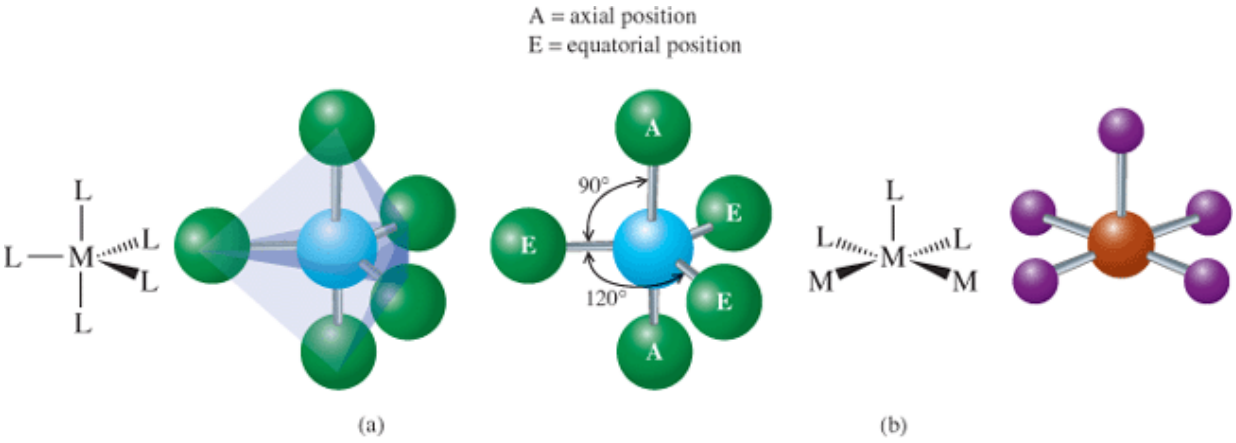


FIGURE 13.16 (a) Trigonal bipyramidal and (b) square pyramidal geometries found in 5-coordinate complexes.

Trigonal bipyramidal geometry is predicted on the basis of VSEPR, but, as we found for 4-coordinate complexes, VSEPR is of limited use when applied to transition metal complexes, especially where the metal ion does not have a d^0 or d^{10} configuration. For example, the $[CuCl_5]^{3-}$ anion is trigonal bipyramidal, while the $[Ni(CN)_5]^{3-}$ anion in the complex $[Cr(en)_3]$ $[Ni(CN)_5]$ simultaneously displays both square pyramidal and trigonal bipyramidal geometries in the same compound.

It is common to refer to the ligands pointing above and below the trigonal plane in a trigonal bipyramidal complex as axial, while the remaining three ligands are called equatorial.

Isomerism in transition metal complexes

We were first introduced to the concept of isomerism in chapter 2, where we discussed constitutional isomers of alkanes. There are a number of different types of isomerism in transition metal complexes, some of which are detailed on the following pages.

Structural isomerism

Structural isomers are molecules with the same molecular formula but with the constituent atoms joined together in different ways. In coordination chemistry, we will consider four types of structural isomerism.

Ionisation isomerism

The purple complex $[CoBr(NH_3)_5]SO_4$ and the red complex $[Co(NH_3)OSO_3]Br$ (figure 13.17) are examples of **ionisation isomers**. The former has bromide acting as a ligand and sulfate as the counterion, while the roles are reversed in the latter, with sulfate coordinated to the metal ion and bromide acting as the counterion.

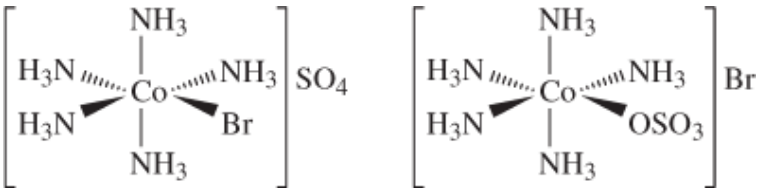


FIGURE 13.17 The ionisation isomers $[CoBr(NH_3)_5]SO_4$ and $[Co(NH_3)OSO_3]Br$.

Hydrate isomerism

This is similar to ionisation isomerism, and results from the different numbers of water molecules that can be coordinated to a metal ion. For example, there are three complexes with the empirical formula $CrCl_3 \cdot 6H_2O$:

- $[Cr(OH_2)_6]Cl_3$ (purple)
- $[CrCl(OH_2)_5]Cl_2 \cdot H_2O$ (blue-green)
- $[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$ (green).

These complexes are **hydrate isomers**.

Coordination isomerism

Coordination isomers result when ligands are exchanged between a complex cation and a complex anion of the same coordination compound. For example, $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are coordination isomers.

Linkage isomerism

Ligands containing more than one donor atom can potentially form **linkage isomers**, which result from the different possible ways in which the ligand can bind to the metal ion. For example, the thiocyanate ligand, NCS^-, can bind using a lone pair on either the N atom, to give the brick-red $[CoNCS(NH_3)_5]^{2+}$ ion, or on the S atom, to give the purple complex $[Co(NH_3)_5SCN]^{2+}$. These complexes are called linkage isomers. The NO_2^- ligand can also form linkage isomers by bonding to a transition metal ion either through the N atom or one of the O atoms. Ligands, such as NCS^- and NO_2^-, with two or more different potential donor atoms are called **ambidentate**.

Stereoisomerism

Stereoisomers are isomers having the same connections between the constituent atoms but different arrangements of those atoms in space. We met an example of stereoisomerism in chapter 2 (p. 42) where we found that the two methyl groups in 1,2-dimethylcyclopentane could either be on the same side or different sides of the five-membered ring; we designated the two possible isomers as *cis* and *trans* respectively. A similar type of isomerism can exist in transition metal complexes and is typified by the square planar complex $[PtCl_2(NH_3)_2]$. The two possible ***cis*–*trans* isomers** of the square planar complex with the empirical formula $[PtCl_2(NH_3)_2]$ are shown in figure 13.18.

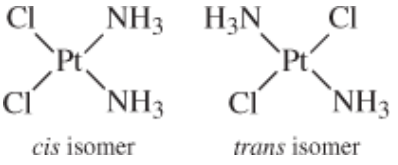


FIGURE 13.18 *cis-trans* isomers of $[Pt(NH_3)_2Cl_2]$.

The ***cis* isomer** has the identical ligands adjacent to each other, while the ***trans* isomer** has them opposite each other. In identifying and naming isomers, *cis* means 'on the same side', and *trans* means 'on opposite sides' we call these two isomers *cis*-$[PtCl_2(NH_3)_2]$ and *trans*-$[PtCl_2(NH_3)_2]$. The two isomers have distinctly different chemical properties, most interesting of which is the fact that the ***cis* isomer** (common name *cisplatin*) is a particularly effective chemotherapy agent against certain types of cancer, while the *trans* isomer shows little activity (see Chemistry

Research on the next page). It should be noted that a tetrahedral arrangement of the ligands around the Pt ion would not give rise to stereoisomers, and this can be used to differentiate between square planar and tetrahedral geometries.

Chemistry Research

Platinum-based anticancer drugs

Professor Trevor Hambley, University of Sydney

At the beginning of the 1970s, 70% of those who developed testicular cancer died within one year, but by the end of that decade this proportion was down to 10% and it is now effectively zero.

The anticancer drug responsible for this dramatic turnaround is known as cisplatin, *cis*-$[PtCl_2(NH_3)_2]$, a very simple coordination complex (see figure 13.19) but the basis of the most widely used group of anticancer drugs in the world. About half of the cancer patients who receive chemotherapy have a platinum-based drug included in their treatment.

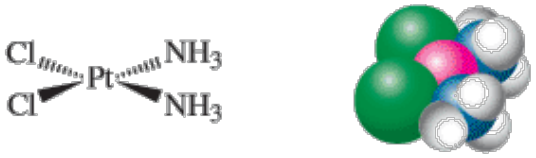


FIGURE 13.19 Models of cisplatin.



FIGURE 13.20 Cyclist Lance Armstrong developed testicular cancer that spread to his brain. Following treatment with cisplatin, he went on to win seven Tours de France, making him the most successful cyclist in this famous race.

Like nearly all anticancer drugs, cisplatin causes serious side effects that limit its use and effectiveness. The research group led by Professor Trevor Hambley is working to develop new, less toxic analogues of the existing drug. They are taking two approaches: the use of complexes in the more inert Pt(IV) oxidation state, and more effective delivery of platinum drugs to tumours rather than to healthy tissues. Pt(II) complexes, such as cisplatin, are 4-coordinate and generally highly reactive, resulting in many reactions in the bloodstream. This leads to side effects and loss of up to 95% of the drug. Pt(IV) complexes are 6-coordinate and much less reactive with molecules in the bloodstream.

Professor Hambley's group has been working to modify Pt(IV) complexes by varying the types of ligand so that the complexes are inert enough to survive in the bloodstream and become active (on reduction to Pt(II)) only after they have been taken up throughout the cells that make up the tumour. His group has also attached fluorescent ligands to platinum complexes to monitor their uptake and distribution in tumours and to help understand the lack of anticancer activity of the geometric isomer of cisplatin, *trans*-$[PtCl_2(NH_3)_2]$.

Octahedral complexes can also show *cis–trans* isomerism. While there are no such possible isomers of complexes of the type $[ML_6]$ and $[ML_5X]$, *cis* and *trans* isomers are possible for $[ML_4X_2]$ species, with the classic example being the complexes *cis*-$[CoCl_2(NH_3)_4]^+$ (violet) and *trans*-$[CoCl_2(NH_3)_4]^+$ (green). The structures of these complexes are given in figure 13.21.

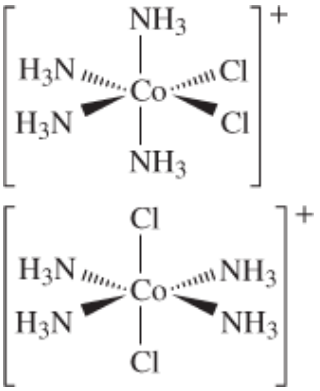


FIGURE 13.21 The structures of the isomers *cis*-$[CoCl_2(NH_3)_4]^+$(top) and *trans*-$[CoCl_2(NH_3)_4]^+$ (bottom).

Note that these are the only possible isomers of this complex; any other arrangement of the ligands is identical to one of the two structures in figure 13.21.

Isomers are also possible for octahedral complexes with the formula $[ML_3X_3]$ and these are depicted in figure 13.22 for the complex $[CoCl_3(NH_3)_3]$.

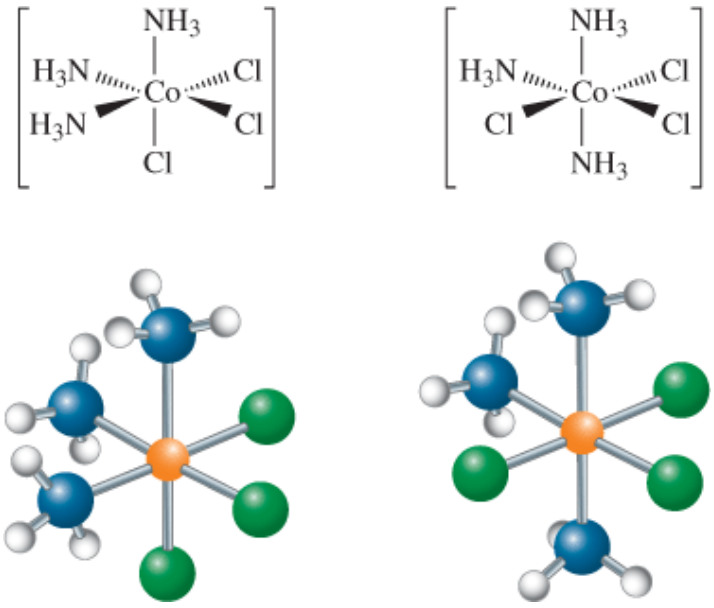


FIGURE 13.22 The *fac* isomer (left) and *mer* isomer (right) of $[CoCl_3(NH_3)_3]$.

These two isomers are designated ***mer* (meridional)** and ***fac* (facial)**. The *mer* isomer has the two sets of three identical ligands lying in perpendicular planes around the meridian of the complex, while the *fac* isomer has each set of three ligands occupying a face of the octahedron, so that the two sets of ligands lie in parallel planes. Again, these are the only possible geometric isomers of these complexes, and there is no other arrangement of ligands that is different from those in figure 13.22.

We will see in chapter 17 that another type of stereoisomerism exists in transition metal complexes containing polydentate ligands. These complexes, with mirror images that are not superimposable on each other, are said to be chiral.

WORKED EXAMPLE 13.4

Identifying and drawing stereoisomers

Draw all the possible stereoisomers of the following transition metal complexes.

(a) $[Co(NH_3)_5OH_2]^{3+}$ (The complex is octahedral.)

(b) $[RhBr_2(NH_3)_4]^+$ (The complex is octahedral.)

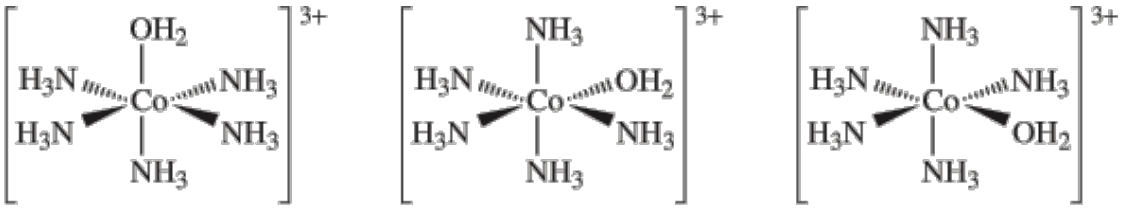
(c) $[PtBrCl(NH_3)(OH_2)]$ (The complex is square planar.)

Analysis

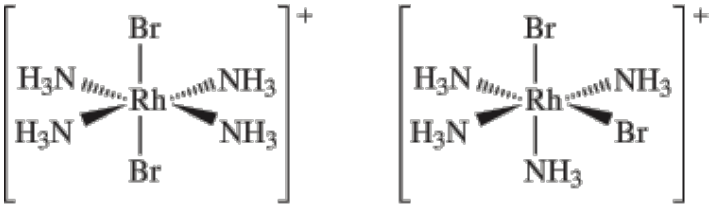
We need to see if changing the relative positioning of the ligands around the central metal ion gives rise to different complexes. If so, then stereoisomers are present.

Solution

(a) In this complex, we have five NH_3 ligands and a single OH_2 ligand arranged in an octahedron around the metal ion. As all the positions in an octahedron are equivalent, we can place the unique aqua ligand anywhere, and its position relative to the five NH_3ligands is the same; there are always four *cis* neighbouring NH_3 ligands and one *trans* NH_3 ligand opposite. The three depictions of the cation below are therefore identical and hence there are no stereoisomers of this complex.

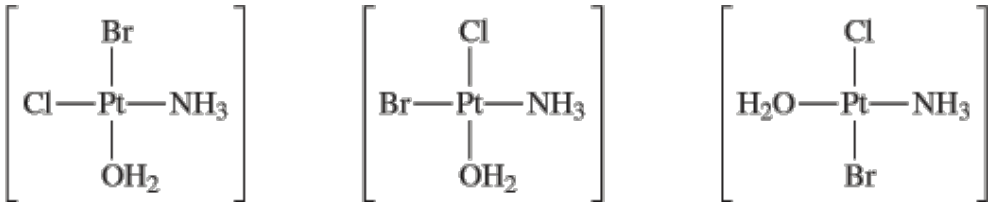


(b) In this complex, we have a set of four NH_3 ligands and a set of two Br^- ligands. In an octahedron, we can place the two Br^- ligands so that they are either adjacent to each other, or on opposite sides from each other. This gives rise to two different complexes, and therefore these are stereoisomers. An inspection of the depictions below should convince you that these are the only stereoisomers possible.

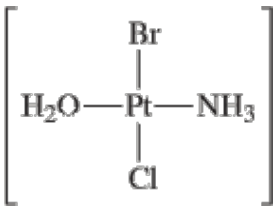


trans *cis*

(c) In this complex, we have four different ligands arranged in a square plane around the metal ion. Therefore, you can anticipate that there should be a number of possible stereoisomers. Begin by drawing one, and then systematically change the positions of the ligands until you obtain no further different complexes. To do this, keep one ligand in the same position and look at the number of different possible ligands that can be placed *trans* to this. You will find that, no matter which ligand you pick, there are only three possible different arrangements, as shown below.



You might think that the following structure is not the same as any of the above three.



However, if you rotate it 180° around the H_2O—Pt—NH_3 axis, you will obtain the third structure above.

PRACTICE EXERCISE 13.4

Determine the number of possible stereoisomers of the following complexes, and sketch their structures.

(a) $[PtBrCl_3]^{2-}$ (The complex is square planar.)

(b) $[CoCl_2(PPh_3)_2]$ (The complex is tetrahedral; note that PPh_3 is shorthand for $P(C_6H_5)_3$, a monodentate phosphane ligand.)

(c)

$[CoCl(NH_3)_3(OH_2)_2]^{2+}$ (The complex is octahedral.)

The nomenclature of transition metal complexes

Chapter 2 introduced the IUPAC rules for naming simple organic compounds and we found that such compounds were named on the basis of the longest carbon chain in the molecule. We cannot use these rules for naming coordination compounds so a separate nomenclature system is necessary. The rules are as follows:

1. Cationic species are named before anionic species. This is the same rule that applies to other ionic compounds, such as NaCl, where we name the cation first followed by the anion (e.g. sodium chloride).
2. The names of anionic ligands always end in the suffix *-o*. Ligands with names ending in *-ide*, *-ite* or *-ate* have this suffix changed to *-ido*, *-ito and -ato*, respectively.

Anion		Ligand name
chloride	Cl^-	chlorido
bromide	Br^-	bromido
cyanide	CN^-	cyanido
oxide	O^{2-}	oxido
carbonate	CO_3^{2-}	carbonato
thiosulfate	$S_2O_3^{2-}$	thiosulfato
thiocyanate	SCN^-	thiocyanato-κ*S* (when bonded through sulfur) thiocyanato-κ*N* (when bonded through nitrogen)
oxalate	$C_2O_4^{2-}$	oxalato
nitrite	NO_2^-	nitrito-κ*O* (when bonded through oxygen) nitrito-κ*N* (when bonded through nitrogen)

When a choice of donor atom exists, the coordinated atom is italicised and preceded by the Greek letter *kappa*, κ.

3. A neutral ligand is usually given the same name as the neutral molecule. Thus the mol ecule ethylenediamine, when serving as a ligand, is called ethylenediamine in the name of the complex. Three very important exceptions to this, however, are water, ammonia and carbon monoxide. These are named as follows when they serve as ligands:
   - H_2O aqua
   - NH_3 ammine (note the double m)
   - CO carbonyl.
4. When there is more than one of a particular ligand, their number is specified by the prefixes *di-* = 2, *tri-* = 3, *tetra-* = 4, *penta-* = 5, *hexa-* = 6 etc. If the name of the ligand already incorporates one of these prefixes (such as ethylenediamine), enclose the ligand in parentheses and use the following prefixes instead: *bis-* = 2, *tris-* = 3, *tetrakis-* = 4. Following this rule, the presence of two Cl^- ligands in a complex would be indicated as *dichlorido-*. If two ethylenediamine ligands are present, we would write bis(ethylenediamine).
5. In the name of the complex, the ligands are named first, in alphabetical order without regard to charge, followed by the name of the metal. For example, the ligand set in the neutral complex $[Co(CN)Cl_2(NH_3)_3]$ would be named as *triamminedichloridocyanido-*: *triammine-* for the three NH_3 ligands, *dichlorido-* for the two Cl^- ligands and *cyanido-* for the CN^- ligand. Notice that, in alphabetising the names of the ligands, we ignore the prefixes *tri-* and *di-*. Thus *triammine-* is written before *dichlorido-* because *ammine-* precedes *chlorido-* alphabetically. For the same reason, *dichlorido-* is written before *cyanido-*.
6. Negative (anionic) complex ions always end in the suffix *-ate*. This suffix is appended to the English name of

the metal atom in most cases. However, if the name of the metal ends in-*ium* or -*ese*, the ending is dropped and replaced by -*ate*.

Metal	Metal as named in an anionic complex
chromium	chromate
manganese	manganate
nickel	nickelate
cobalt	cobaltate
zinc	zincate
platinum	platinate
vanadium	vanadate

For metals with symbols derived from their Latin names, the suffix -*ate* is appended to the Latin stem.

Metal	Stem	Metal as named in an anionic complex
iron	ferr-	ferrate
copper	cupr-	cuprate
silver	argent-	argentate
gold	aur-	aurate

Mercury, antimony and tungsten are the exceptions; in an anion, they are named mercurate, antimonate and tungstate, respectively. For neutral or positively charged complexes, the metal is always specified with the English name for the element, without any suffix.

7. The oxidation state of the metal in a complex may be written in Roman numerals within parentheses following the name of the metal, or the charge on the coordination entity may be specified in Arabic numbers followed by the charge sign, all enclosed in parentheses. For example:
   - $[Co(NH_3)_6]^{3+}$ is the hexaamminecobalt(III) ion or the hexaamminecobalt(3+) ion.
   - $[CuCl_4]^{2-}$ is the tetrachloridocuprate(II) ion or the tetrachloridocuprate(2-) ion.

   Notice that there are no spaces between the name of the ligands and the name of the metal, and there is no space between the name of the metal and the parentheses that enclose the oxidation state expressed in either Roman or Arabic numerals.
8. The number of counterions need not be specified, as it can be inferred from the charge on the complex ion. For example, $K_4[NiCl_6]$ would be named potassium hexachloridonickelate(II), not tetrapotassium hexachloridonickelate(II). Note also that there is a space between the names of the cation and anion.
9. Include any stereochemical descriptors (e.g. *cis*, *trans*, *mer*, *fac*) at the start of the name, italicised and hyphenated. The following are some additional examples. Study them carefully to see how the rules given on pp. 528–30 apply, then try worked examples 13.5 and 13.6 and practice exercises 13.5 and 13.6

$[Ni(CN)_4]^{2-}$	tetracyanidonickelate(II) ion
$K_3[CoCl_6]$	potassium hexachloridocobaltate(III)
$[CoCl_2(NH_3)_4]^{-}$	tetraamminedichloridocobalt(III) ion
$[Ag(NH_3)_2]^{+}$	diamminesilver(I) ion
$[Ag(S_2O_3)_2]^{3-}$	dithiosulfatoargentate(I) ion
$[Mn(en)_3]Cl_2$	tris(ethylenediamine) manganese(II) chloride
$[PtCl_2(NH_3)_2]$	diamminedichloridoplatinum(II)

Naming Coordination Complexes

What is the IUPAC name for each of the following coordination compounds?

(a) $[Ni(OH_2)_6]SO_4$

(b) $[CrCl_2(en)_2]Cl$

(c) $K_2[CoCl_4]$

Analysis

We simply follow the guidelines given on pp. 528–30 for naming coordination compounds.

Solution

(a) The nickel ion is surrounded by six ligands, so we use the prefix *hexa-*. The ligands are water molecules, which have the special name *aqua*, so the ligand set is named *hexaaqua-*. The complex is cationic, and the 2- charge on sulfate means that the cation has a 2+ charge. As the aqua ligands are neutral, the oxidation state of Ni is Ni(II). Therefore, the name of the complex is hexaaquanickel(II) sulfate.

(b) The chromium ion is coordinated to two en ligands and two Cl^- ligands. Naming the ligands alphabetically puts the Cl^- ligands first, followed by the en ligands. The two Cl^- ligands are named *dichlorido-*, while, as we have seen in the guidelines, two en ligands are named bis(ethylenediamine). Hence, the ligand set is named dichloridobis(ethylenediamine). The presence of a single Cl^- counterion means that the charge on the complex cation is 1+; the oxidation state of the metal ion must be Cr(III), as it has two Cl^- ions coordinated to it. Therefore, the name of the complex is dichloridobis(ethylenediamine) chromium(III) chloride.

(c) The cation, potassium, is named first. The complex anion contains a cobalt ion surrounded by four Cl^- ligands, so the ligand set is named *tetrachlorido-*. The complex is an anion with a 2- charge, so the oxidation state of the metal ion is Co(II). Since the complex is an anion, the metal is given the suffix *-ate*. Therefore, the name of the complex is potassium tetrachloridocobaltate(II).

Is our answer reasonable?

Verify that the numerical prefixes give the correct total number of ligands, that the ligands are named alphabetically and that the overall species is charge neutral. This should ensure that your answer is correct.

PRACTICE EXERCISE 13.5

Name the following coordination compounds.

(a) $[Co(NH_3)_5(OCO_2)]NO_3$

(b) $[Mo(CO)_3(NH_3)_3]$

(c) $[Cr(OH_2)_5OH]Cl_2$

(d) $K_3[Fe(CN)_6]$

(e) $[CrCl_2(en)_2]_2SO_4$

Having learned how to name coordination compounds, you should be able to determine the formula from the name.

WORKED EXAMPLE 13.6

Writing a Formula from the Name of a Coordination Compound

Determine the formulae of the following coordination compounds.

(a) *fac*-triamminetriiodidoruthenium(III)

(b) sodium hexacyanidoferrate(II)

Analysis

Construct the formula by breaking the name down, one piece at a time. Begin by determining the number and type of ligands around the metal ion. From these, and the oxidation state of the metal ion, you can then determine the correct number of counterions (if any).

Solution

(a) The prefix *triammine*- corresponds to three NH_3 ligands and *triiodido*- to three I^- ligands. Therefore, there are six ligands surrounding the Ru(III) ion. The *fac*- prefix means that each set of three ligands is arranged such that they occupy a face of an octahedron. The formula of the complex is *fac*-$[RuI_3(NH_3)_3]$.

(b) The prefix *hexacyanido*- means that there are six CN^- ligands around the Fe(II) ion, and this gives the anion a charge of 4-. Sodium is the cation, so four of these are required to balance the charge on the complex anion. The formula of the complex is $Na_4[Fe(CN)_6]$.

Is our answer reasonable?

Conversion from the name to the formula is usually fairly straightforward, and our answers do correspond to the names. As shown in (b), make sure you include the correct number of cations and anions to ensure charge neutrality.

PRACTICE EXERCISE 13.6

Determine the formulae of the following coordination compounds.

(a) tris(ethylenediamine) ruthenium(II) chloride

(b) potassium hexachloridoplatinate(IV)

(c) ammonium diaquatetracyanidoferrate(II)

(d) *trans*-dichloridobis(ethylenediamine) cobalt(III) chloride

The chelate effect

In chapter 11, we quantified the strength of Brønsted-Lowry acids using K_a, the equilibrium constant for donation of a proton to water. As the formation of transition metal complexes from their constituent metal ions and ligands is also an equilibrium process, we can use an analogous method to quantify the extent of such reactions. Consider, for example, the formation of a hypothetical complex $[ML_n]^{x+}$ from the metal ion, M^{x+}, and the ligands, nL, in aqueous solution according to the equation:

$$M^{x+}(aq) + nL(aq) \rightleftharpoons [ML_n]^{x+}(aq)$$

(Note that, for simplicity, we have assumed that the ligand is neutral.) The equilibrium constant for this process, which we can write in the same way as we have done in preceding chapters, is called the **cumulative formation constant (β_n)**. Therefore, for the above equilibrium:

$$\beta_n = \frac{\left[ML_n^{x+}(aq)\right]}{\left[M^{x+}(aq)\right][L(aq)]^n}$$

Obviously, the larger the value of β_n, the further to the right-hand side the equilibrium position lies, and therefore the more complete the formation of the complex. Table 13.3 gives values of β_n for a number of transition metal complexes, and you can see that, in all cases, the equilibrium for the formation reaction lies very much towards products. However, there is a range of nearly 44 orders of magnitude in the values of β_n, showing that the formation reactions of some complexes proceed further towards completion than others.

TABLE 13.3 β_n values for a variety of transition metal complexes containing monodentate and polydentate ligands at 25 °C

Ligand	Metal	Equilibrium	*n*	β_n
NH_3	Co(II)	$Co^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Co(NH_3)_6]^{2+}(aq)$	6	5.0×10^4
	Co(III)	$Co^{3+}(aq) + 6NH_3(aq) \rightleftharpoons [Co(NH_3)_6]^{3+}(aq)$	6	4.6×10^{33}
	Ni(II)	$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq)$	6	2.0×10^8
	Cu(II)	$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$	4	1.1×10^{13}
en	Co(II)	$Co^{2+}(aq) + 3en(aq) \rightleftharpoons [Co(en)_3]^{2+}(aq)$	3	1.0×10^{14}
	Co(III)	$Co^{3+}(aq) + 3en(aq) \rightleftharpoons [Co(en)_3]^{3+}(aq)$	3	5.0×10^{48}
	Ni(II)	$Ni^{2+}(aq) + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq)$	3	4.1×10^{17}
	Cu(II)	$Cu^{2+}(aq) + 2en(aq) \rightleftharpoons [Cu(en)_2]^{2+}(aq)$	2	4.0×10^{19}
$EDTA^{4-}$	Co(II)	$Co^{2+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Co(EDTA)]^{2-}(aq)$	1	2.8×10^{16}
	Co(III)	$Co^{3+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Co(EDTA)]^{-}(aq)$	1	2.5×10^{41}

Inspection of the data in table 13.3 reveals some interesting trends. For example, coordination of the same ligand to different metal ions gives very different β_n values, showing that a given ligand binds more strongly to some metal ions than to others. Ligands can also show different affinities for various oxidation states of the same metal ion. For example, notice the very different values for the Co(II) and Co(III) complexes listed, with Co(III) favoured in each case by a factor of up to 10^{34}. Of particular interest are the values for complexes of the monodentate ligand NH_3 and the bidentate ligand en. For example, $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ have very similar structures, with Nibonded to six N atoms in both cases, but β_3 for $[Ni(en)_3]^{2+}$ is larger than β_6 for $[Ni(NH_3)_6]^{2+}$ by a factor of 10^9. This trend is repeated in all of the complexes of NH_3 and ethylenediamine listed in table 13.3 and is found to be fairly general for complexes containing these ligands.

The larger values of β_n for complexes containing polydentate ligands than for analogous complexes containing monodentate ligands is called the **chelate effect**, and this is best explained with reference to the *dissociation*, rather than formation, reactions of the two Nicomplexes discussed above:

$$[Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l) \rightleftharpoons [Ni(OH_2)_6]^{2+}(aq) + 6NH_3(aq) \quad K_{Ni(NH_3)_6^{2+}} = \frac{\left[Ni(OH_2)_6^{2+}\right][NH_3]^6}{\left[Ni(NH_3)_6^{2+}\right]} = 5.0 \times 10^{-9} \left(25.0\,^{\circ}C\right)$$

$$[Ni(en)_3]^{2+}(aq) + 6H_2O(l) \rightleftharpoons [Ni(OH_2)_6]^{2+}(aq) + 3en(aq) \quad K_{[Ni(en)_3]^{2+}} = \frac{\left[Ni(OH_2)_6^{2+}\right][en]^3}{\left[Ni(en)_3^{2+}\right]} = 2.4 \times 10^{-18} \left(25.0\,^{\circ}C\right)$$

Note that the expressions for K are simply the reciprocals of those for β_n for each complex. Therefore, the values of K are simply $1/\beta_n$ for the respective complexes.

Recall from chapter 9 (p. 362) that $\Delta G^{\ominus}$ for a reaction is related to the equilibrium constant for that reaction by the equation $\Delta G^{\ominus} = -RT\ln K$. Therefore, a large negative value of $\Delta G^{\ominus}$ leads to a large equilibrium constant for the reaction, meaning that the forward reaction will proceed essentially to completion. We also learned in chapter 8 (p. 326) that $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$, and that the relative magnitudes and signs of both $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are crucial in determining the value and sign of $\Delta G^{\ominus}$, and hence the value of K. If we examine the two dissociation reactions above, we can see that both involve breaking six Ni—N bonds and this should result in similar positive values of $\Delta H^{\ominus}$ for the two reactions. However, the two reactions differ in their values of $\Delta S^{\ominus}$. While dissociation of $[Ni(NH_3)_6]^{2+}$ gives no net change in the number of species in solution, and would thus be expected to have a $\Delta S^{\ominus}$ value around zero, dissociation of $[Ni(en)_3]^{2+}$ gives a net decrease in the number of species in solution, and hence has a negative $\Delta S^{\ominus}$ value. Remembering that the $\Delta H^{\ominus}$ values are similar, we therefore expect $\Delta G^{\ominus}$ for dissociation of $[Ni(NH_3)_6]^{2+}$ to be smaller and less positive than that for $[Ni(en)_3]^{2+}$. This means that $K_{[Ni(NH_3)_6]^{2+}}$ should be greater than $K_{[Ni(en)_6]^{2+}}$, as is indeed found.

We can also rationalise the chelate effect by considering the mechanisms of the dissociation reactions. The initial mechanistic process that occurs in both cases is cleavage of a single Ni—N bond; in the case of $[Ni(NH_3)_6]^{2+}$, this leads to the loss of one NH_3 ligand, which is immediately replaced by a water molecule:

$$[Ni(NH_3)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Ni(NH_3)_5(OH_2)]^{2+}(aq) + NH_3(aq)$$

However, cleavage of an Ni—N bond in $[Ni(en)_3]^{2+}$ leads to a situation in which one end of one of the en ligands becomes detached from the complex but remains close to the metal ion because the other donor atom of the en ligand is still bonded to the metal ion. Therefore, there is a significant probability that the 'dangling' donor atom can reattach to the metal ion before the other end of the ligand detaches (figure 13.23); from this, it is apparent that it should be more difficult to lose a bidentate ligand than a monodentate ligand.

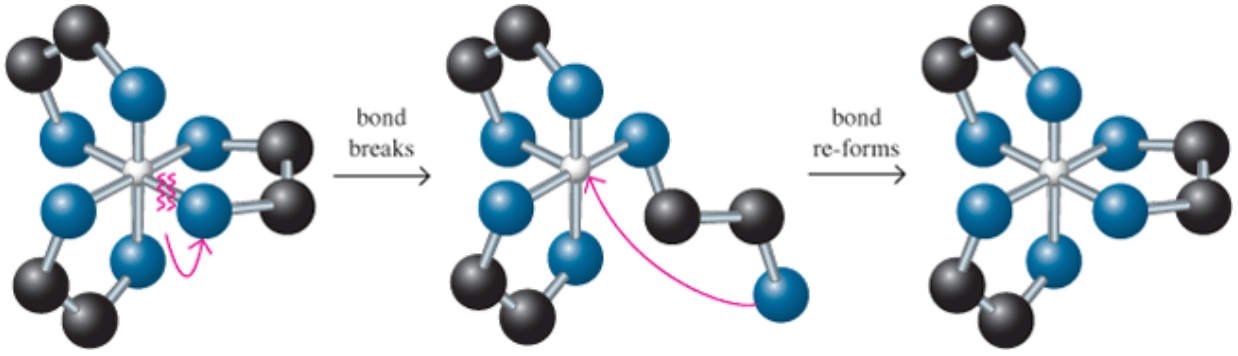


FIGURE 13.23 The chelate effect. Breaking one Ni—N bond in $[Ni(en)_3]^{2+}$ leaves the en ligand dangling but 'tethered' to the metal by the second nitrogen atom (hydrogen atoms have been omitted for clarity).

The loss of a ligand becomes progressively more difficult as the number of donor atoms increases. Therefore, in general, the more donor atoms a ligand contains, the larger is the value of β_n for its complexes.

We can obtain some appreciation of the magnitudes of β_n values by carrying out calculations similar to those we have performed for other equilibrium systems in earlier chapters. For example, worked example 13.7 looks at a reaction

used to extract gold from ores.

WORKED EXAMPLE 13.7

Calculations Involving β_n

The small amounts of gold in low-grade ores (figure 13.24) can be extracted using a combination of oxi dation and complexation. Elemental gold is oxidised to Au^+, which forms a complex with cyanide anions according to the equation:



FIGURE 13.24 Gold in low-grade ores can be extracted using oxidation and complexation.

$$Au^+(aq) + 2CN^-(aq) \rightleftharpoons [Au(CN)_2]^-(aq) \quad \beta_2 = 2 \times 10^{38}$$

Suppose that a sample of ore containing 2.5×10^{-3} mol of gold is extracted with 1.0 L of 4.0×10^{-2} m aqueous KCN solution under oxidising conditions. Calculate the concentrations of the three species involved in the complexation equilibrium.

Analysis

We treat this in a similar fashion to problems we have seen in earlier chapters by using a concentration table. However, in this case, we assume complete initial formation of $[Au(CN)_2]^-$. We are justified in this assumption because of the enormous value of β_2. We then realise that a very small amount of Au^+ and CN^- will be formed by dissociation of $[Au(CN)_2]^-$ and, using the concentration table and the value of β_2, we can determine the equilibrium concentrations.

Solution

We assume all of the gold is initially converted to $[Au(CN)_2]^-$, so our initial concentrations for the concentration table are:

$$\begin{aligned} [Au(CN)_2]^- &= 2.5 \times 10^{-3} M \\ [Au^+] &= 0 M \end{aligned}$$

We obtain the starting $[CN^-]$ from $[CN^-]_{added} - [CN^-]_{converted\ to\ [Ag(CN)_2^-]}$, so:

$$\begin{aligned} [CN^-] &= \left[4 \times 10^{-2} - (2 \times 2.5 \times 10^{-3})\right] M \\ &= 3.5 \times 10^{-2} M \end{aligned}$$

The system then comes to equilibrium through dissociation of $[Au(CN)_2]^-$ to form both Au^+ and CN^-. The concentration table is then:

	$Au^+(aq) + 2CN^-(aq) \rightleftharpoons [Au(CN)_2]^-$

Initial concentration (m)	0	3.5×10^{-2}	2.5×10^{-3}
Change in concentration (m)	$+x$	$+2x$	$2 - x$
Equilibrium concentration (m)	x	$3.5 \times 10^{-2} + 2x$	$2\ 2.5 \times 10^{-3} - x$

As $\beta_2 = 2 \times 10^{38}$, we know that the dissociation of $[Au(CN)_2]^-$ will proceed only to a tiny extent. We can, therefore, assume with confidence that $(2.5 \times 10^{-3} - x) \approx 2.5 \times 10^{-3}$ and $(3.5 \times 10^{-2} + 2x\ 2) \approx 3.5 \times 10^{-2}$. We can now substitute these values into the expression for β_2 and solve for the only remaining unknown, $[Au^+]$:

$$\beta_2 = \frac{[Au(CN)_2]^-}{[Au^+][CN^-]^2} = \frac{2.5 \times 10^{-3}}{[Au^+](3.5 \times 10^{-2})^2} = 2 \times 10^{38}$$

Therefore:

$$\begin{aligned} [Au^+] &= \frac{2.5 \times 10^{-3}}{(2 \times 10^{38})(3.5 \times 10^{-2})^2} \\ &= 1.0 \times 10^{-38}\,M \\ [CN^-] &= 3.5 \times 10^{-2}\,M \\ [Au(CN)_2]^- &= 2.5 \times 10^{-3}\,M \end{aligned}$$

The tiny value of $[Au^+]$ shows the extraordinarily high affinity of CN^- for Au^+ in aqueous solution.

Is our answer reasonable?

Owing to the large value of β_2, we expect an extremely low concentration of Au^+ in solution, which is what we have found. Our assumptions are therefore reasonable and formation of $[Au(CN)_2]^-$ is essentially complete.

PRACTICE EXERCISE 13.7

Dissolution of 0.275 g of silver nitrate in 0.85 L of 0.250 M ammonia results in the formation of the complex $[Ag(NH_3)_2]^+$ according to the equation:

$$Au^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \quad \beta_2 = 1.6 \times 10^7$$

Calculate the equilibrium concentrations of all species involved in the complexation equilibrium.

Inert and labile transition metal complexes

The magnitude of β_n for a complex is a measure of how far the formation reaction for that complex proceeds towards completion. For example, if β_n is small, the complex shows little tendency to form from the free metal ion and ligand(s); if β_n is large, the complex forms almost completely.

We might be tempted to say that the larger the value of β_n, the more *stable* the complex; this is true from a thermodynamic viewpoint, because the larger the value of β_n, the larger and more negative the value of $\Delta G^\ominus$ for the formation of a particular complex. However, we find that many complexes with large β_n values are, in fact, quite

unstable with respect to exchange of ligands. This is illustrated by the complex $[Ni(CN)_4]^{2-}$, for which $\beta_4 = 3.2 \times 10^{30}$. This extremely large value means that addition of CN^- to a solution containing Ni(II) ions results in essentially complete formation of $[Ni(CN)_4]^{2-}$. However, addition of $^{14}CN^-$ (cyanide containing a radioactive ^{14}C label) to a solution of $[Ni(CN)_4]^{2-}$ results in very rapid incorporation of $14CN^-$ into the complex, as shown in the following equation:

$$[Ni(CN)_4]^{2-} + {}^{14}CN \xrightarrow{\text{rapig}} \left[Ni({}^{14}CN)(CN)_3\right]^{2-} + CN^-$$

This means that the cyanide ligands in $[Ni(CN)_4]^{2-}$ are not bonded strongly to the Ni(II) ion, so they exchange very rapidly with added CN^-. We say that the $[Ni(CN)_4]^{2-}$ ion is **labile**, meaning that it undergoes rapid ligand exchange. $[Ni(CN)_4]^{2-}$ is, therefore, an example of a thermodynamically stable, but kinetically labile, transition metal complex. The opposite situation is observed for the Co(III) complex $[Co(NH_3)_6]^{3+}$. The equilibrium constant for the reaction:

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \rightleftharpoons [Co(OH_2)_6]^{3+} + 6NH_4^+$$

is of the order of 10^{25} at 25 °C, corresponding to a $\Delta G^{\ominus}$ value of -143 kJ mol^{-1}. This means that the $[Co(NH_3)_6]^{3+}$ ion is thermodynamically unstable with respect to formation of $[Co(OH_2)_6]^{3+}$ in acidic solution. Despite this, $[Co(NH_3)_6]^{3+}$ can be recovered unchanged after several days in 1.0 M H_3O^+, meaning that the NH_3 ligands cannot easily exchange with H_2O. We say that $[Co(NH_3)_6]^{3+}$ is **inert** to ligand substitution and, therefore, is an example of a thermodynamically unstable, but kinetically inert, transition metal complex. Most firstrow transition metal complexes are labile, but complexes containing metals with a d^3 or d^6 electron configuration are often inert, with Cr(III) and Co(III) being the classic examples of inert metal centres. It is important, therefore, that you are careful when using the word ‘stable’, and that you realise that thermodynamic stability and kinetic stability are entirely separate concepts.

Electrochemical aspects of transition metal complexes

Electrochemistry provides another convenient method of quantifying the thermodynamic stability of transition metal complexes. As we saw in chapter 12 (table 12.1), the reduction potentials of simple aqueous transition metal ions span a wide range of values and, therefore, electrochemical behaviour. Thus, the Ag^+(aq) ion is moderately oxidising $E^{\ominus}_{Ag^+/Ag} = +0.80\,V$ while the Cr^{3+}(aq) to ion shows neglibile oxidising ability $(E^{\ominus}_{Cr^+/Cr} = -0.74\,V)$. However, coordination of ligands to aqueous transition metal ions can result in the formation of complexes having very different electrochemical behaviours from those of the parent aqueous transition metal ions. The classic example of this is provided by the Co^{3+}(aq) (or $[Co(OH_2)_6]^{3+}$) ion. Under standard conditions in aqueous solution, this ion is extremely strongly oxidising $(E^{\ominus}_{Co^{3+}/Co^{2+}} = +1.9\,V)$, and as a result is generally stable only under ice-cold acidic conditions. However, replacement of the six H_2O ligands with six NH_3 or three ethylenediamine (en) ligands results in enormous stabilisation of the resulting $(E^{\ominus}_{[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}} = 0.1\,V)$ and $(E^{\ominus}_{[Co(en)_3]^{3+}/[Co(en)_3]^{2+}} = -0.25\,V)$ ions. This observation is general for the majority of N-donor ligands and, as a result, Co(III) complexes in which the metal ion is bonded to six oxygen atoms are rather rare.

When a transition metal ion is surrounded by anionic ligands, the resulting complex generally becomes more difficult to reduce, as addition of an electron to a negatively charged complex is unfavourable on electrostatic grounds. An example of this is the anionic Fe(III) complex $[Fe(CN)_6]^{3-}$, for which $E^{\ominus}_{[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}} = +0.28\,V$, significantly less than that for the cationic Fe^{3+}(aq) ion $(E^{\ominus}_{Fe^{3+}/Fe^{2+}} = +0.77\,V)$.

The correct choice of ligand can assist in stabilising transition metal ions that are unstable with respect to **disproportionation**. This is a redox reaction in which the metal ion is simultaneously oxidised and reduced. The most celebrated example is the Cu^+(aq) ion, for which the following $E^{\ominus}$ values have been obtained.

$$E^{\ominus}_{Cu^{2+}/Cu^{+}} = 0.16\,V$$
$$E^{\ominus}_{Cu^{+}/Cu} = 0.52\,V$$

The disproportionation of Cu^{+} proceeds according to the equation:

$$2Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$$

for which $E^{\ominus} = E_R - E_L = 0.52\,V - 0.16\,V = +0.36\,V$ (assuming that Cu^{+} is reduced at the right-hand electrode). The positive value of $E^{\ominus}$ shows that this reaction is spontaneous under standard conditions, and aqueous solutions of Cu^{+} are often found to be unstable. However, use of strong-field ligands (see p. 572) such as CN^{-} or various phosphanes gives Cu(I) complexes which show significant stability. Note that disproportionation is not limited to transition metal ions, and species such as O_2^{-} (superoxide) and HOCl (hypochlorous acid) can disproportionate.

Bonding in transition metal complexes

Earlier in this chapter, we stated that two of the defining characteristics of transition metal complexes are that they are usually coloured and that they are often paramagnetic. It is not unusual for a given metal ion to form complexes with different ligands to give a rainbow of colours, as illustrated in figure 13.25 for a series of Co(III) complexes.



FIGURE 13.25 Aqueous solutions of the Co(III) complexes (from left to right) $[Co(O_2CO)(en)_2]^{+}$, *trans*-$[CoCl_2(en)_2]^{+}$, $[Co(en)_3]^{3+}$, $[CoCl(NH_3)_5]^{2+}$ and $[Co(NH_3)5OH_2]^{3+}$. As the metal ion is the same in all cases, the variety of colours arises from the different ligands surrounding the Co(III) ion.

Also, because transition metal ions often have incompletely filled *d* orbitals, we expect to find many of them with unpaired *d* electrons, and such compounds should therefore be paramagnetic. However, for a given metal ion in a particular oxidation state, the number of unpaired electrons is not necessarily the same from one complex to another. Consider, for example, the Fe(II) complexes $[Fe(OH_2)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$. As Fe^{2+} has the electron configuration $[Ar]3d^6$, both contain six *d* electrons, but four of these are unpaired in the $[Fe(OH_2)_6]^{2+}$ ion, while all of them are paired in the $[Fe(CN)_6]^{4-}$ ion. As a result, the $[Fe(OH_2)_6]^{2+}$ ion is para-magnetic and the $[Fe(CN)_6]^{4-}$ ion is diamagnetic. We can explain both the colours and magnetic properties of transition metal complexes using **crystal field theory**, a theory of bonding that looks at how the energies of the *d* orbitals on the metal ion are influenced by the surrounding ligands.

Crystal field theory of bonding in octahedral coordination complexes

Crystal field theory is based on the premise that the ligands surrounding the metal ion in a transition metal complex exert an electric field that affects the energies of the *d* orbitals on the metal ion to different extents. It assumes that the interaction between the metal and the ligands is purely electrostatic, an unrealistic situation, given that all metal-ligand bonds exhibit some degree of covalency. Nevertheless, crystal field theory can explain many of the unusual features of transition metal complexes and is conceptually straightforward.

We begin by looking at the electron distributions (figure 13.26) and energies of the five *d* orbitals in a free transition metal ion.

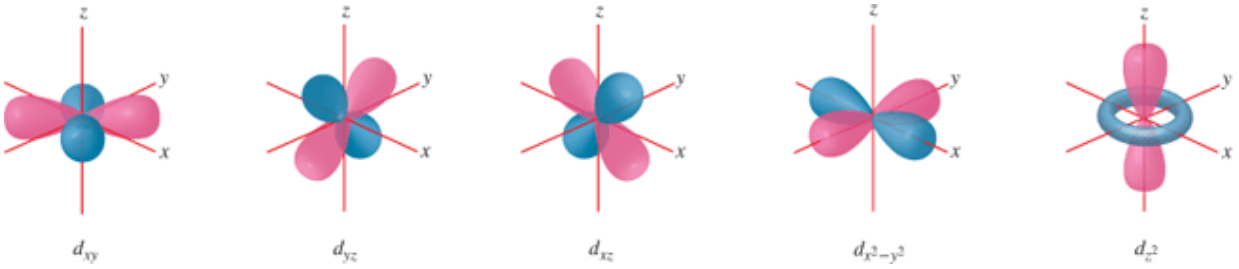


FIGURE 13.26 The directional properties of the five *d* orbitals in a free transition metal ion.

The d_{xy}, d_{xz} and d_{yz} orbitals all have lobes pointing between the *x*-, *y*- and *z*-axes, while the lobes of the $d_{x^2-y^2}$ and d_{z^2} orbitals point along the axes. In the absence of any ligands, the five *d* orbitals are **degenerate**, meaning they are all of the same energy. However, this is not the case in the presence of ligands, where we find that the degeneracy is removed. We illustrate this by considering the formation of an octahedral transition metal complex by the introduction of six ligands at bonding distance along the *x*-, *y*- and *z*-axes, as shown in figure 13.27 on the next page, and looking at the effect of this on the energies of the five *d* orbitals.

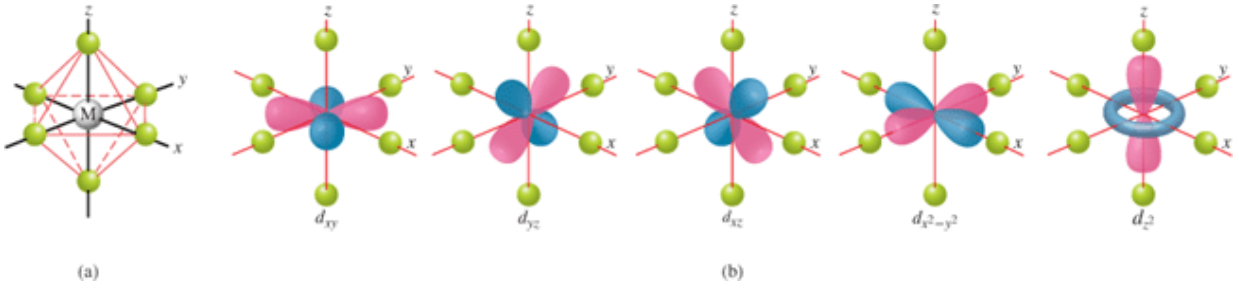


FIGURE 13.27 (a) An octahedral ML_6 complex and
(b) the orientation of the metal orbital with respect to the ligands in an octahedral ML_6 complex.

In an isolated atom or ion, all the *d* orbitals of a given *d* subshell are degenerate. Therefore, an electron has the same energy regardless of which *d* orbital it occupies. In an octahedral complex, however, this is no longer the case. As the

lobes of the $d_{x^2-y^2}$ orbitals point directly towards the ligands, an electron in either of these orbitals is nearer the electron pairs of the ligands than if it was in a d_{xy}, d_{xz} or d_{yz} orbital, with lobes pointing between the ligands. Since the electron itself is negatively charged and is repelled by the ligand electrons, an electron in the $d_{x^2-y^2}$ or d_{z^2} orbital is of higher energy than one in a d_{xy}, d_{xz} or d_{yz} orbital. Therefore, we can see that introduction of the ligands removes the degeneracy of the five *d* orbitals, splitting them into two sets of degenerate orbitals; the lower energy set consists of the d_{xy}, d_{xz} and d_{yz} orbitals, and the higher energy set comprises the $d_{x^2-y^2}$ and d_{z^2} orbitals (figure 13.28). The three lower energy orbitals are collectively called the t_{2g} orbitals while the two higher energy orbitals are called the e_g orbitals. These labels refer to the symmetry of the sets of orbitals, and are obtained using a branch of mathematics called group theory, which is described in advanced chemistry courses.

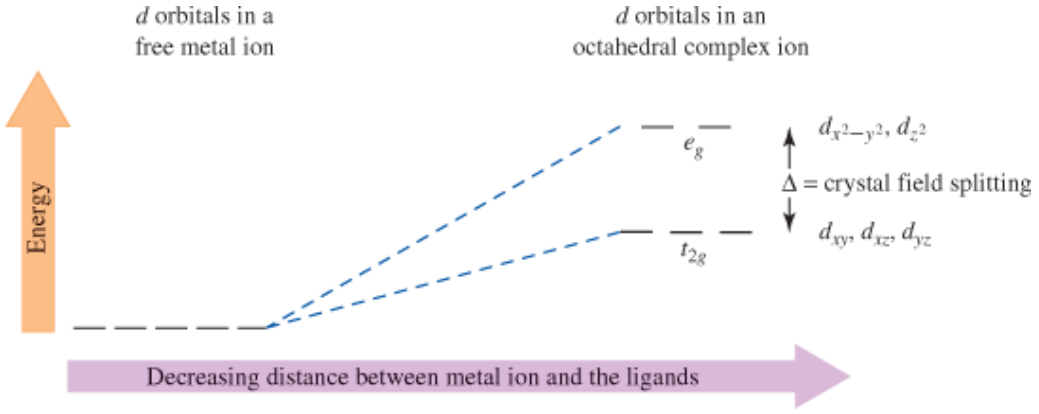


FIGURE 13.28 The changes in the energies of the *d* orbitals of a metal ion as an octahedral complex is formed. As the ligands approach the metal ion, the initially degenerate *d* orbitals split into two new sets of degenerate orbitals.

Figure 13.28 shows that, regardless of which orbital the electron occupies, its energy increases because it is repelled by the electrons of the approaching ligands. However, the electron is repelled more (and has a higher energy) if it is in an orbital that points directly at the ligands than if it occupies an orbital that points between them. In an octahedral complex, the energy difference between the two sets of *d*-orbital energy levels is called the **crystal field splitting energy** (CFSE). It is usually given the symbol Δ_o in octahedral complexes (delta oh, the 'o' standing for octahedral), and its magnitude depends on the following factors.

- *The nature of the ligand:* Some ligands produce a larger splitting of the energies of the *d* orbitals than others. For example, for a given metal ion, CN^- nearly always gives a large value of Δ_o, and F^- always gives a small value. This is due to the more extensive orbital interactions between the metal and ligand that occur in the case of CN^-. We will discuss this further later in this section.
- *The oxidation state of the metal:* For a given metal and ligand, the size of Δ_o increases with an increase in the oxidation state of the metal. As electrons are removed from the metal, the charge on the ion becomes more positive and the ion becomes smaller. This means that the ligands are attracted to the metal more strongly and they can approach the metal ion more closely. As a result, they also approach the *d* orbitals along the *x*-, *y*- and *z*-axes more closely, causing greater repulsion. This produces a greater splitting of the t_{2g} and e_g orbitals and a correspondingly larger value of Δ_o.
- *The position of the transition metal in the periodic table:* For a given ligand and oxidation state, the magnitude of Δ_o increases going down a group. In other words, an ion of an element in the first row of transition elements has a smaller value of Δ_o than the ion of a heavier member of the same group. Thus, comparing complexes of Ni^{2+} and Pt^{2+} with the same ligand, we find that the platinum complexes have the larger crystal field splitting. The explanation of this is that, in the larger Pt^{2+} ion, the *d* orbitals are larger and more diffuse and extend further from the nucleus in the direction of the ligands. This produces a larger repulsion between the ligands and the orbitals

that point at them.

The final point to be made here concerns the overall energetics of the orbital splitting. Figure 13.28 shows an overall energy increase on going from the degenerate *d* orbitals of a free metal ion to the *d* orbitals in an octahedral complex, and this is primarily due to electron-electron repulsion. However, the dominant energetic contribution actually arises from the large attractive electrostatic interactions between the positively charged metal ion and the ligands. Therefore, despite the slight overall *d*-orbital energy increase that occurs on complex formation, the metal complex is still of much lower energy than the infinitely separated metal ion and ligands.

Electron configurations in octahedral transition metal complexes

Having shown that the *d* orbitals in a transition metal complex are not degenerate, we now look at how these orbitals are populated with *d* electrons. We learned in chapter 4 that orbitals are filled in order of increasing energy (the Aufbau principle); a set of degenerate orbitals has a single electron placed in each of the orbitals before any pairing of electrons takes place (Hund's rule); and no two electrons of the same spin may occupy the same orbital (the Pauli exclusion principle). These rules give us the ground-state electron configuration of any chemical species. We will, therefore, consider the situations outlined in figure 13.29 for octahedral complexes having d^1, d^2 and d^3 electron configurations.

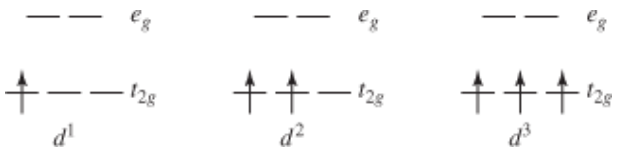


FIGURE 13.29 Orbital occupancies for d^1, d^2 and d^3 electron configurations.

There is no ambiguity about the way in which the orbitals are filled for the electron configurations in figure 13.29; the electrons are placed in the lowest energy t_{2g} orbitals with parallel spins. Ordinarily, we would then place the fourth electron, spin down, in one of the t_{2g} orbitals. However, the energy difference between the t_{2g} and e_g sets of orbitals is relatively small in transition metal complexes, and we must weigh the energetic advantage of placing the fourth electron in a low-energy t_{2g} orbital against the energetic disadvantage that results from placing an electron in an already occupied orbital. This latter energy is called the **pairing energy (*P*)** and is due primarily to the interelectronic repulsions that result from having two electrons in the same orbital. The magnitude of *P*, compared with the crystal field splitting energy, Δ_o, determines which of the two possible electron configurations is favoured. If $P > \Delta_o$, the energetically favourable electron configuration is that in which the fourth electron occupies an e_g orbital. Such a configuration is called the **high-spin** configuration, as the electron spins are maximised. Conversely, when $P < \Delta_o$, the complex adopts the **low-spin** configuration in which the fourth electron is added to one of the lower energy orbitals and is paired with one of the t_{2g} electrons. In this case, the electron spins are minimised and the lowest number of unpaired electrons results. These possibilities are shown in figure 13.30 for the d^4 Cr(II) complexes $[Cr(OH_2)_6]^{2+}$ and $[Cr(CN)_6]^{4-}$.

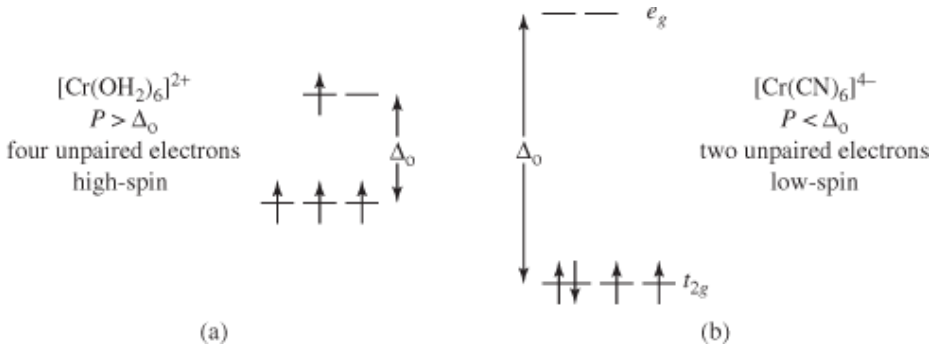


FIGURE 13.30 The two possible electron configurations for a d^4 complex.

(a) When Δ_o is small, as for $[Cr(OH_2)_6]^{2+}$, the high-spin configuration is favoured.

(b) A large value of Δ_o favours the low-spin configuration, as shown for $[Cr(CN)_6]^{4-}$.

Because of its relatively small value of Δ_o, $[Cr(OH_2)_6]^{2+}$ adopts the high-spin configuration, while $[Cr(CN)_6]^{4-}$, which has a significantly larger value of Δ_o, is low-spin. In octahedral complexes, high-spin and low-spin possibilities exist only for d^4, d^5, d^6 and d^7 electron configurations (figure 13.31). There is only one possible configuration for each of the d^8, d^9 and d^{10} configurations (figure 13.32).

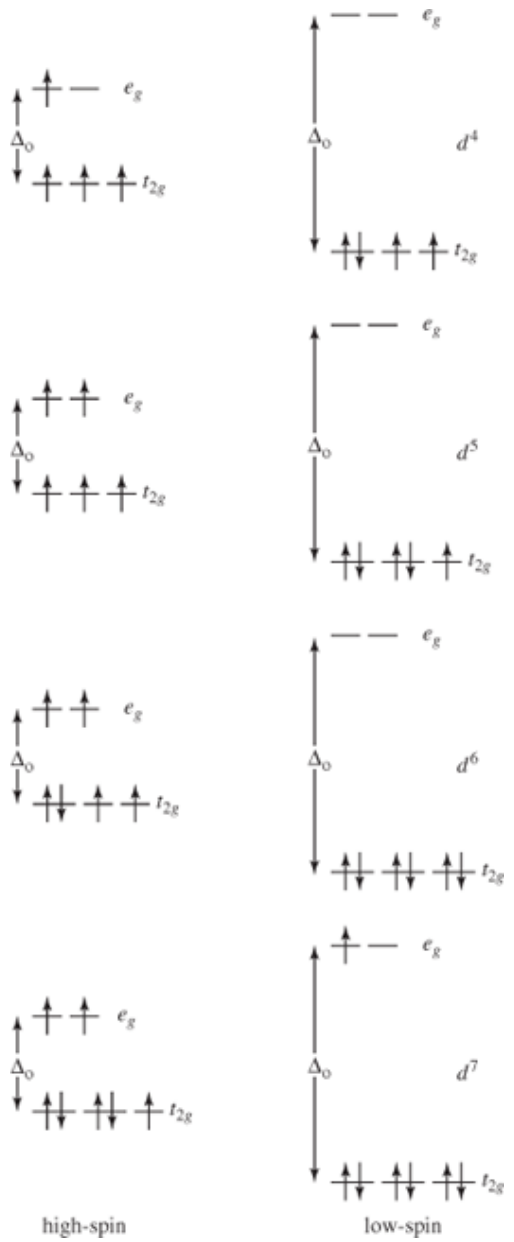


FIGURE 13.31 Low-spin and high-spin electron configurations for d^4-d^7 octahedral transition metal complexes. Note that the number of unpaired electrons is different for the low-spin and high-spin configuration in all cases.

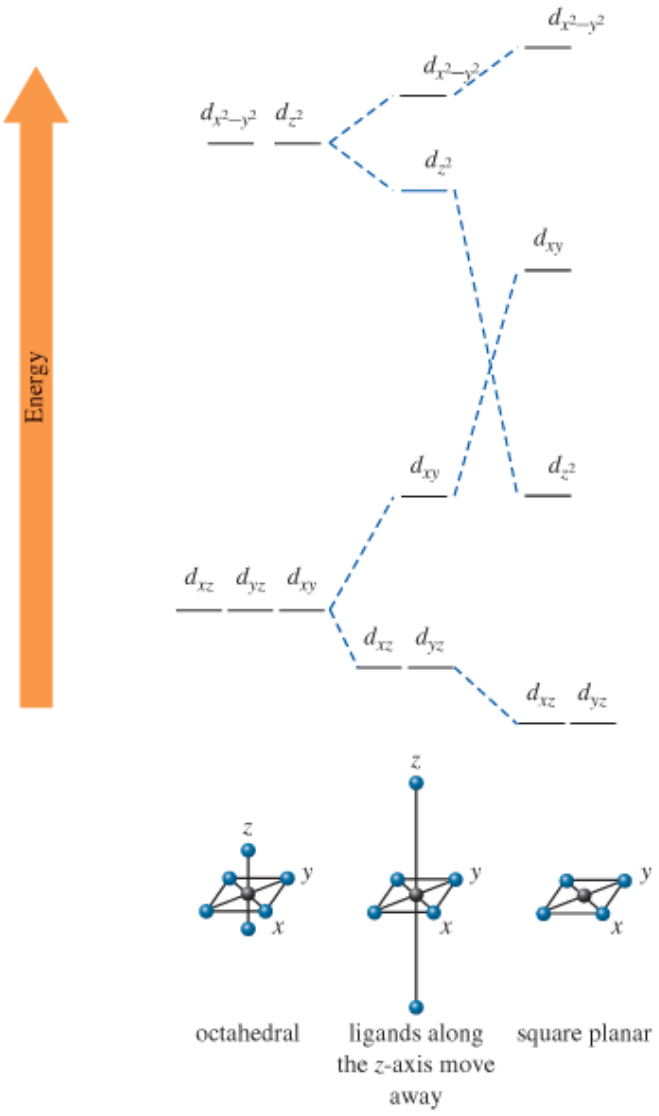


FIGURE 13.32 Electron configurations for d^8, d^9 and d^10 octahedral transition metal complexes.

Crystal field theory applied to 4-coordinate complexes

As mentioned earlier, 4 is the second most common coordination number for metal ions in coordination compounds. We can apply crystal field theory to the two possible 4-coordinate geometries, square planar and tetrahedral, using the same principles we learned earlier.

Square planar complexes

We can form a square planar complex from an octahedral complex simply by removing the two axial ligands that lie along the *z*-axis. This lowers the energy of any of the *d* orbitals with a *z* component (d_{z^2}, d_{xz} and d_{yz}) as electronic repulsion between the electrons in these orbitals and the ligand electrons is reduced. Removing the axial ligands along the *z*-axis allows closer approach to the metal by the ligands in the *xy*-plane; this means that the energies of the orbitals in this plane ($d_{x^2-y^2}$ and d_{xy}) are raised slightly, with the energy of the $d_{x^2-y^2}$ orbital being more affected as its lobes point directly towards the ligands. Figure 13.33 shows these energy changes and the resulting *d*-orbital splitting diagram for a square planar complex.

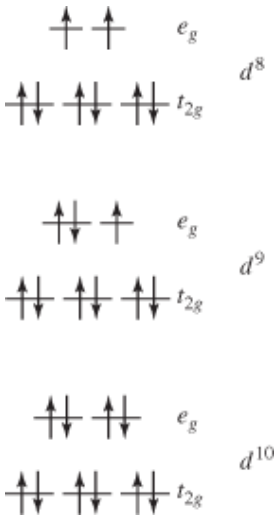


FIGURE 13.33 The derivation of a *d*-orbital splitting diagram (not to scale) for a square planar complex by removal of axial ligands from an octahedral complex.

Tetrahedral complexes

The derivation of a *d*-orbital splitting diagram for a tetrahedral complex is not as conceptually straightforward as that for an octahedral or square planar complex, as none of the four ligands lies directly along the *x*-, *y*- or *z*-axes (figure 13.34).



FIGURE 13.34 The *d*-orbital splitting diagram for a tetrahedral complex.

Notice that the order of the orbitals is exactly opposite to that for an octahedral complex (figure 13.28). In a tetrahedral complex, the crystal field splitting energy is termed Δ_t, and it can be shown that $\Delta t \approx \frac{4}{9}\Delta_o$ for the same metal ion with the same ligands. This small value of Δ_t is usually less than the pairing energy, *P*, so tetrahedral complexes almost always adopt high-spin electron configurations. Note that high-spin and low-spin configurations are theoretically possible for d^3, d^4, d^5 and d^6 tetrahedral complexes.

The colours of transition metal complexes

We saw in chapter 4 that excited-state atoms emit photons of particular energies only. A similar situation occurs when atoms, ions or molecules absorb light; we find that these species absorb photons of certain energies only, rather than absorbing all photons irrespective of their energy. Absorption of a photon by an octahedral transition metal complex can occur if its energy exactly matches Δ_o, the energy difference between the t_{2g} and e_g sets of orbitals. This then leads to an **electronic transition** from a t_{2g} orbital to a higher energy e_g orbital. Such electronic transitions, which involve electrons in the t_{2g} and e_g sets of orbitals only, are called ***d-d* transitions**. In many octahedral transition metal complexes, the energy difference, Δ_o, corresponds to photons of visible light, as shown in figure 13.35 for the d^1 complex $[Ti(OH_2)_6]^{3+}$. This is the reason that many transition metal complexes appear coloured.

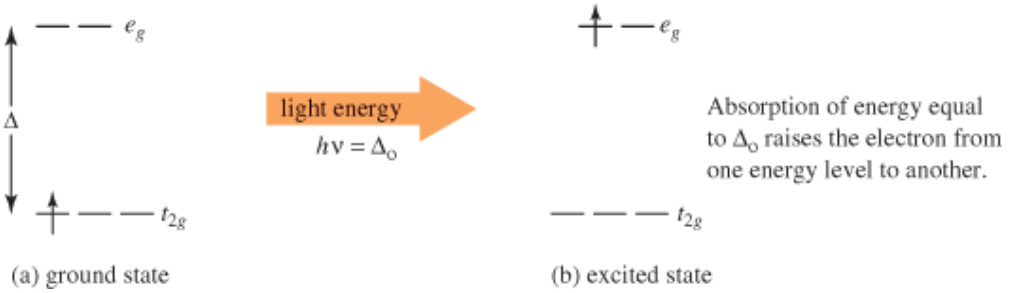


FIGURE 13.35 Absorption of a photon by $[Ti(OH_2)_6]^{3+}$:

(a) The electron distribution in the ground state of the $[Ti(OH_2)_6]^{3+}$ ion;

(b) Absorption of a photon results in an electronic transition from the t_{2g} set of *d* orbitals to the higher energy e_g set.

As you know, white light contains photons with energies that correspond to all of the colours in the visible spectrum, as shown in figure 13.36.

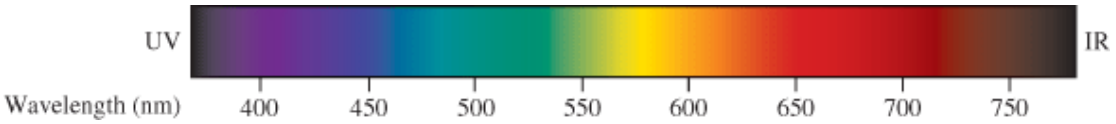


FIGURE 13.36 The visible spectrum, showing the colours as a function of wavelength.

If we shine white light through a solution of a coloured transition metal complex, the light that emerges after passing through the solution contains all the colours except those that have been absorbed, and it is these transmitted colours that we perceive when we look at the solution. If we know what colour the solution appears, we can determine which colour is being absorbed by using a colour wheel, like that shown in figure 13.37.

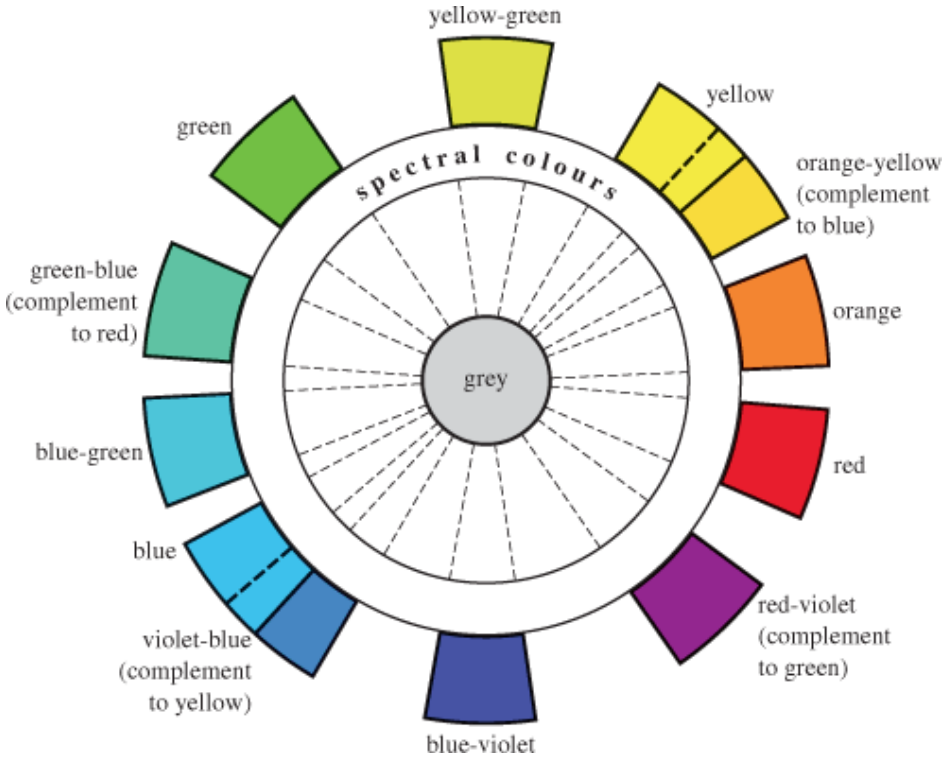


FIGURE 13.37 A colour wheel. Colours opposite each other are called complementary colours. When a substance absorbs light of a particular colour, the light that is reflected or transmitted has the colour of its complement. Thus, something that absorbs red light appears green-blue, and vice versa.

The colour lying opposite any colour on the wheel is called its **complementary colour**; for example, red-violet is the complementary colour of green, while green-blue is the complementary colour of red. If a substance absorbs a particular colour when illuminated with white light, the perceived colour of the reflected or transmitted light is the complementary colour. In the case of the $[Ti(OH_2)_6]^{3+}$ ion, the electronic transition from the t_{2g} set to the e_g set occurs on absorption of green light and this is why a solution of this ion appears red-violet. We can quantify the absorption of visible light using a UV/visible spectrophotometer, a device that determines both the wavelength and intensity of light absorbed by chemical species. Spectrophotometers output a plot of **absorbance (*A*)** versus wavelength, where absorbance is defined as:

$$A = \log\frac{I_o}{I}$$

with I_0 being the intensity of the incident light and I the intensity of the transmitted light. Note that absorbance is a dimensionless quantity.

Figure 13.38 shows the UV/visible spectrum of the red-violet $[Ti(OH_2)_6]^{3+}$ ion, and we can see that this displays a single peak, with a maximum absorbance at 514 nm.

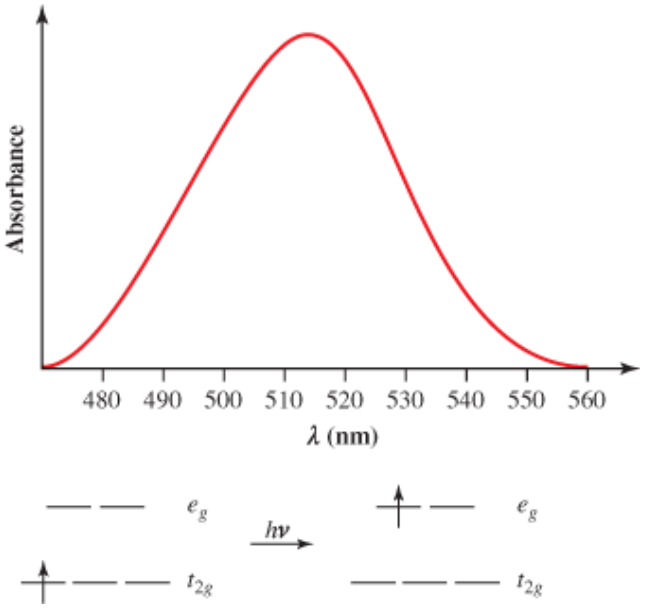


FIGURE 13.38 The UV/visible spectrum of the $[Ti(OH_2)_6]^{3+}$ ion. The peak corresponds to an electronic transition of the single *d* electron from the t_{2g} to the e_g orbital set.

As Ti(III) is a d^1 transition metal ion, we know that this absorbance band is due to the promotion of the single *d* electron from the t_{2g} set of orbitals to the e_g set of orbitals, and we can use the highest point on the peak to calculate

the energy difference between these sets of orbitals — in other words, we can calculate the value of Δ_o for $[Ti(OH_2)_6]^{3+}$ from this spectrum. Recall from chapter 4 that there is an inverse relationship between wavelength (λ) and energy (E), given by the equation:

$$E = \frac{hc}{\lambda}$$

where $h = 6.626 \times 10^{-34}$ J s (Planck's constant) and $c = 2.998 \times 10^{8}$ m s^{-1} (the speed of light). We can now find the energy corresponding to a photon of wavelength 514 nm by using the equation:

$$\begin{aligned} E &= \frac{(6.626 \times 10^{-34}\,\text{Js}) \times (2.998 \times 10^{8}\,\text{m s}^{-1})}{514 \times 10^{-9}\,\text{m}} \\ &= 3.86 \times 10^{-19}\,\text{J} \end{aligned}$$

This value tells us that the t_{2g} and e_g orbitals are separated by 3.86×10^{-19} J in a single $[Ti(OH_2)_6]^{3+}$ ion. It is usual to report the value of Δ_o for a complex on a molar basis, rather than for an individual ion, and we do this by multiplying E by the Avogadro constant (6.022×10^{23} mol^{-1}). Therefore:

$$\begin{aligned} E &= (3.86 \times 10^{-19}\,\text{J}) \times (6.022 \times 10^{23}\,\text{mol}^{-1}) \\ &= 232 \times 10^{3}\,\text{Jmol}^{-1} \\ &= 232\,\text{KJ mol}^{-1} \end{aligned}$$

Therefore, Δ_o for $[Ti(OH_2)_6]^{3+}$ = 232 kJ mol^{-1}. It should be noted that the *exact* value of t Δ_o can be determined in this way only for a small number of metal complexes. Electron-electron repulsions in complexes with more than one *d* electron mean that the exact determination of Δ_o for such complexes is difficult, and, indeed, beyond the scope of this book. However, the previous treatment does give a fair approximation of Δ_o in these cases and we will continue to use it throughout this chapter.

We have already seen in a series of Co(III) complexes that the nature of the ligands is critical in determining the colour of transition metal complexes (figure 13.25) and must therefore influence the value of Δ_o. The greater the value of Δ_o, the further apart in energy are the t_{2g} and e_g orbitals and, therefore, the shorter the wavelength of light required to promote an electron from the t_{2g} set to the e_g set of orbitals. This can be illustrated by looking at the Ti(III) complexes $[TiF_6]^{3-}$ and $[Ti(NCS)_6]^{3-}$, which have maximum absorbance wavelengths (λ_{max}) at 526 nm and 543 nm, respectively. These are at a longer wavelength than that of $[Ti(OH_2)_6]^{3+}$, which has a maximum absorbance wavelength of 514 nm.

The Δ_o values corresponding to these absorption maxima are 232 kJ mol^{-1} for $[Ti(OH_2)_6]^{3+}$, 227 kJ mol^{-1} for $[TiF_6]^{3-}$ and 220 kJ mol -1 for $[Ti(NCS)_6]^{3-}$, meaning that the separation of the t_{2g} and e_g orbitals varies significantly with the identities of the ligands for the same metal in the same oxidation state (figure 13.39).

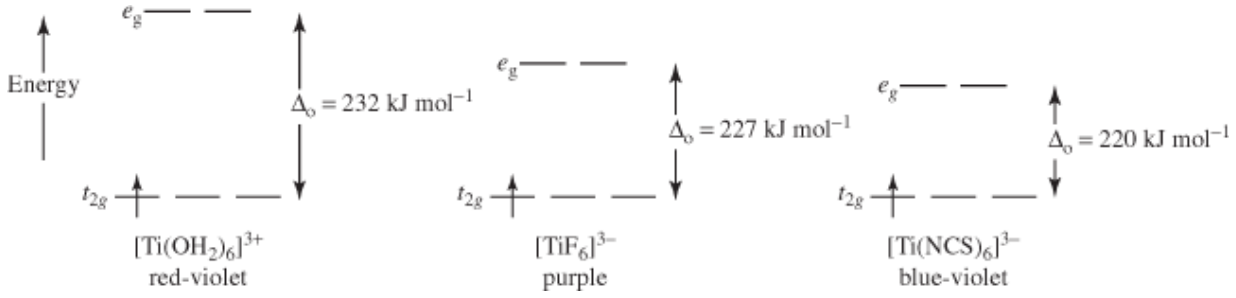


FIGURE 13.39 Energy separations between their t_{2g} and e_g orbitals for $[Ti(OH_2)_6]^{3+}$, $[TiF_6]^{3-}$ and $[Ti(NCS)_6]^{3+}$

A ligand that produces a large crystal field splitting with one metal ion also produces a large value of Δ_o in complexes with other metals. For example, CN^- nearly always gives a very large value of Δ_o regardless of the metal to which it is bound. Complexes containing NH_3 have lower values of Δ_o than complexes containing CN^-, while Δ_o values for complexes containing H_2O are smaller still. Thus, ligands can be arranged in order of the magnitude of their crystal field splitting energies. This sequence is called the **spectrochemical series**. Such a series containing some common ligands arranged in order of decreasing Δ_o values is:

$$CO \approx CN^- > NO_2^- > en > NH_3 > H_2O > C_2O_4^{2-} > OH^- > F^- > Cl^- > Br^- > I^-$$

For a given metal ion, the carbonyl ligand produces the largest value of Δ_o, and iodide produces the smallest. Ligands such as CO, CN^- and NO_2^-, which give large values of Δ_o, are called **strong-field** ligands, while the halide ions and others that induce small *d*-orbital splittings are called **weak-field** ligands. The *d*-orbital splittings induced by strong-field ligands are often so large that the energy gap between the t_{2g} and e_g sets of orbitals is greater than the energy of visible photons. Therefore, electronic transitions between the t_{2g} and e_g orbitals in octahedral complexes containing only CO or CN^- ligands are often caused only by UV photons, so such complexes are usually very pale yellow or colourless.

Octahedral complexes of Zn(II) and high-spin Mn(II) are also often colourless, or nearly so, but for a very different reason; Zn(II) is a d^{10} metal ion, meaning that the t_{2g} and e_g sets of orbitals are full (figure 13.40).

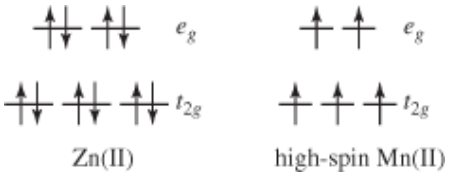


FIGURE 13.40 The *d*-electron configurations for complexes of Zn(II) (left) and high-spin Mn(II) (right).

No electronic transition between the t_{2g} and e_g orbitals is possible, as the e_g orbitals are unable to accommodate an extra electron. High-spin Mn(II) has a d^5 electron configuration as shown in figure 13.40; to promote an electron from a t_{2g} orbital to an e_g orbital, we would require the electron involved to change its spin during the transition, otherwise a situation would result in which two electrons with the same spin occupy a single orbital, in violation of the Pauli exclusion principle. We say, therefore, that the $t_{2g} \rightarrow e_g$ electronic transition in such complexes is spin forbidden; the probability of such a transition occurring is very low, so these complexes are usually very pale in colour.

We might expect complexes containing transition metal ions with a d^0 electron configuration to be colourless, as obviously there are no possible *d-d* transitions between the t_{2g} and e_g orbitals, and this is borne out in many cases. However, ions such as $[MnO_4]^-$ (purple) and $[Cr_2O_7]^{2-}$ (orange) are very intensely coloured, despite the metal ion having a - d^0 configuration in each case. The colour in such compounds is due to **ligand-to-metal charge transfer (LMCT) transitions**, which involve the formal transfer of an electron on the ligand to an orbital on the metal ion. While such transitions usually occur in the ultraviolet part of the spectrum and are, therefore, invisible to the eye, some low-energy LMCT transitions are observed, such as those in $[MnO_4]^-$ and $[Cr_2O_7]^{2-}$. LMCT transitions have a much higher probability of occurring than transitions between t_{2g} and e_g orbitals, and this explains the extremely intense colour of, for example, the $[MnO_4]^-$ ion. In some complexes where the metal ion contains occupied *d* orbitals, an electron can be formally transferred in the opposite direction, i.e. from the metal to the ligand. Such processes are called **metal-to-ligand charge transfer (MLCT) transitions** and often occur in complexes having aromatic, pyridine-based ligands. These transitions also have high probabilities and lead to very intensely coloured complexes. One of the best known examples of a complex that displays an MLCT transition is $[Ru(bipy)_3]^{2+}$, which contains three bidentate 2,2'-bipyridine ligands.

It should be noted that it is not the nature of the ligands alone that ultimately determines the colour of a transition metal complex. For example, the isomeric complexes *cis*-$[CoCl_2(en)_2]^+$ and *trans*-$[CoCl_2(en)_2]^+$, which contain identical ligands coordinated to a Co(III) centre, are violet and green, respectively. Other factors such as the arrangement of the ligands and the metal- ligand bond lengths can also be important.

WORKED EXAMPLE 13.8

Colours of Transition Metal Complexes

A student prepared five Co(III) complexes in an undergraduate chemistry laboratory and stored them in sample tubes. However, the student forgot to label the tubes and, at the start of the next laboratory session, could not remember which complex was which. To identify them, the student recorded the UV/visible

spectra of the complexes and found that the five complexes exhibited maximum absorbance values in the visible region at 506 nm, 490 nm, 534 nm, 441 nm and 471 nm. The five complexes prepared by the student were $[CoCl(NH_3)_5]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5OH]^{2+}$, $[CoCN(NH_3)_5]^{2+}$ and $[Co(NH_3)_5OH_2]^{3+}$. Match the UV/visible data to the complexes.

Analysis

We have five very similar complexes, all of which contain a $[Co(NH_3)_5]^{3+}$ moiety and differ only in the nature of the sixth ligand. Therefore, we should be able to use the spectrochemical series to decide the order of the UV/visible absorption maxima across the five complexes; the strongest field ligand should have the largest energy gap between the t_{2g} and e_g orbitals, and should therefore have the shortest wavelength absorption maximum.

Solution

We begin by ordering the five ligands according to their positions in the spectrochemical series, from strongest field to weakest field. The order is therefore:

$$CN^- > NH_3 > OH_2 > OH^- > Cl^-$$

We would expect the complex containing CN^- to have the largest energy gap between the t_{2g} and e_g sets of orbitals, as CN^- is the strongest field ligand, and therefore this complex will exhibit the shortest wavelength (highest energy) absorption maximum. The complex containing Cl^- should have the smallest energy gap between the t_{2g} and e_g sets of orbitals, as Cl^- is the weakest field ligand, and therefore this complex will exhibit the longest wave-length (lowest energy) absorption maximum. The remaining three complexes will be ordered according to the positions of the ligands in the spectrochemical series above. Therefore, the identities of the complexes are:

$$[CoCN(NH_3)_5]^{2+}: \quad \lambda_{max} = 441\,nm$$
$$[Co(NH_3)_6]^{3+}: \quad \lambda_{max} = 471\,nm$$
$$[Co(NH_3)_5OH_2]^{3+}: \quad \lambda_{max} = 490\,nm$$
$$[Co(NH_3)_5OH]^{2+}: \quad \lambda_{max} = 506\,nm$$
$$[CoCl(NH_3)_5]^{2+}: \quad \lambda_{max} = 534\,nm$$

PRACTICE EXERCISE 13.8

The octahedral complex $[CoCl_6]^{4-}$ and the tetrahedral complex $[CoCl_4]^{2-}$ both contain Co(II). Which is larger: Δ_o for $[CoCl_6]^{4-}$ or Δ_t for $[CoCl_4]^{2-}$? Explain your answer.

The absorbance of a solution of a transition metal complex (and indeed, of any solution) is related to the concentration of the absorbing species by the **Beer-Lambert law** (also often called **Beer's law**), which states that:

$$A = \varepsilon cl$$

where A = absorbance (dimensionless), ε = molar absorption coefficient (mol^{-1} L cm^{-1}), c = concentration of absorbing species (mol L^{-1}) and l = pathlength of cell (cm). The somewhat unusual units of ε arise from the fact that UV/visible spectra are generally measured using cells of dimensions 1 cm × 1 cm.

The ε values for transition metal complexes depend on both the geometry of the metal ion and the type of electronic transition occurring and, as such, can be useful in characterising these species. For example, *d-d* transitions for

octahedral complexes generally have ε values <100 mol^{-1} L cm^{-1} and, as a result, such complexes are usually weakly coloured. Tetrahedral complexes are often more intensely coloured, with ε values for *d-d* transitions in these lying *d* in the range 200-250 mol^{-1} L cm^{-1}. More intense still, as discussed on the previous page, are LMCT and MLCT transitions, which can have ε values up to 10^4 mol^{-1} L cm^{-1}.

You will notice that the UV/visible spectra arising from *d-d* transitions in transition metal complexes look very different from the atomic spectra we saw in chapter 4 (p. 120). While the latter display sharp lines, indicative of electronic transitions between well-defined, quantised energy levels, the former show broad bands, an observation seemingly at odds with the definite energies of the t_{2g} and e_g sets of orbitals between which these electronic transitions occur. The broad bands can be rationalised by considering vibrations of the complexes. Consider for example the octahedral $[Ti(OH_2)_6]^{3+}$ ion, the UV/visible spectrum of which is given in figure 13.38; if all the $[Ti(OH_2)_6]^{3+}$ ions in the sample exhibited identical octahedral geometry with all Ti—O bond distances the same, then the *d-d* absorbance band would indeed be much narrower than that observed. However, vibrations within the cations at room temperature ensure that there is a variety of Ti—O bond distances and, therefore, geometries at any given time. As the energies of the t_{2g} and e_g sets of orbitals depend on the Ti—O bond distances, this therefore leads to a range of energy differences between the t_{2g} and e_g sets, which in turn results in broad absorption bands. Single atoms cannot undergo vibrations in the same way as molecules or polyatomic ions, and so their spectra consist of sharp lines. This is illustrated in figure 13.41.

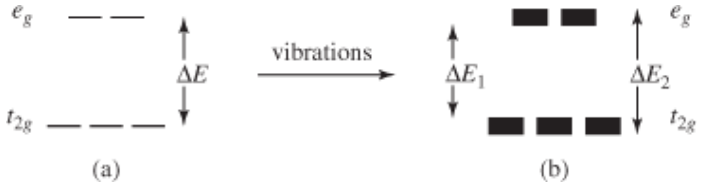


FIGURE 13.41

(a) In the absence of vibrations, the energies of the t_{2g} and e_g sets of orbitals are precisely defined, and an electronic transition between these therefore result in a narrow spectral line.

(b) When vibrations occur, they result in a range of energies for each of the t_{2g} and e_g sets of orbitals. Electronic transitions between these therefore span the range of energies between ΔE_1 and ΔE_2, thereby leading to broad bands.

The magnetic properties of transition metal complexes

As we have seen both in chapter 4 and earlier in this chapter, a paramagnetic substance is one that is attracted into a magnetic field. For a substance to be paramagnetic, it must contain unpaired electrons, the number of which determines the magnitude of its response to a magnetic field. This response can be measured by using a very accurate balance to determine the mass difference of a sample of the complex in the presence and absence of a magnetic field. This allows us to calculate the **magnetic moment (μ)** of the complex and, hence, to determine the number of unpaired electrons it contains. The magnetic moment of a complex is measured in Bohr magnetons (μ_B) and is defined as:

$$\mu = \sqrt{n(n+2)}\mu_B$$

where *n* is the number of unpaired electrons in the complex. Therefore, a complex containing one unpaired electron should have $\mu = \sqrt{3} = 1.73\mu_B$ while the value of μ for a complex containing three unpaired electrons would be $\mu = \sqrt{15} = 3.87\mu_B$. Note that this equation applies exactly only to complexes in which the orbital motion of the unpaired electrons between degenerate *d* orbitals is negligible. We will assume that this is the case in the examples presented.

Having introduced the concept of high-spin and low-spin electron configurations, we can now explain the unusual magnetic behaviour of the $[Fe(OH_2)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ ions discussed on p. 566. Both complexes contain d^6 Fe(II) metal ions, but $[Fe(OH_2)_6]^{2+}$ is paramagnetic (μ ≈ 4.9 μ_B) while $[Fe(CN)_6]^{4-}$ is diamagnetic (μ ≈ 0 μ_B). We know from the spectrochemical series that H_2O induces a much smaller value of Δ_o than does CN^-, meaning that $[Fe(OH_2)_6]^{2+}$ is high-spin while $[Fe(CN)_6]^{4-}$ is low-spin, as shown in figure 13.42.

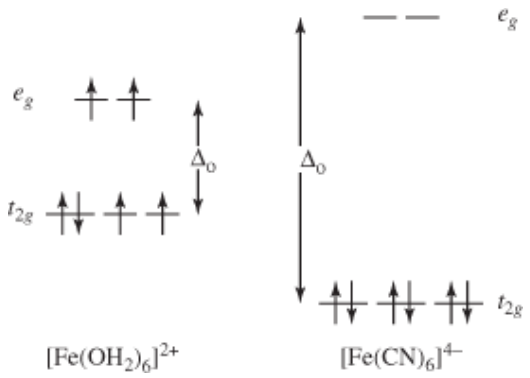


FIGURE 13.42 The distribution of *d* electrons in $[Fe(OH_2)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$. The magnitude of Δ_o for the cyanide complex is much larger than that for the complex containing water. This produces a maximum pairing of electrons in the t_{2g} orbitals in $[Fe(CN)_6]^{4-}$, and a corresponding low-spin configuration for this complex.

Therefore, $[Fe(OH_2)_6]^{2+}$ contains four unpaired electrons and is paramagnetic, while $[Fe(CN)_6]^{4-}$ has no unpaired electrons and is diamagnetic.

Magnetic measurements allow us to distinguish between high-spin and low-spin possibilities in transition metal complexes. For example, the magnetic moments of the d^4 Cr(II) complexes $[Cr(OH_2)_6]^{2+}$ and $[Cr(CN)_6]^{4-}$ are 4.9 μ_B and 2.8 μ_B, respectively. The value of 4.9 μ_B for $[Cr(OH_2)_6]^{2+}$ is consistent with the presence of four unpaired electrons and, therefore, a high-spin $(t_{2g})^3(e_g)^1$ configuration. The value of 2.8 μ_B for $[Cr(CN)_6]^{4-}$ arises from two unpaired electrons, which suggests a low-spin $(t_{2g})^4(e_g)^0$ configuration.

WORKED EXAMPLE 13.9

The magnetic Behaviour of Octahedral Transition Metal Complexes

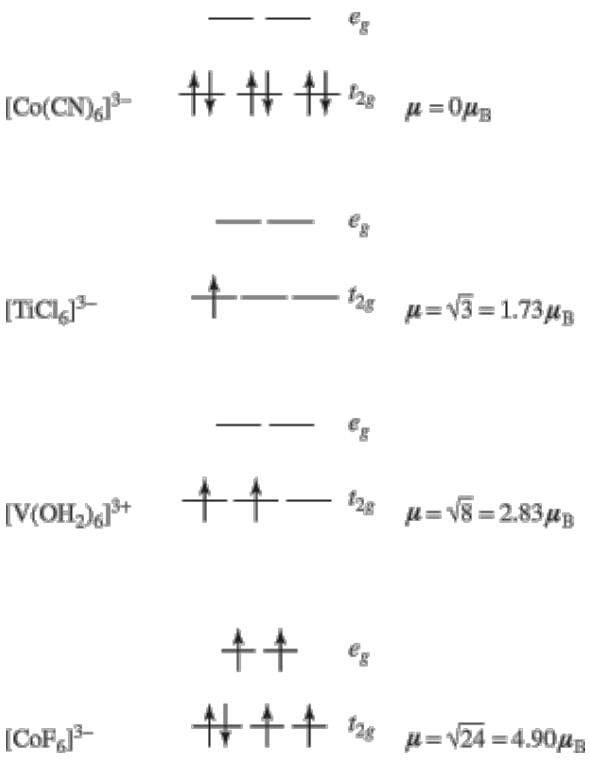
Predict whether the following octahedral transition metal complex ions are paramagnetic or diamagnetic: $[Co(CN)_6]^{3-}$, $[TiCl_6]^{3-}$, $[V(OH_2)_6]^{3+}$, $[CoF_6]^{3-}$. If they are paramagnetic, estimate their magnetic moments.

Analysis

We can calculate the *d*-electron configurations of the complexes by first determining the oxi dation states and then numbers of *d* electrons for each metal ion. Where high-spin and low-spin possibilities occur, we use the position of the ligand in the spectrochemical series to decide between the two configurations.

Solution

The oxidation states are Co(III), Ti(III), V(III) and Co(III), which correspond to d^6, d^1, d^2 and d^6 electron configurations, respectively. High-spin and low-spin poss ibilities exist for both $[Co(CN)_6]^{3-}$ and $[CoF_6]^{3-}$. We know from the spectrochemical series on p. 572 that CN^- is a strong-field ligand, while F^- is a weak-field ligand. We therefore predict that $[Co(CN)_6]^{3-}$ is d^6 low-spin and diamagnetic, while $[CoF_6]^{3-}$ is d^6 high-spin, with four unpaired electrons, and paramagnetic. $[TiCl_6]^{3-}$ must be paramagnetic, as it contains an odd number of *d* electrons, while $[V(OH_2)_6]^{3+}$ is also paramagnetic, as the two *d* electrons occupy two of the t_{2g} orbitals with parallel spins. Therefore, the electron configur ations and magnetic moments are as shown on the right.



Is our answer reasonable?

Provided we have counted the *d* electrons correctly and filled the orbitals in the appropriate fashion, our answers should be correct.

PRACTICE EXERCISE 13.9

Determine how many unpaired electrons are contained in the following octahedral complex ions: $[NiCl_6]^{2-}$, $[CuCl_6]^{4-}$, $[ZnCl_6]^{4-}$. Estimate the magnetic moments of these complexes.

It is important to realise that the simple paramagnetic complexes we have discussed, while attracted into a magnetic field, do not themselves act as permanent magnets. The presence of unpaired electrons is not sufficient in itself for a substance to act as a permanent magnet; for this, a substance must have a nonzero magnetic field that persists over time. In the absence of an external magnetic field, the unpaired electron spins in a paramagnetic material are aligned randomly; therefore, the tiny magnetic fields resulting from each electron spin cancel each other and the net magnetic moment is zero. Application of an external magnetic field results in the electron spins aligning, and this ordering of the spins results in a net magnetic moment within the material. However, when the external magnetic field is removed, the electron spins again align randomly and the individual magnetic fields again cancel each other. In order to act as a permanent magnet, these unpaired spins must behave cooperatively to give a nonzero magnetic moment in the absence of an external magnetic field. Of all the metals in the periodic table, only five, iron, cobalt, nickel, dysprosium and gadolinium, have this ability and can therefore act as permanent magnets. They display a property called **ferromagnetism**, which means that all of the electron spins are oriented in the same direction in the absence of a magnetic field.

Figure 13.43 shows the difference between paramagnetic and ferromagnetic materials. Ferromagnetic materials display the alignment of electron spins within small areas called domains in the absence of a magnetic field. Again, because the ordering of the domains is randomised, the individual magnetic fields due to each domain cancel out and there is no net magnetic moment. When an external magnetic field is applied, each domain aligns with all the others, and this alignment remains when the magnetic field is switched off, resulting in the material having a nonzero magnetic moment and behaving as a permanent magnet. Many of you will have observed this behaviour when you

have magnetised a needle; stroking a needle with a permanent magnet causes the individual domains within the needle (made of steel, a ferromagnetic material) to align, and this alignment remains when the permanent magnet is removed.

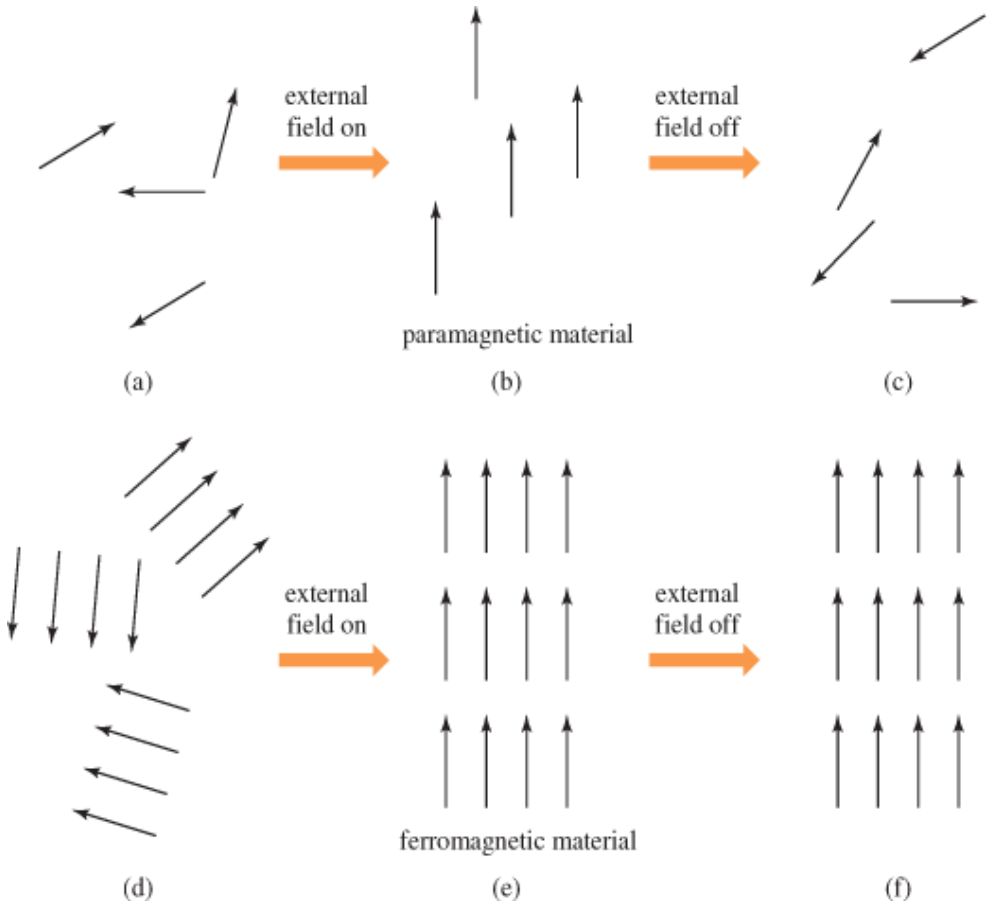


FIGURE 13.43 The differing behaviours of paramagnetic and ferromagnetic materials. Each arrow represents a single electron spin. In a paramagnetic material:

(a) in the absence of an external magnetic field, the directions of the electron spins are randomised;

(b) applying an external magnetic field causes the electron spins to align;

(c) when the external magnetic field is switched off, the electron spins again randomise. In a ferromagnetic material;

(d) in the absence of an external magnetic field, there is short-range ordering of the electron spins in individual domains within the material;

(e) applying an external magnetic field causes all the electron spins within all the domains to align;

(f) when the external magnetic field is switched off, the electron spins remain aligned to give a permanent magnet.

While magnetic materials are widely used in data storage (the magnetic strips on the back of your ATM and credit

cards, for instance), nanoscale magnetic materials offer potentially enormous possibilities as replacements for current silicon-based technology in computers (see p. 577). Central to this is the development of both magnetic nanoparticles, which are well-defined magnetic particles with a diameter of less than 100 nm and generally comprising collections of metal atoms or metal oxides, and single-molecule magnets, in which individual molecules containing unpaired electrons with aligned spins act as magnets. Both areas are currently the focus of extensive worldwide research.

Chemistry Research

Low-spin versus high-spin electronic states — spin crossover

Professor Sally Brooker, University of Otago, Dunedin

The development of nanoscale devices that could be used as molecular computers is currently of intense interest. These will be far smaller and more powerful than today's computers based on silicon chips; they will likely result from a 'bottom-up' approach rather than the current 'top-down' approach used to etch smaller and smaller circuits onto silicon chips to improve performance. The latter approach cannot continue indefinitely as ultimately the limit of the performance of silicon will be reached and 'short circuits' will result. Chemistry researchers are particularly well placed to contribute strongly to the 'bottom-up' approach as we are good at making molecules. Molecules with a range of functions will be required and we focus here on those able to act as switches.

As you have learned in this chapter, octahedral coordination complexes with d^4 - d^7 electron configurations can potentially exist in either the low-spin (LS) state ($\Delta_o > P$) or the high-spin (HS) state ($\Delta_o < P$). However, for some complexes, the values of Δ_o and P are similar, leading to the observed spin state being dependent on the conditions. Such complexes are called spin crossover complexes. Most commonly, the spin state of such complexes is determined by varying the temperature and monitoring the number of unpaired electrons. At low temperature, the metal ion in a monometallic spin crossover complex is in the LS state but switches to the HS state at high temperature. This switching behaviour (usually reversible) between LS and HS states can be considered akin to an on/off switch or a binary code, 0/1.

Most spin crossover complexes contain a single metal ion, but at the University of Otago our focus is on complexes containing two, three or four metal ions. For example, we have observed unprecedented spin crossover behaviour in a dicobalt complex (figure 13.44), and more recently we have determined the crystal structure of an unusual mixed spin state diiron complex (figure 13.45).

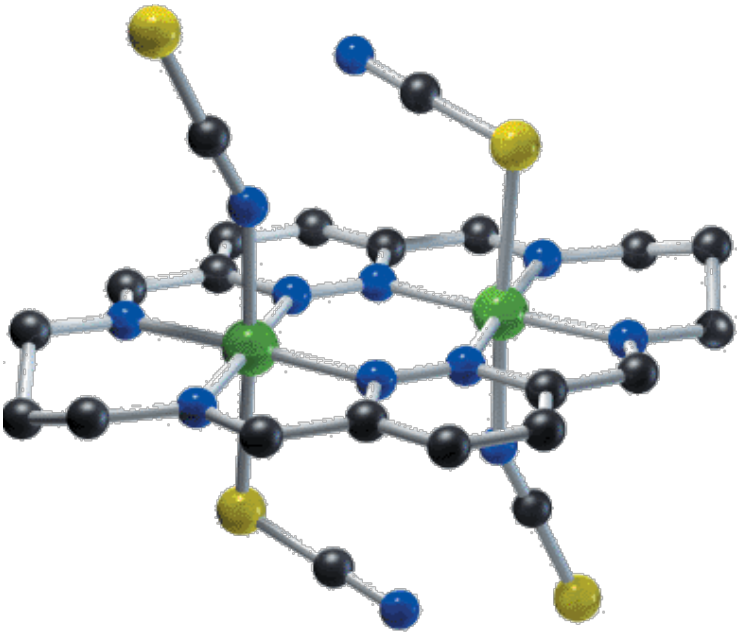


FIGURE 13.44 The crystal structure of $[Co_2L(NCS)_2(SCN)_2]$, where L is a neutral macrocyclic ligand. The cobalt(II) ions are green, nitrogen atoms are blue, carbon atoms are black and sulfur atoms are yellow.

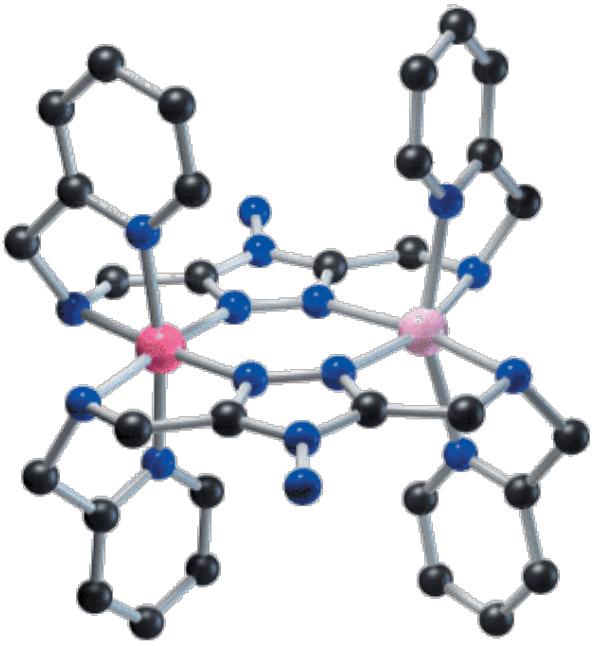


FIGURE 13.45 The crystal structure of $[Fe_2(PMAT)_2](BF_4)_4 \cdot DMF$, where PMAT is a neutral polydentate ligand. The iron(II) ions are pink, nitrogen atoms are blue and carbon atoms are black.

For a complex containing two metal ions, there are three possible spin states ([LS-LS], [LS-HS] and [HS-HS]) and, therefore, 3-state switching is possible. However, at ambient pressures $[Fe_2(PMAT)_2](BF_4)_4$ exists in only two different states; at room temperature it is pale yellow [HS-HS] (figure 13.46a), whereas at low temperature it is purple [LS-HS] (figure 13.46b). Interestingly, even when this complex is placed under pressure at very low temperatures, we cannot force it to adopt the third possible state, [LS-LS].

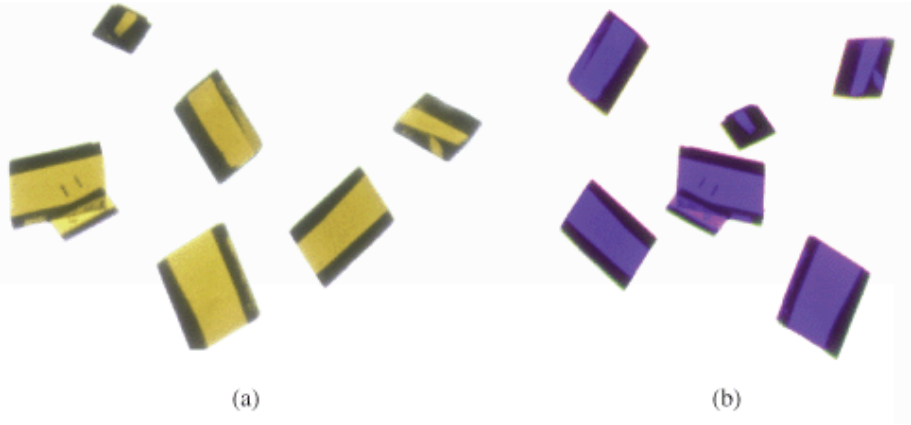


FIGURE 13.46 Crystals of
(a) HS-HS $[Fe_2(PMAT)_2](BF_4)_4$(yellow) and
(b) LS-HS $[Fe_2(PMAT)_2](BF_4)_4$ (purple).

Clearly, for a complex containing four metal ions, 5-state switching, from the fully LS form [LS-LS-LS-LS] through all of the mixed spin states to the fully HS form [HS-HS-HS-HS], is possible in principle, although it has yet to be realised.

We grow crystals of the new spin crossover complexes we make in order to work out the three-dimensional arrangements of atoms within the molecules that these crystals contain. Knowing the structure of these new molecules is vital to understanding, and subsequently finetuning, the properties exhibited by our molecules. Studies in this area aim to develop better understanding and control of spin crossover. Improved understanding of the effect of the exact nature of the ligands on the crystal field splitting energy (Δ_o) experienced by the metal ion(s), and hence on the spin crossover behaviour of such systems, may ultimately lead to applications in molecular computers.

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13.5 Transition Metal Ions in Biological Systems

Almost 90% of the atoms that make up the human body are either hydrogen or oxygen. Most of these are in water, which constitutes around 70% of our bodies. The organic molecules that make up the body, as well as the molecules involved in biosynthesis and energy production, consist almost entirely of C, H, N and O. These four elements account for 99% of all the atoms present in a human. Another seven elements — Na, K, Ca, Mg, P, S and Cl — are also essential for all known life-forms. These seven add another 0.9% to the total atom count of a human being. The remaining 0.1%, the so-called trace elements, are required by most organisms.

Although trace elements are present in only minute amounts, they are essential for healthy function. Of these trace elements, nine are transition metals, namely the elements V, Cr, Mn, Fe, Co, Ni, Cu and Zn from the first row of the transition metals and Mo (molybdenum) from the second row. Many of these are natural constituents of proteins, biological macromolecules made of long chains of amino acids that are described in chapter 24. These metalloproteins play three essential roles in biochemistry. Some act as transport and storage agents, moving small molecules from place to place within an organism. Others are enzymes, catalysts for a diverse group of biochemical reactions. Both transport and catalysis depend on the ability of transition metals to bind and release ligands. The third role of metalloproteins is to serve as redox reagents, adding or removing electrons in many different reactions. Transition metals are ideal for this purpose because of their ability to cycle between two or more oxidation states.

Transport and storage metalloproteins

Organisms extract energy from food by using molecular oxygen to oxidise fats and carbohydrates. For most animals, the movement and storage of O_2 is accomplished by the iron-containing proteins haemoglobin and myoglobin. The iron atom in haemoglobin binds O_2 and transports this vital molecule from the lungs to various parts of the body where oxidation takes place. Haemoglobin makes O_2 about 70 times more soluble in blood than in water. Whereas haemoglobin transports O_2, myoglobin stores O_2 in tissues, such as muscle, that require large amounts of oxygen. Haemoglobin and myoglobin have closely related structures and contain one (myoglobin) or four (haemoglobin) haem groups (figure 13.47). These are essentially iron-porphyrin complexes, as shown in figure 13.48 on the next page.

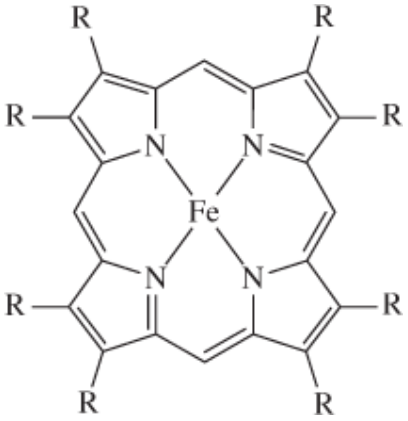


FIGURE 13.47 The haem group, as found in haemoglobin and myoglobin.

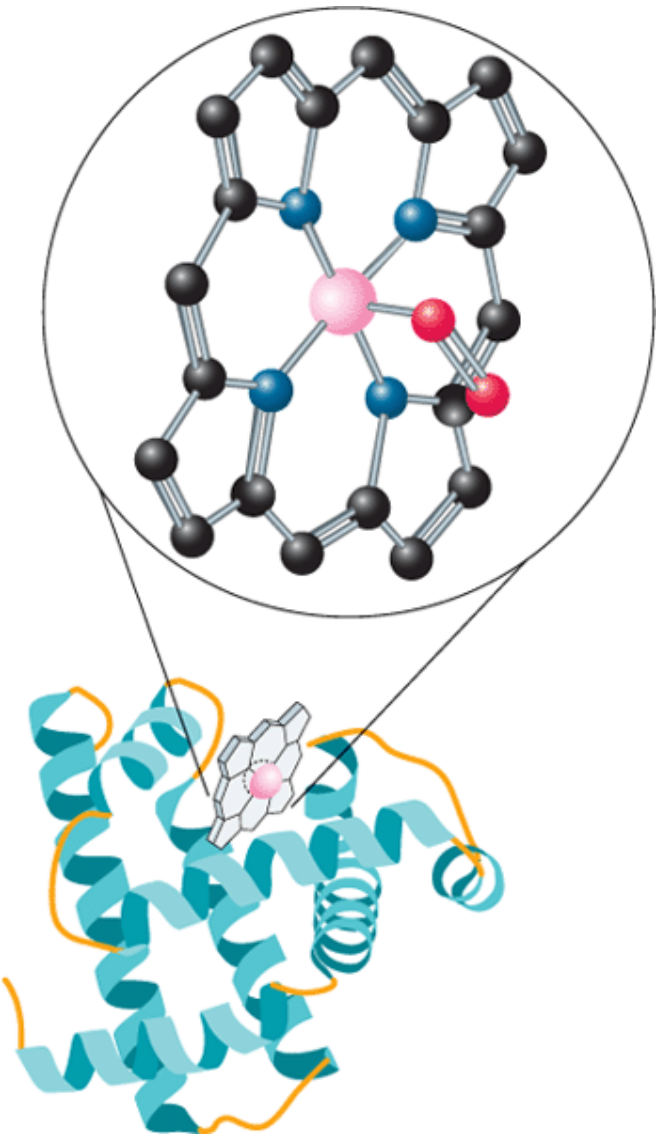


FIGURE 13.48 A ribbon depiction of the structure of myoglobin, determined by X-ray crystallography, showing the haem unit embedded in a pocket created by the folding of the protein chain. (Fe is shown as pink and O as red.)

In myoglobin, the haem group is bound to a polypeptide chain of 153 amino acids arranged in helical arrays, and the ribbon structure of myoglobin is shown in figure 13.48. The polypeptide chain folds to create a 'pocket' in the protein for a haem group.

Haemoglobin is made up of four polypeptide chains, each of which is similar in shape and structure to a myoglobin molecule. Each haem unit in both myoglobin and haemoglobin contains one Fe^{2+} ion bound to four nitrogen donor atoms in a square planar arrangement. This leaves the metal with two axial coordination sites to bind other ligands. One of these sites is occupied by an N-donor ligand from a protein side chain that holds the haem in the pocket of the protein, while the sixth coordination site is where reversible binding of O_2 takes place. Ordinarily, interaction of an Fe(II) ion with molecular O_2 would result in irreversible oxidation to Fe(III) $E^{\ominus}_{O_2/H_2O} = 0.82\,V$ at pH = 7, $E^{\ominus}_{Fe^{3+}/Fe^{2+}} = 0.77\,V$ but, remarkably, as a result of the protein surrounding the haem, both haemoglobin and myoglobin are able to bind O_2 without being irreversibly oxidised (oxidation of haemoglobin gives a compound called methaemoglobin, which cannot bind O_2).

In the lungs, haemoglobin 'loads' four oxygen molecules and then moves through the blood-stream. In tissues, the concentration of O_2 is very low, but there is plenty of CO_2, the end-product of metabolism. The concentration of CO_2 has an important effect on haemoglobin-oxygen binding. Like oxygen, CO_2 can bind to haemoglobin. However, CO_2 binds to specific amino acid side chains of the protein, rather than to the haem group. Binding CO_2 to the protein causes the shape of the haemoglobin molecule to change in ways that reduce the equilibrium constant for O_2 binding. The reduced binding constant allows haemoglobin to release its O_2 molecules in oxygen-deficient, CO_2-rich tissue.

The bloodstream carries this deoxygenated haemoglobin back to the lungs, where it releases CO_2 and binds four more molecules of O_2. This CO_2 effect does not operate in myoglobin, which binds and stores the oxygen released by haemoglobin.

Carbon monoxide seriously impedes transport of O_2. The deadly effect of inhaled CO results from its reaction with haemoglobin. A CO molecule is almost the same size and shape as O_2, so it fits into the binding pocket of the haemoglobin molecule. In addition, the carbon atom of CO forms a stronger bond with Fe(II) than does O_2. Under typical conditions in the lungs, haemoglobin binds CO over 200 times more strongly than it binds O_2. Haemoglobin complexed to CO cannot transport oxygen so, when a significant fraction of haemoglobin contains CO, oxygen 'starvation' occurs at the cellular level, leading to loss of consciousness and death.

An adult human contains only about 4 g of iron, most of it in the form of haem-containing proteins. Yet the daily requirement of iron in the diet is only about 7-18 mg, indicating that the body recycles iron. The recycling of iron requires a transport system and a storage mechanism. Iron is transported by a protein called transferrin, which collects iron in the spleen and liver, where haemoglobin is degraded, and carries it to the bone marrow where fresh red blood cells are synthesised. The protein ferritin stores iron in the body. A ferritin molecule consists of a protein coat and an iron-containing core. The outer coat is made up of 24 polypeptide chains, each comprising about 175 amino acids, which pack together to form a sphere. The sphere is hollow, and channels through the protein coat allow movement of iron in and out of the molecule. The core of the protein contains hydrated iron(III) oxide, $Fe_2O_3{\cdot}H_2O$. The protein retains its shape whether or not iron is stored on the inside. When filled to capacity, one ferritin molecule holds as many as 4500 iron atoms, but the core is only partially filled under normal conditions. In this way, the protein can provide iron as needed for haemoglobin synthesis or to store iron if an excess is absorbed by the body.

Metalloenzymes

As we have seen in this section, molecular oxygen is essential to life. However, the superoxide ion, O_2^-, which is the product of one-electron reduction of O_2, can damage cells and is thought to play a role in the ageing process. The enzyme superoxide dismutase (SOD) is abundant in virtually every type of aerobic organism; its role in cells is to destroy superoxide ions. The active site of the SOD enzyme, the region of the enzyme where the catalytic reaction occurs, contains one copper ion and one zinc ion, each of which displays a tetrahedral geometry. As figure 13.53 shows, the two metals are held close together by a histidine ligand (histidine is an amino acid, chapter 24) that forms a bridge between the Cu(II) and Zn(II) ions.

Chemistry Research

Chelating ligands to treat Fe overload

Professor Paul V Bernhardt, University of Queensland

Professor Paul Bernhardt at the University of Queensland and Professor Des Richardson at the University of Sydney carry out research into new ligands that can coordinate iron in the quest for new drugs to treat iron overload.

Iron is an essential element to humans (and all other life forms) as it is involved in vital biological processes such as respiration, DNA synthesis and energy production. In excess, however, Fe is potentially highly toxic. This condition is referred to as Fe overload. The toxicity of excess Fe is linked to oxidative stress caused by so-called 'Fenton chemistry' where Fe(II) catalyses the breakdown of hydrogen peroxide to toxic hydroxyl radicals:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH + OH^-$$

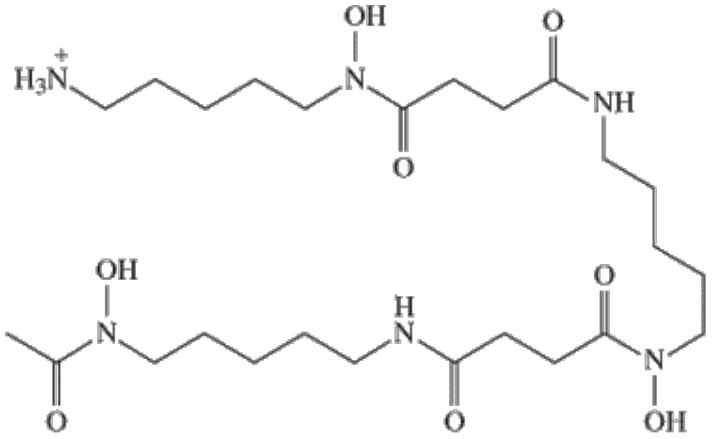
causing DNA damage and affecting normal cell function.

Fe overload can arise in several ways, but if untreated it may lead to irreversible damage to the heart and liver. Coordination chemistry offers a solution to the problem of Fe overload by the administration of ligands (Fe chelators) as drugs that form stable complexes with Fe and enable its removal (figure 13.49); humans have no way of actively excreting excess Fe from their bodies. The first and most successful drug has been

desferrioxamine (DFO), a hexadentate ligand that forms an exceptionally stable Fe(III) complex (figure 13.51). This compound has been used for more than 40 years as a drug to treat Fe overload.



FIGURE 13.49 The structure of the metal-containing site of superoxide dismutase, as determined by X-ray crystallography. The Zn^{2+} and Cu^{2+} cations lie in close proximity, with a histidine side chain (in the box) acting as a bridge between the metals.



desferrioxamine (Desferal, DFO)

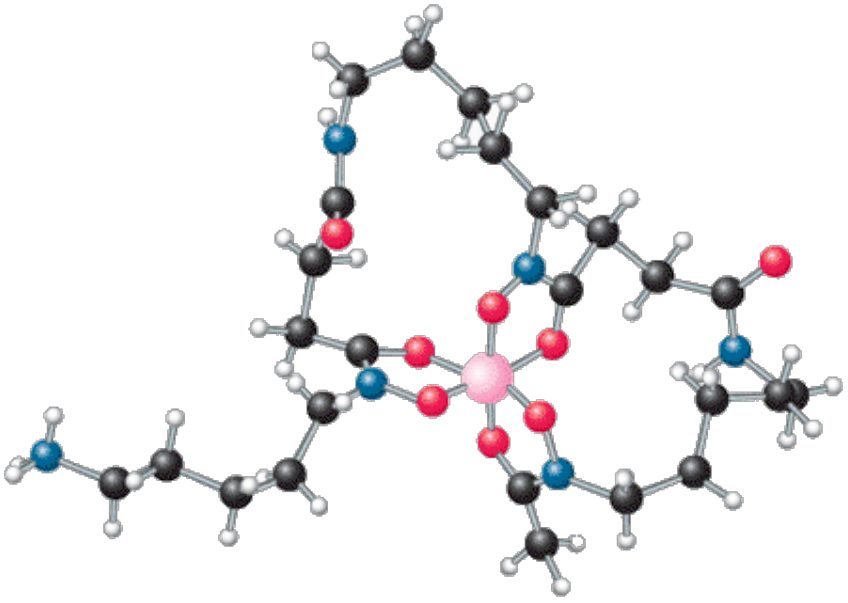


FIGURE 13.50 Fe overload can be successfully treated by the administration of Fe chelators that form stable complexes with Fe.

The main drawback of DFO therapy is that the compound cannot be taken orally but instead is administered by slow injections over periods of hours several days per week; inevitably many patients fail to comply with this strict routine. This has driven research aimed at finding alternative Fe chelators that can be taken orally but at the same time are active in chelating Fe and are nontoxic. A recent breakthrough is the appearance of the drug deferasirox (figure 13.51), in this case a tridentate Fe chelator, which is taken orally once daily to control severe Fe overload.

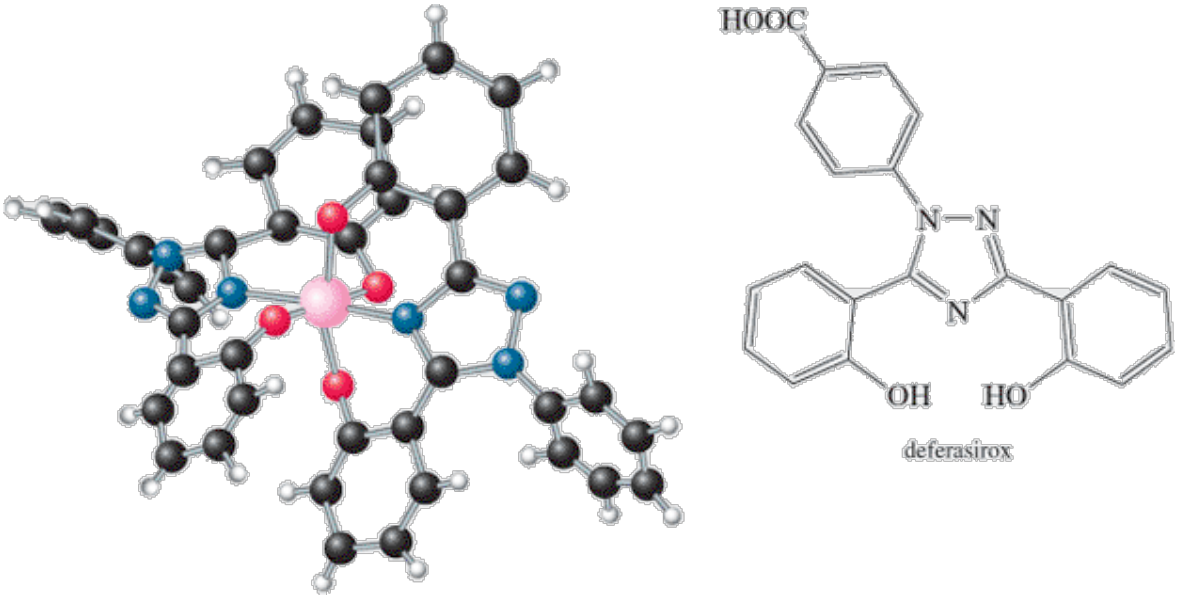
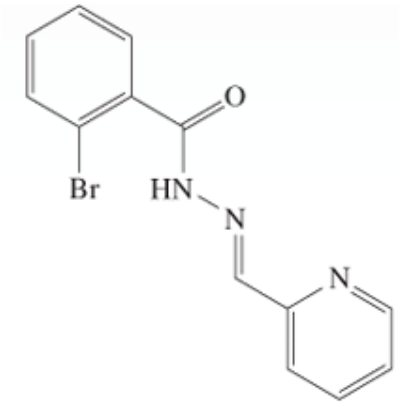
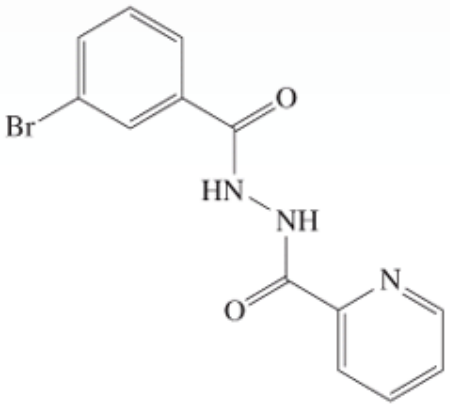


FIGURE 13.51 Chemical structure of desferrioxamine (DFO, deferoxamine) and its Fe(III) complex.

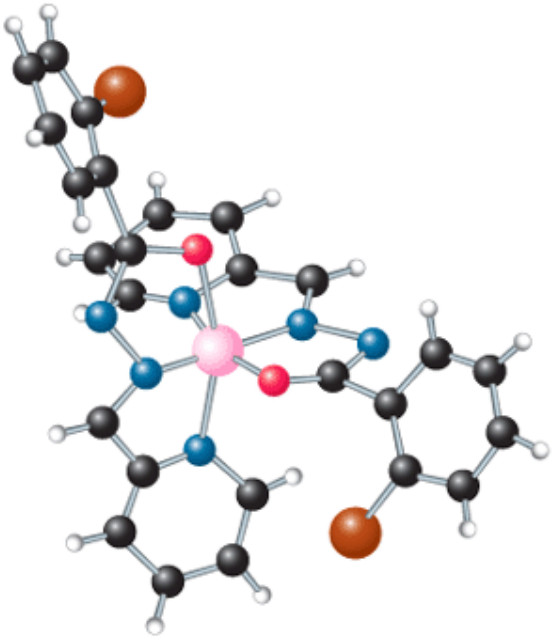
The Bernhardt and Richardson research groups are also developing alternative, potentially orally active, Fe chelating drugs. The two ligands in figure 13.52 (PCBBH and BBPH) appear similar but their Fe coordination chemistry is very different. PCBBH binds only Fe(II) (and not Fe(III)) while BBPH binds only Fe(III) (and not Fe(II)). Both ligands are very effective in removing excess Fe from living cells, and compounds from this family may eventually prove effective alternatives to existing pharmaceuticals.



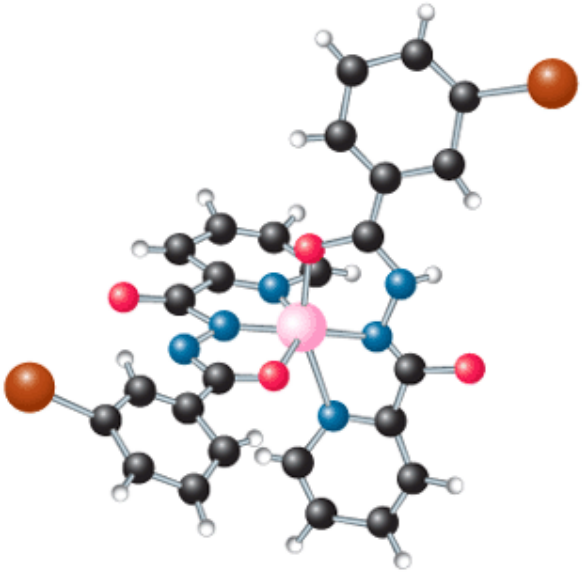
PCBBH (Fe(II) chelator)



BBPH (Fe(III) chelator)



Fe(II) complex of PCBBH



Fe(III) complex of BBPH

FIGURE 13.52 Chemical structure of deferasirox and the crystal structure of an Fe(III) complex of a closely related ligand.

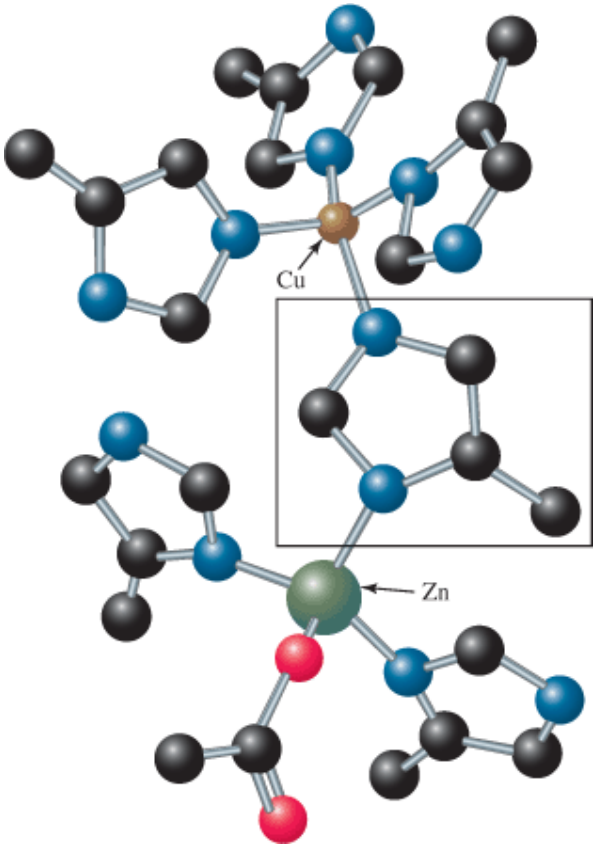


FIGURE 13.53 Molecular structures of new biologically active Fe chelators and their Fe complexes.

It is thought that O_2^- initially binds to the Cu centre, which eventually leads to disproportionation (also called dismutation) of O_2^- and formation of O_2 and H_2O_2. The role of the Zn(II) ion is thought to be purely structural. Interest in superoxide dismutase has increased in recent years with the discovery that a mutation in the gene coding for SOD is linked to certain types of the neurodegenerative disease amyotrophic lateral sclerosis (ALS), and this is currently an area of intense research.

Electron transfer proteins

The many redox reactions that take place within an animal or a plant cell make use of metallo-proteins with a wide range of electron transfer potentials. Some of these proteins play key roles in respiration, photosynthesis and nitrogen fixation, while others simply shuttle electrons to or from enzymes that require electron transfer as part of their catalytic activity. In many other cases, a complex enzyme may incorporate its own electron transfer centres. There are three general categories of transition metal redox centres: cytochromes, blue copper proteins and iron-sulfur proteins. Cytochromes are iron-containing proteins that incorporate haem groups and that facilitate electron transfer by cycling the iron between the (II) and (III) states. A typical blue copper redox protein contains a single copper atom in a distorted tetrahedral environment. The copper centre can cycle between the Cu(I) and Cu(II) oxidation states, thereby aiding electron transfer. Iron-sulfur proteins display a variety of nuclearities (one, two or four iron centres) and

geometries; the two available oxidation states of iron, Fe(II) and Fe(III), allow electron transfer to take place.

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13.6 Isolation and Purification of Transition Metals

The production and purification of metals from their ores is called **metallurgy**. This technology has an ancient history and may represent one of the earliest useful applications of chemistry. Metallurgical advances have had profound influences on the course of human civilisation, so much so that historians speak of the Bronze Age (about 3000 to 5000 years ago) and the Iron Age (starting about 3000 years ago). Metallurgy has also had an enormous impact on the his tories of both New Zealand and Australia, with gold rushes in the nineteenth century contributing significantly to the economy and social fabric of both countries. Australia is one of the most important mineral producers in the world, and the mining industry is a major source of overseas earnings. In this section, we discuss some of the techniques of metallurgy as applied to transition metals, and we also look at some of the areas in which transition metals are used.

Nearly all transition metals are readily oxidised, so most ores are compounds in which the transition metal has a positive oxidation state. Examples include oxides (TiO_2, rutile; Fe_2O_3, haematite; Cu_2O, cuprite), sulfides (ZnS, sphalerite; MoS_2, molybdenite) and carbonates ($FeCO_3$, siderite). Other minerals contain oxoanions ($MnWO_4$, wolframite) and those with even more complex structures such as carnotite, $K_2(UO_2)_2(VO_4)_2{\cdot}3H_2O$. Figure 13.54 shows in schematic fashion some of the alternative paths leading from ores to pure metals, all of which involve reduction as the essential chemical process.

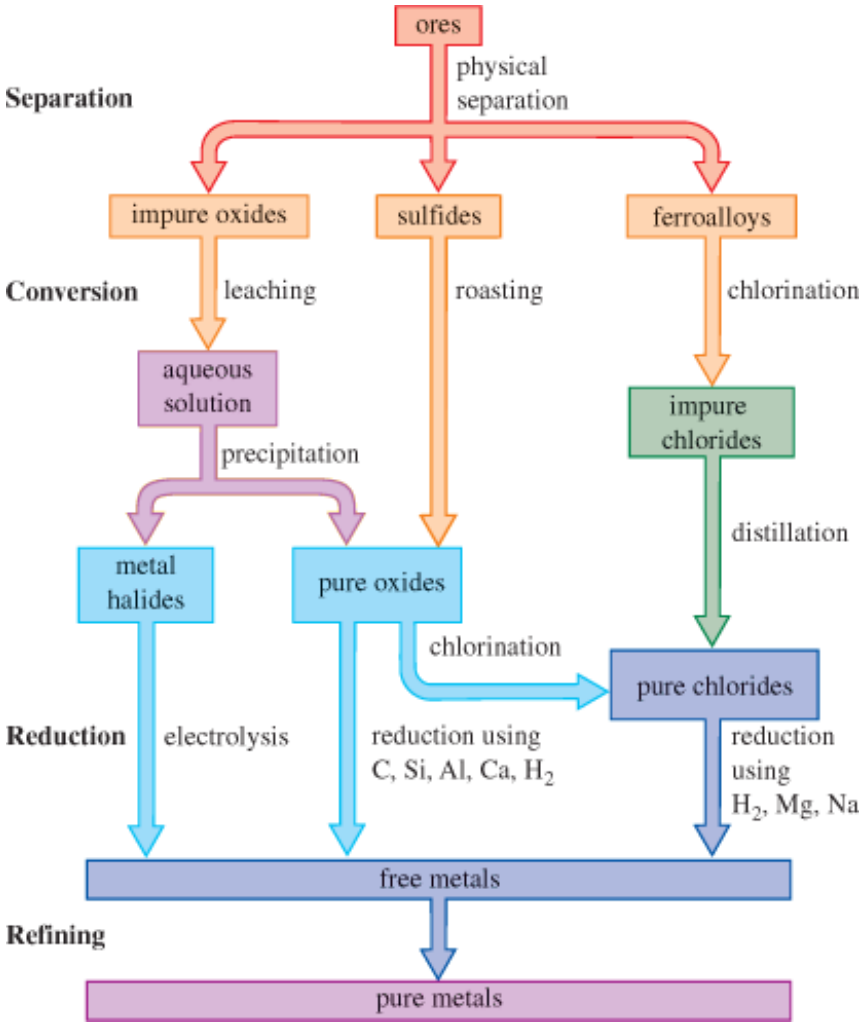


FIGURE 13.54 Metallurgy includes separation, conversion, reduction and refining steps. The starting material is an impure ore, and the end-product is pure metal.

The four main steps in the conversion of an ore to a pure metal are *separation*, *conversion*, *reduction* and *refining*. Separation involves the removal of a particular compound of some desired metal from other contaminants. The conversion step entails chemical treatment of the separated material to convert it into a form that can be easily reduced. Chemical or electrolytic reduction then gives the impure metal, which is

finally refined to the pure metal.

Separation

Ore obtained from a mining operation contains a desired mineral contaminated with other components, which may include sand, clay and organic matter. This economically valueless portion of the ore, which is called gangue (pronounced ‘gang’), must be removed before the metal can be extracted and refined. Ores can be separated into components by physical or chemical methods.

Flotation, a common physical separation process, was discovered and developed in Australia, and was first used on a large scale at Broken Hill in the early years of the twentieth century. During flotation, the ore is crushed and mixed with water to form a thick slurry. As shown in figure 13.55, the slurry is transferred to a flotation vessel and mixed with oil and a surfactant (in this case, a detergent).

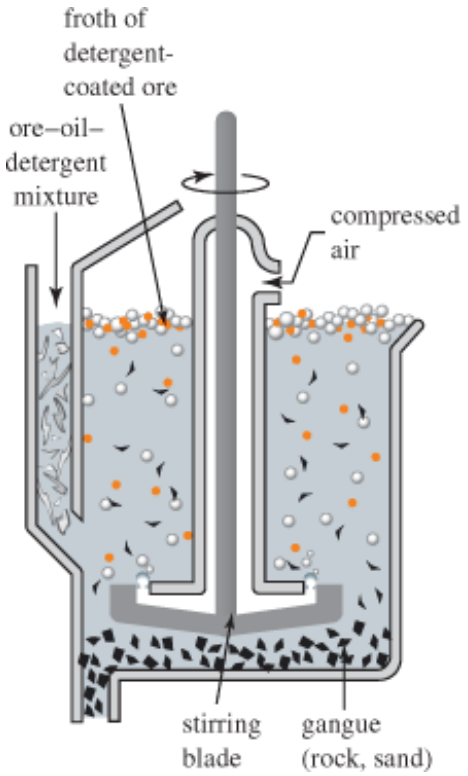


FIGURE 13.55 In the flotation process, detergent-coated mineral particles float to the surface of the mixture, where they become trapped in the froth. The gangue settles to the bottom.

The polar head groups of the detergent coat the surface of the mineral particles, but the nonpolar tails point outwards, making the detergent-coated mineral particles hydrophobic. Air is blown vigorously through the mixture, carrying the oil and the coated mineral to the surface, where they become trapped in the froth. Because the gangue has a much lower affinity for the detergent, it absorbs water and sinks to the bottom of the flotation vessel. The froth is removed at the top, and the gangue is removed at the bottom.

Leaching is a chemical separation technique that uses solubility properties to separate the components of an ore. For example, modern gold production depends on the extraction of tiny particles of gold from gold-bearing rock deposits. After the rock is crushed, it is treated with an aerated aqueous basic solution of sodium cyanide, resulting in the formation of the soluble coordination complex $[Au(CN)_2]^-$, as we saw in worked example 13.7:

$$4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l) \rightarrow 4[Au(CN)_2]^-(aq)4OH^-(aq)$$

Conversion

Sulfide ores may be treated chemically to convert them to oxides before extraction can occur. The process of oxidising an ore by heating to a high temperature in the presence of air is known as roasting. When sulfide ore is roasted, sulfide anions are oxidised and molecular oxygen is reduced. The conversion of sphalerite, ZnS, (figure 13.56) is a typical example:



FIGURE 13.56 Sphalerite.

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

Unfortunately, roasting produces copious amounts of highly polluting SO_2 gas that, in the past, seriously damaged the environment around sulfide ore smelters. Today, zinc and other metals can be extracted from sulfides by reaction with aqueous acid to generate free sulfur or sulfate ions rather than SO_2. Here are two examples:

$$2ZnS(s) + 4H_3O^+(aq) + O_2(g) \rightarrow 2Zn^{2+}(aq) + 2S(s) + 6H_2O(l)$$

$$3CuS(s) + 8NO_3^-(aq) + 8H_3O^+(aq) \rightarrow 3Cu^{2+}(aq) + 8NO(g) + 3SO_4^{2-}(aq) + 12H_2O(l)$$

Taking into account the cost of SO_2 pollution of the atmosphere, these more elaborate aqueous separation procedures are economically competitive with conversion by roasting. Also, in the case of CuS, the liberated $SO_4^{2-}(aq)$ can be converted to H_2SO_4 for use in the manufacture of fertiliser (see chapter 14, p. 622).

Reduction

Once an ore is in suitably pure form, it can be reduced to the free metal. This is accomplished either chemically or electrolytically. Electrolysis is costly because it requires huge amounts of electrical energy. For this reason, chemical reduction is used unless the metal is too reactive for chemical reducing agents to be effective. Mercury is reduced easily enough that roasting the sulfide ore frees the metal. The sulfide ion is the reducing agent, and both O_2 and the metal ion gain electrons:

$$HgS(s) + O_2(g) \rightarrow Hg(l) + SO_2(g)$$

However, this reduction produces SO_2, which must be removed from the exhaust gases. One of the most common chemical reducing agents for metallurgy is coke, a form of carbon made by heating coal at high temperature in the absence of O_2 until all of the volatile impurities have been removed. Metals such as Co, Ni, Fe and Zn that have cations with a moderately negative reduction potential can be reduced by coke. For example, direct reaction with coke in a furnace frees nickel from its oxide:

$$NiO(s) + C(s) \rightarrow Ni(l) + CO(g)$$

Refining

Chemical reduction of an ore usually gives metal that is not pure enough for its intended use. Further refining of the metal removes undesirable impurities. Several important metals, including Cu, Ni, Zn and Cr, are refined by electrolysis, either from an aqueous solution of the metal salt or from anodes prepared from the impure metal. To give one example, Zn(II) ions, obtained by dissolving ZnS or ZnO in acidic solution, can be reduced while water is oxidised:

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$

$$6H_2O(l) \rightarrow O_2(g) + 4H_3O^+(aq) + 4e^-$$

$$2Zn^{2+}(aq) + 6H_2O(l) \rightarrow 2Zn(s) + O_2(g) + 4H_3O^+(aq)$$

Table 13.4 on the next page provides a summary of the chemical species and processes involved in the metallurgy of many transition metals. The following survey of several metals provides further examples of the four phases of metallurgy.

TABLE 13.4 Metallurgy of transition metals

Metal	Ore	Separation method	Intermediate	Reducing agent
Ti	TiO_2	chlorination	$TiCl_4$	Mg
Cr	$FeCr_2O_4$	roasting	Cr_2O_3	Al
Mn	MnO_2		Mn_2O_3	Al
Fe	Fe_3O_4	slag formation	(a)	C
Co	CoAsS	roasting	CoO	C
Ni	Ni_9S_8	complexation	$Ni(CO)_4$	H_2
Cu	$CuFeS_2$	leaching	Cu^{2+}(b)	
Zn	ZnS	roasting	ZnO	C
Mo	MoS_2	roasting	MoO_3	H_2
W	$CaWO_4$	leaching	WO_4^{2-}, WO_3	H_2
Au	Au	leaching	$[Au(CN_2)]^-$	Zn
Hg	HgS	roasting	(c)	S^{2-}

(a) $CaSiO_3$ is formed as an impurity.
(b) SO_4^{2-} is formed as an impurity.
(c) SO_2 is formed as an impurity.

Iron and steel

Iron has been the dominant structural material of modern times and, despite the growth in importance of aluminium and plastics, it still ranks first in total use. Worldwide production of steel (iron strengthened by additives) is in the order of 900 million tonnes per year. Australia produces about 18% of the world's iron ore, third behind China and Brazil, with most coming from mines in Western Australia (figure 13.57). Significant deposits of ironsands are found on the west coast of the North Island of New Zealand.



FIGURE 13.57 Iron ore stockpiles in the Pilbara region of Western Australia.

The most important iron ores are two oxides, haematite, Fe_2O_3, and magnetite, Fe_3O_4. The production of iron from its ores involves several chemical processes that take place in a blast furnace. As shown in figure 13.58, this is an enormous chemical reactor in which heating, reduction and purification occur together.

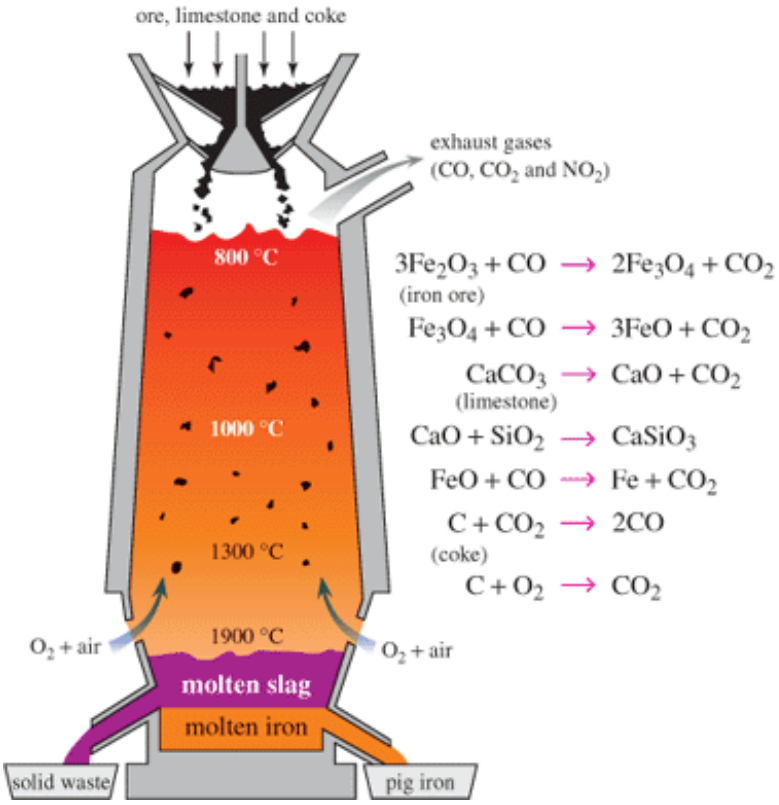




FIGURE 13.58 A diagrammatic view showing the chemical reactions occurring within the pictured blast furnace.

The raw materials placed in a blast furnace include the ore (usually haematite) and coke, which serves as the reducing agent. The ores always contain various amounts of silicon dioxide, SiO_2, which is removed chemically by reaction with limestone, $CaCO_3$. To begin the conversion process, pellets of ore, coke and limestone are mixed and fed into the top of the furnace, and a blast of hot air is blown in at the bottom. As the starting materials fall through the furnace, the burning coke generates intense heat:

$$2C(s) + O_2(g) \rightarrow 2CO(g) \quad \Delta H^{\ominus} = -221\,KJmol^{1}$$

The result is a temperature gradient ranging from about 800 °C at the top of the furnace to 1900 °C at the bottom.

The reduction of iron oxide takes place in several stages in different temperature zones within the furnace. The reducing agent is CO produced from burning coke. The key reactions are:

$$3Fe_2O_3(s) + CO(g) \rightarrow 2Fe_3O_4(s) + CO_2(g)$$
$$Fe_3O_4(g) + CO(g) \rightarrow 3FeO(s) + CO_2(g)$$
$$FeO(s) + CO(g) \rightarrow Fe(I) + CO_2(g)$$

Once liberated from its oxides, the iron melts when the temperature reaches 1500 °C and collects in a pool at the bottom of the furnace.

While heating and reduction occur, limestone decomposes into calcium oxide and CO_2. The CaO then reacts with SiO_2 impurities in the ore to generate calcium silicate:

$$CaCO_3(s) \xrightarrow{heat} CaO(s) + CO_2(g)$$
$$CaO(s) + SiO_2(s) \xrightarrow{heat} CaSiO_3(I)$$

At blast furnace temperatures, calcium silicate is a liquid, called slag. Being less dense than iron, slag pools on the surface of the molten metal. Both products are drained periodically through openings in the bottom of the furnace. Although this chemistry is complex, the basic process is reduction of iron oxide by carbon in an atmosphere depleted of oxygen. Archaeologists have found ancient smelters in Tanzania that exploited this chemistry to produce iron around 2000 years ago. Early African peoples used a hole lined with termite residue as a fuel before adding iron ore. Charred reeds and charcoal provided the reducing substance. Finally, a chimney of mud was added. When this furnace was ‘fired’, a pool of iron collected in the bottom.

The iron formed in a blast furnace, called pig iron, contains impurities that make the metal brittle. These include phosphorus and silicon from silicate and phosphate minerals that contaminate the original ore, as well as carbon and sulfur from the coke. This iron is refined in a converter furnace. Here, a stream of O_2 gas blows through molten impure iron. Oxygen reacts with the nonmetal impurities, converting them to oxides. As in the blast furnace, CaO is added to convert SiO_2 into liquid calcium silicate, in which the other oxides dissolve. The molten iron is analysed at intervals until its impurities have been reduced to satisfactory levels. Then the liquid metal, now in a form called steel, is poured from the converter and allowed to solidify. Most steels contain various amounts of other elements that are added deliberately to give the metal particular properties. These additives may be introduced during the converter process or when the molten metal is

poured off. One of the most important additives is manganese, which adds strength and hardness to steel. Manganese is added to nearly every form of steel in amounts ranging from less than 1% to more than 10%; in fact, more than 80% of all the manganese produced is incorporated into steel.

Titanium

The metallurgy of titanium illustrates the purification of one metal by another. The major titanium ores are rutile, TiO_2, and ilmenite, $FeTiO_3$, and Australia provides a significant proportion of the world's supply of these (about 30% of ilmenite and 55% of rutile). These ores are converted to titanium(IV) chloride by a redox reaction with chlorine gas and coke. For rutile:

$$TiO_2(s) + C(s) + 2Cl_2(g) \xrightarrow{500\,^{\circ}C} TiCl_4(g) + CO_2(g)$$

In this reaction, carbon is oxidised and chlorine is reduced. When the hot gas cools, titanium tetrachloride (bp = 140 °C) condenses to a liquid that is purified by distillation. Titanium metal is obtained by reduction of $TiCl_4$ with molten magnesium metal at high temperature. The reaction gives solid titanium metal (mp = 1660 °C) and liquid magnesium chloride (mp = 714 °C):

$$TiCl_4(g) + 2Mg(l) \xrightarrow{850\,^{\circ}C} Ti(s) + 2MgCl_2(l)$$

Copper

Copper is found mainly in the sulfide ore chalcopyrite, $FeCuS_2$(figure 13.59), but chalcocite, Cu_2S, cuprite, Cu_2O, and malachite, $Cu_2CO_3(OH)_2$, are also important, while elemental copper nuggets can also be found in parts of the world. Copper ores often have concentrations of copper less than 1% by mass, so achieving economic viability requires mining operations on a huge scale. The extraction and purification of copper from chalcopyrite is complicated by the need to remove the iron. The first step in the process is flotation, which concentrates the ore to around 15% Cu by mass. In the next step, the concentrated ore is roasted to convert $FeCuS_2$ to CuS and FeO:

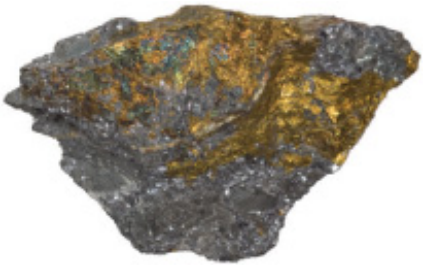


FIGURE 13.59 Chalcopyrite.

$$2FeCuS_2(s) + 3O_2(g) \rightarrow 2CuS(s) + 2FeO(s) + 2SO_2(g)$$

Copper(II) sulfide is unaffected if the temperature is kept below 800 °C. Heating the mixture of CuS and FeO to 1400 °C in the presence of silica, SiO_2, causes the material to melt and separate into two layers. The top layer is molten $FeSiO_3$ formed from the reaction of SiO_2 with FeO. As this takes place, the copper in the bottom layer is reduced from CuS to Cu_2S. This bottom layer consists of molten Cu_2S contaminated with FeS. Reduction of the Cu_2S takes place in a converter furnace following the same principle that converts impure iron into steel. Silica is added, and oxygen gas is blown through the molten mixture. Iron impurities are converted first to FeO and then to $FeSiO_3$, which is a liquid that floats to the surface. At the same time,

Cu_2S is converted to Cu_2O, which reacts with more Cu_2S to give copper metal and SO_2:

$$2Cu_2S(l) + 3O_2(g) \rightarrow 2Cu_2O(l) + 2SO_2(g)$$
$$2Cu_2O(l) + Cu_2S(l) \rightarrow 6Cu(l) + SO_2(g)$$

Copper metal obtained from the converter furnace must be refined to better than 99.95% purity before it can be used to make electrical wiring. This is accomplished by electrolysis, as illustrated in figure 13.60.

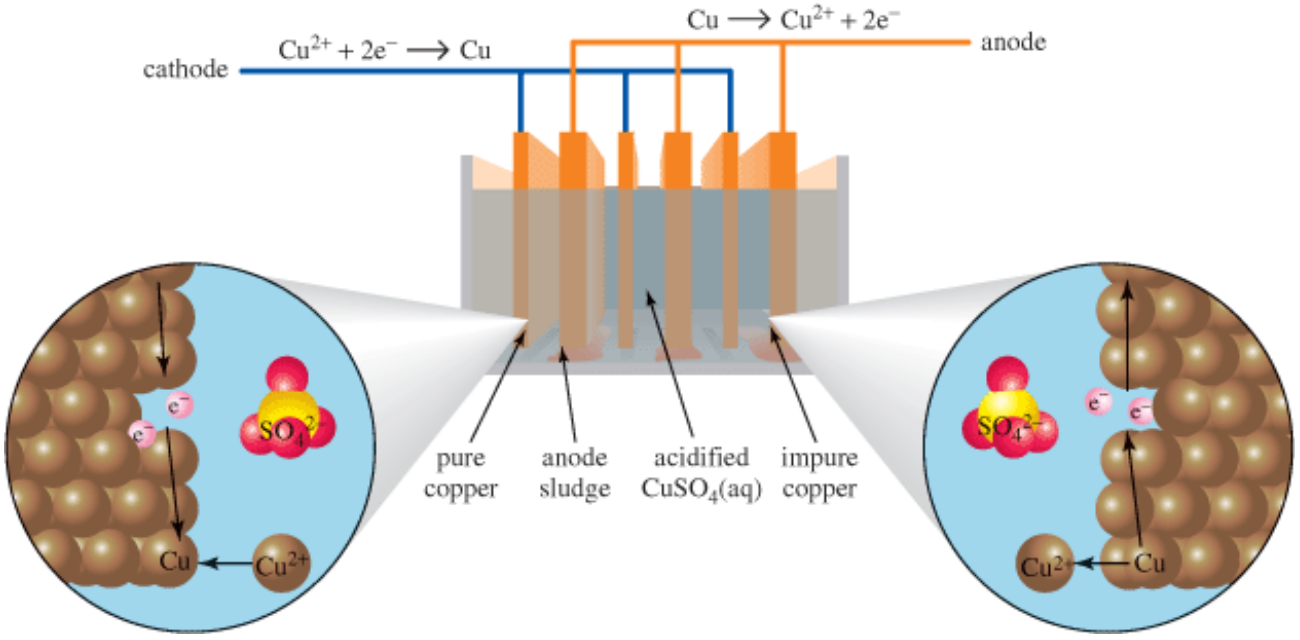


FIGURE 13.60 Diagram of an electrolytic cell for the purification of copper.

The impure copper is formed into slabs that serve as anodes in electrolytic cells. The cathodes are constructed from thin sheets of very pure copper. These electrodes are immersed in a solution of $CuSO_4$ dissolved in dilute sulfuric acid. Application of a controlled voltage causes oxidation in which copper, along with iron and nickel impurities, is oxidised to its cations. Less reactive metal contaminants, including silver, gold and platinum, are not oxidised. As the electrolysis proceeds and the anode dissolves, these and other insoluble impurities fall to the bottom of the cell. The metal cations released from the anode migrate through the solution to the cathode. Because Cu(II) is easier to reduce than Fe(II) and Ni(II), careful control of the applied voltage makes it possible to reduce Cu(II) to Cu metal, leaving Fe(II) and Ni(II) dissolved in solution.

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13.7 Applications of Transition Metals

A complete discussion of all the transition metals is beyond the scope of a first-year chemistry course. Instead, we provide a brief survey of several metals that highlights the diversity and utility of this group of elements.

Titanium

Titanium, the ninth most abundant element in the Earth's crust, is characterised by its high strength, its low density (-57% that of steel) and its stability at very high temperatures. When alloyed with small amounts of aluminium or tin, titanium has the highest strength-to-weight ratio of all the engineering metals. Its major use is in the construction of aircraft frames and jet engines. Because titanium is also highly resistant to corrosion, it is used in the construction of pipes, pumps and vessels for the chemical industry and for surgical implants (figure 13.61). Because it is difficult to purify and fabricate, titanium is an expensive metal. For example, although titanium bicycles are highly prized by avid cyclists, they are quite expensive, frequently costing well over $1000 for just the frame. The most important compound of titanium is titanium(IV) oxide, TiO_2. More than 2 million tonnes of TiO_2 are produced worldwide every year, the majority by the controlled combustion of $TiCl_4$:



FIGURE 13.61 Titanium plates and pins are used to hold this broken leg together.

$$TiCl_4(g) + O_2(g) \xrightarrow{1200^\circ C} TiO_2(s) + 2Cl_2(g)$$

The Cl_2 produced in the combustion reaction is recycled to produce more $TiCl_4$ from rutile ore.

Titanium dioxide is brilliant white, owing to the d^0 electron configuration of the Ti(IV) ions, highly opaque, chemically inert and nontoxic. Consequently, it finds wide use as a pigment in paints and other coatings, paper, sunscreens, cosmetics and toothpaste. TiO_2 is also finding increasing use in solar cells and self-cleaning windows because of its electrochemical properties.

Chromium

Chromium makes up just 0.012% of the Earth's crust, yet it is an important industrial metal. The main use of chromium is in metal alloys. Stainless steel, for example, contains as much as 20% chromium. Nichrome, a 60 : 40 alloy of nickel and chromium, is used to make heat-radiating wires in electrical devices such as toasters and hair dryers. Another important application of chromium metal is as a protective and decorative coating for the surface of metal objects. The only important ore of chromium is chromite, $FeCr_2O_4$. Reduction of chromite with coke gives ferrochrome, an iron-chromium compound:

$$FeCr_2O_4(s) + 4C(s) \rightarrow FeCr_2(s) + 4CO(g)$$

Ferrochrome is mixed directly with molten iron to form chromium-containing stainless steel.

Chromium compounds of high purity can be produced from chromite ore without reduction to the free metal. The first step is the roasting of chromite ore in the presence of sodium carbonate:

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{1100^\circ C} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

The product is converted to sodium dichromate by reaction with sulfuric acid:

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

When the resulting solution is concentrated by evaporation, $Na_2Cr_2O_7 \cdot 2H_2O$ precipitates from the solution. This compound is the most important source of chromium compounds for the chemical industry. It is the starting material for most other chromium-containing compounds of commercial importance, including $(NH_4)_2Cr_2O_7$ (ammonium dichromate), Cr_2O_3 (chromium(III) oxide) and CrO_3 (chromium(VI) oxide).

Pure chromium metal is made by a two-step reduction sequence. First, sodium dichromate is reduced to chromium(III) oxide by heating in the presence of charcoal:

$$Na_2Cr_2O_7 + 2C \xrightarrow{\text{heat}} Cr_2O_3 + Na_2CO_3 + CO$$

Dissolving Cr_2O_3 in sulfuric acid gives an aqueous solution of Cr(III) cations:

$$Cr_2O_3(s) + 6H_3O^+(aq) \rightarrow 2Cr^{3+}(aq) + 9H_2O(l)$$

Electrolysis of this solution reduces the cations to pure Cr metal, which forms a hard, durable film on the surface of the object serving as the cathode. The name ‘chromium’ is derived from the Greek *chroma* meaning ‘colour’, because compounds of this metal display a wide variety of colours (figure 13.62)



FIGURE 13.62 Chromium compounds display a striking range of colours. Shown here are Na_2CrO_4 (yellow), $K_2Cr_2O_7$ (orange), $CrCl_3$ (green) and CrO_3 (dark purple).

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Chromium compounds have been used for many years as pigments in paints and other coatings; for example, $Na_2Cr_2O_7$ is bright orange, Cr_2O_3 is green and the salts of CrO_4^{2-} are bright yellow. However, in recent years, the use of chromium pigments has diminished because chromium in the VI oxidation state is carcinogenic.

Chromium is also important in converting animal hides into leather. In the tanning process, hides are treated with basic solutions of Cr(III) salts, which cause cross-linking of collagen proteins. The hides toughen and become pliable and resistant to biological decay.

Copper, silver and gold

The first three pure metals known to humanity were probably copper, silver and gold (figure 13.63), collectively known as the coinage metals because they found early use as coins. All three can be found in nature in their pure elemental form, and all have been highly valued throughout civilisation. The oldest known gold coins were used in Egypt around 5400 years ago. At about the same time, copper was obtained in the Middle East from charcoal reduction of its ores. The first metallurgy of silver was developed in Asia Minor (Turkey) about 500 years later. All three of these metals are excellent electrical conductors and are highly resistant to corrosion. These properties, coupled with its relatively low cost, make copper one of the most useful metals in modern society. About half of all copper produced is for electrical wiring, and the metal is also widely used for plumbing pipes.



FIGURE 13.63 Gold, silver and bronze have been widely used in medals and coins because they do not corrode.

Copper is used to make several important alloys, the most important of which are bronze and brass. Both alloys contain copper mixed with smaller amounts of tin and zinc in various proportions. The amount of tin in bronze exceeds that of zinc, whereas the opposite is true for brass. The discovery of bronze around 5000 years ago launched the advance of civilisation known today as the Bronze Age. Because bronze is harder and stronger than other metals known in antiquity, it became a mainstay of the civilisations of India and the Mediterranean, being used for tools, cookware, weapons, coins and objects of art. Today, the principal use of bronze is for bearings, fittings and machine parts.

Copper is resistant to oxidation, but over time the metal acquires a coating of green corrosion called

patina (figure 13.64). The green compound is a mixed salt of Cu(II), hydroxide, sulfate and carbonate ions that is formed by air oxidation in the presence of carbon dioxide and small amounts of sulfur dioxide:



FIGURE 13.64 Over time, copper metal develops a green coating called patina.

$$3Cu + 2H_2O + SO_2 + 2O_2 \rightarrow Cu_3(OH)_4SO_4$$
$$2Cu + H_2O + CO_2 + O_2 \rightarrow Cu_2(OH)_2CO_3$$

Although trace amounts of copper are essential for all forms of life, the metal is toxic in large amounts. Thus, copper(II) salts, particularly $CuSO_4 \cdot 5H_2O$, are used as pesticides and wood preservatives. Wood soaked in solutions of Cu(II) or coated with paints containing Cu(II) resist degradation by bacteria, algae and fungi.

Silver is usually found as a minor component of ores of more abundant metals such as copper and zinc. Most commercial silver is produced as a by-product of the production of these common metals. For example, electrolytic refining of copper generates a solid anodic residue that is rich in silver and other precious metals. The silver from this residue can be isolated by oxidising the metal into nitrate-containing solutions, silver nitrate being one of the few soluble silver salts. The pure metal is then deposited electrolytically. Silver is used for tableware in the form of sterling silver, an alloy containing small amounts of copper to make the metal harder. Silver is also used in jewellery, mirrors and batteries, and, prior to the advent of digital cameras, one of its main uses was in photography. Silver does not form a simple oxide by direct oxidation in air, but the metal does form a black tarnish with oxygen and trace amounts of hydrogen sulfide in the atmosphere:

$$4Ag + 2H_2S + O_2 \rightarrow \underset{\text{black}}{2Ag_2S} + 2H_2O$$

The extraction of gold by leaching has been described on p. 584. Gold is used extensively in the manufacture of jewellery. Interestingly, Au(I) compounds are very effective in the treatment of rheumatoid arthritis, and there is recent evidence that certain gold-containing compounds have anticancer properties.

Zinc and mercury

Zinc and mercury are found in the Earth's crust as sulfide ores, the most common of which are sphalerite, ZnS, and cinnabar, HgS; the isolation and purification of the metals from these is described on pp. 583-4. Most of the world's zinc output is used to prevent the corrosion of steel. Zinc is easier to oxidise than iron, as shown by the more negative reduction potential of Zn(II):

$$Fe^{2+} + 2e^- \rightarrow Fe \quad E^\ominus = -0.447\,V$$
$$Zn^{2+} + 2e^- \rightarrow Zn \quad E^\ominus = -0.7618\,V$$

Consequently, a zinc coating oxidises preferentially and protects steel from corrosion. Zinc coatings are applied in several ways: by immersion in molten zinc, by paint containing powdered zinc and by electroplating. Zinc is also combined with copper and tin to make brass and bronze, and large amounts of zinc are used to make several types of batteries. Zinc oxide is the most important zinc compound. Its principal industrial use is as a catalyst to shorten the time of vulcanisation in the production of rubber. The compound is also used as a white pigment in paints, cosmetics and photocopy paper. In everyday life, ZnO is used as a common sun-screen (figure 13.65).



FIGURE 13.65 ZnO is a common sunscreen.

The use of mercury for extracting silver and gold from their ores has been known for many centuries. Gold and silver form amalgams with liquid mercury, which can then be removed by distillation to leave the pure precious metal. The Romans mined the mineral cinnabar, HgS, from deposits in Spain 2000 years ago, and in the sixteenth century the Spanish shipped mercury obtained from the same ore deposits to the Americas for the extraction of silver. Mercury is an important component of street lamps and fluorescent lights. It is used in thermometers and barometers and in gas-pressure regulators, electrical switches and electrodes.

The platinum metals

Six of the transition metals — Ru, Os, Rh, Ir, Pd and Pt — are known collectively as the platinum metals. The group is named for the most familiar and most abundant of the six. These elements are usually found mingled together in ore deposits, and they share many common features. Although they are rare (total annual production is only about 200 tonnes), the platinum metals play important roles in modern society. They are valuable by-products of the extraction of common metals such as copper and nickel, and the anodic residue that results from copper refining is a particularly important source. The chemistry involved in their purification is too complicated to describe here, except to note that the final reduction step involves reaction of molecular hydrogen with metal halide complexes.

By far the most important use of the platinum metals is for catalysis. The largest single use is in catalytic

converters in the exhaust systems of cars. Platinum is the principal catalyst, but catalytic converters also contain rhodium and palladium. These elements catalyse a wide variety of reactions in the chemical and petroleum industries. For example, platinum metal is the catalyst for ammonia oxidation in the production of nitric acid:

$$4NH_3 + 5O_2 \xrightarrow{\text{Pt gauze, } \sim 900\,^{\circ}C} 4NO + 6H_2O$$

Palladium is used as a catalyst for hydrogenation reactions in the food industry, and a rhodium catalyst is used in the production of acetic acid:

$$CH_3OH + CO \xrightarrow{\text{Rh catalyst, } 175\,^{\circ}C} CH_3COOH$$

Osmium and iridium hold the distinction of being the two most dense elements in the periodic table, with a tennis ball-sized sphere of either metal weighing a quite astonishing 3.4 kg.

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SUMMARY

Metals in the periodic table

The majority of known elements are metals, and they occur in distinct sections of the periodic table. Metals in groups 1, 2 and 13-16 are called main-group metals, while those in groups 3-12 are called transition metals. Compounds of the former are usually diamagnetic and colourless while those of the latter are often paramagnetic and coloured. Transition metal ions form complexes in which the metal ion is coordinated to one or more ligands. Complexes can be positively or negatively charged or neutral.

Transition metals

Transition metals are characterised by *d* valence orbitals, and can exist in more than one oxidation state. The *nd* orbitals in transition metal ions are always of lower energy than the (*n* + 1)*s* orbitals so are filled with electrons first. Transition metal ions are Lewis acids.

Ligands

Ligands are Lewis bases that contain one or more electron pairs and can be negatively charged, neutral or, very rarely, positively charged. The atom on which a lone pair is located is called a donor atom; common donor atoms are F, Cl, Br, I, O, S, N and P, although organic compounds with C donor atoms are also known. Ligands that bind to a metal ion using only one donor atom are called mono dentate, those using two are called bidentate and those using two or more are collectively called polydentate. When polydentate ligands bind to a single transition metal ion, they form one or more chelate rings, and complexes containing these are called chelates.

Transition metal complexes

The study of transition metal complexes is called coordination chemistry. Transition metal complexes form as a result of a Lewis acid–Lewis base interaction between a transition metal ion and a ligand. The bonds between the metal ion and the ligand are sometimes called coordinate, donor covalent or dative bonds, while the complexes are often called coordination compounds. Complexes are written enclosed in square brackets, while the counterions (if any) that balance the charge are written outside the square brackets.

The most common coordination number of the central metal ion in transition metal complexes is 6, followed by 4 and 5. Most 6-coordinate complexes display an octahedral geometry. The 4-coordinate complexes adopt either a square planar or tetrahedral geometry, while 5-coordinate complexes are usually trigonal bipyramidal or square pyramidal.

There are numerous isomeric possibilities in transition metal complexes. Structural isomers have the same molecular formula, but different orders of attachments of the constituent atoms. Four important types in coordination chemistry are ionisation isomers, coordination isomers, linkage isomers and hydrate isomers. Linkage isomers are formed with ambidentate ligands, ligands with two or more different types of donor atom. Stereoisomers have the same connections between the constituent atoms, but different arrangements of the atoms in space. An example of such isomerism are *cis*-*trans* isomers; a *cis* isomer has two groups on the same side of some reference plane and a *trans* isomer has the groups on different sides. Meridional (*mer*) and facial (*fac*) isomers are also possible in complexes of the form $[ML_3X_3]$. Transition metal complexes are named according to IUPAC rules.

The formation of transition metal complexes can be quantified by the cumulative formation constant (β_n), which is the equilibrium constant for the process:

$$M^{x+}(aq) + nL(aq) \rightleftharpoons \left[ML_n\right]^{x+}(aq)$$

where $\beta_n = \frac{[ML_n^{x+}(aq)]}{[M^{x+}(aq)][L(aq)]^n}$

β_n values for most transition metal complexes are extremely large, with those for complexes containing bidentate or polydentate ligands being significantly greater than those for the corresponding mono dentate ligands, a manifestation of the chelate effect. Complexes that readily exchange their ligands are said to be labile, while those with slow rates of ligand exchange are called inert.

Crystal field theory can be used to describe the bonding in transition metal complexes, and it predicts that the *d* orbitals, which are degenerate in a free transition metal ion, are split by interactions with the ligand electrons. In an octahedral complex, they are split into a lower energy t_{2g} set of three orbitals and a higher energy e_g set of two orbitals. The energy difference between these sets of orbitals is called the crystal field splitting energy (CFSE), which is given the symbol Δ_o. The way in which these orbitals are filled with electrons depends on the comparative magnitudes of Δ_o and the pairing energy, *P*. If $P > \Delta_o$, a high-spin configuration results; if $P < \Delta_o$, a low-spin configuration results. In octahedral complexes, these possibilities arise only for d^4, d^5, d^6 and d^7 configurations. Different *d*-orbital splitting diagrams are obtained for the 4-coordinate square planar and tetrahedral geometries.

Transition metal complexes are often coloured because of electronic transitions between the nondegenerate *d* orbitals; the colour of the complex is complementary to that absorbed. We quantify the absorbed light by measuring the absorbance with a spectrophoto-meter, and we can calculate the value of Δ_o from the wavelength of the absorbance peak in the UV/visible spectrum. The position of this peak is found to depend on the nature of the ligands, and we can arrange the ligands in order of the magnitude of their crystal field splitting energies to give the spectrochemical series. Ligands giving a large Δ_o are called strong-field while those that induce small splittings are called weak-field. In addition to electronic transitions between the *d* orbitals, very intense ligand-to-metal charge transfer transitions can also occur in transition metal complexes.

Transition metal ions in biological systems

The transition metals V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Mo are essen-tial for healthy biological function. Transition metal ions are important constituents of proteins and enzymes involved in transport and storage (Fe in haemoglobin and ferritin), catalysis (Cu and Zn in superoxide dismutase) and electron transfer (Fe in cytochromes and iron-sulfur proteins and Cu in blue copper proteins). The ability of the transition metal ion to adopt more than one oxidation state and coordination number is crucial to the operation of these biological systems.

Isolation and purification of transition metals

Metallurgy is the study of the production and purification of metals from their ores. As ores contain metals in positive oxidation states, reduction is required to liberate the free metals. The four steps involved in isolating a pure metal from its ore are separation, conversion, reduction and refinement. The reduction step is carried out either chemically or electrolytically, depending on the ore. Iron is the most important metal and is obtained from its ore using a blast furnace, with coke as the reductant. Titanium is isolated from TiO_2 by conversion to $TiCl_4$ and reduction with molten Mg, while copper is obtained from its sulfide and oxide ores and purified by electrolysis.

Applications of transition metals

Transition metals have a vast number of uses. Titanium has high strength and low density, making it useful for aircraft and bike frames and jet engines. Most chromium is used to make steel and other alloys. Copper, silver and gold, the coinage metals, are quite resistant to direct oxidation; copper is

mainly used in electrical wiring, while some gold complexes are useful for treating arthritis. Zinc is used to galvanise iron, while mercury is used in thermometers and fluorescent lights. Ru, Os, Rh, Ir, Pd and Pt constitute the platinum metals and are chemically important as solid catalysts in industrial processes as well as catalytic converters in cars.

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Determining *d*-electron configurations *(section 13.2)*

This allows us to calculate the number of *d* electrons in any transition metal ion. Neutral atoms have valence electron configurations of $(n + 1)s^2nd^{x-2}$, where *x* is the group number of the metal in the periodic table and *n* is the principal quantum number. The *nd* orbitals are filled before the $(n + 1)s$ orbitals in transition metal ions.

Cumulative formation constant (β_n) *(section 13.4)*

This quantifies the extent to which the formation reaction of a transition metal complex occurs. For the equilibrium:

$$M^{x+}(aq) + nL(aq) \rightleftharpoons [ML_n]^{x+}(aq)$$

$$\beta_n = \frac{[ML_n{}^{x+}(aq)]}{[M^{x+}(aq)]\,[L(aq)]^n}$$

Naming transition metal complexes *(section 13.4)*

The IUPAC rules allow us to determine the correct name of any transition metal complex.

1. Cationic species are named before anionic species.
2. The names of anionic ligands always end in the suffix *-o*. Ligands with names ending in *-ide*, *-ite* and *-ate* have this suffix changed to *-ido*, *-ito* and *-ato*, respectively.
3. A neutral ligand is usually given the same name as the neutral molecule, except aqua for H_2O, ammine for NH_3 and carbonyl for CO.
4. The number of a particular ligand is specified by the prefixes *di-* = 2, *tri-* = 3, *tetra-* = 4, *penta-* = 5, *hexa-* = 6 etc.
5. Ligands are named first, in alphabetical order without regard to charge, followed by the name of the metal.
6. Negative (anionic) complex ions always end in the suffix *-ate*. For neutral or positively charged complexes, the metal is always specified with the English name for the element, without any suffix.
7. The oxidation state of the metal in the complex is written in Roman numerals within parentheses following the name of the metal.
8. The number of counterions need not be specified.
9. Include any stereochemical descriptors (e.g. *cis*, *trans*, *mer*, *fac*) at the start of the name, italicised and hyphenated.

Crystal field theory *(section 13.4)*

This allows us to determine the *d*-orbital splitting diagrams for transition metal complexes of any geometry, and hence the *d*-electron configuration in these complexes. It is based on the crystal field splitting energy, which is the energy difference (Δ_o) between the d_{xy}, d_{xz} and d_{yz} orbital set and the $d_{x^2-y^2}$ and $d_z{}^2$ orbital set.

The spectrochemical series *(section 13.4)*

The position of a ligand in the spectrochemical series tells us the magnitude of the *d*-orbital splitting it can induce. In order of decreasing Δ_o values, the series is:

$$CO = CN^- > NO_2^- > en > NH_3 > H_2O > C_2O_4^{2-} > OH^- > F^- > Cl^- > Br^- > I^-$$

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METALS IN THE PERIODIC TABLE AND TRANSITION METALS

13.1 The following compounds can be purchased from chemical supply companies. Determine the oxidation state of the transition metal in each:

(a) $MnCO_3$,

(b) $MoCl_5$,

(c) Na_3VO_4,

(d) Au_2O_3,

(e) $Fe_2(SO_4)_3 \cdot 5H_2O$,

(f) $NiSO_4$,

(g) $KMnO_4$,

(h) $(NH_4)_2WO_4$,

(i) $PbCrO_4$,

(j) $ZrOCl_2 \cdot 8H_2O$.

13.2 Give the names and symbols for the elements that have the following valence configurations:

(a) $4s^1 3d^5$,

(b) $5s^2 4d^{10}$,

(c) $4s^1 3d^{10}$,

(d) $5s^1 4d^8$,

(e) $4s^2 3d^2$,

(f) $5s^1 4d^4$.

13.3 Write valence electron configurations for the following transition metal cations:

(a) Mn^{2+},

(b) Ir^{3+},

(c) Ni^{2+},

(d) Mo^{2+},

(e) Ti^{2+},

(f) Fe^{3+},

(g) Pt^{2+},

(h) Nb^{3+}.

LIGANDS

13.4 To be a ligand, a substance should also generally be a Lewis base. Explain.

13.5 Give the names of two molecules that are electrically neutral, monodentate ligands.

13.6 Give the formulae of four ions that have 1- charges and are monatomic, monodentate ligands.

13.7 What must be true about a ligand classified as bidentate?

13.8 What is a chelate? Use Lewis structures to illustrate how the oxalate ion, $C_2O_4^{2-}$, functions as a chelating ligand.

13.9 How many potential donor atoms does $EDTA^{4-}$ have?

TRANSITION METAL COMPLEXES

13.10 The formation of the complex ion $[Cu(OH_2)_5]^{2+}$ is described as a Lewis acid-base reaction.

(a) Explain this statement.
(b) What are the formulae of the Lewis acid and the Lewis base in this reaction?
(c) What is the formula of the ligand?
(d) What is the name of the species that provides the donor atom?
(e) What atom is the donor atom, and why is it so designated?
(f) What is the name of the species that is the acceptor?

13.11 Why are substances that contain complex ions often called coordination compounds?

13.12 Use Lewis structures to illustrate the formation of $[Cu(NH_3)_4]^{2+}$ and $[CuCl_4]^{2-}$ ions from their respective

13.13 How does a salt of $EDTA^{4-}$ in shampoo make the shampoo work better in hard water? (Hard water generally contains high concentrations of metal ions such as Ca^{2+} and Mg^{2+}.)

13.14 The cobalt(III) ion, Co^{3+}, forms a 1 : 1 complex with $EDTA^{4-}$. What is the net charge, if any, on this complex, and what would be a suitable formula for it (using the symbol EDTA)?

13.15 Which complex has a higher β_n value, $[Cr(NH_3)_6]^{3+}$ or $[Cr(en)_3]^{3+}$? Why?

13.16 What is a coordination number? What structures are generally observed for complexes in which the central metal ion has a coordination number of 4?

13.17 What is the most common structure observed for coordination number 6?

13.18 Sketch the structure of an octahedral complex that contains only identical monodentate ligands.

13.19 What are isomers?

13.20 Define ‘stereoisomerism’.

13.21 What are *cis* and *trans* isomers?

13.22 What is cisplatin? Draw its structure.

13.23 On appropriate coordinate axes, sketch and label the five *d* orbitals.

13.24 Which *d* orbitals point between the *x*-, *y*- and *z*-axes and which point along the axes?

13.25 Explain why an electron in a $d_{x^2-y^2}$ or d_{z^2} orbital in an octahedral complex experiences greater repulsion by the ligands than an electron in a d_{xy}, d_{xz} or d_{yz} orbital.

13.26 Sketch the *d*-orbital energy level diagram for a typical octahedral complex.

13.27 Explain how the same metal in the same oxidation state can form complexes of different colours.

13.28 If a complex appears red, what colour light does it absorb? What colour light is absorbed if the complex appears yellow?

13.29 What does the term ‘spectrochemical series’ mean? How can the order of the ligands in the series be determined?

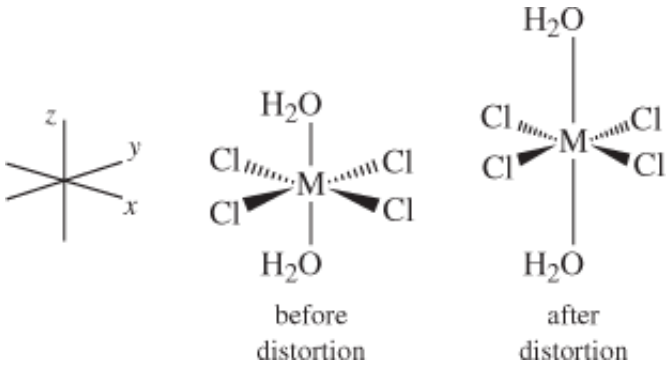
13.30 What do the terms ‘low-spin complex’ and ‘high-spin complex’ mean?

13.31 For which *d*-orbital electron configurations are both high-spin and low-spin complexes possible in octahedral complexes?

13.32 Sketch what happens to the *d*-orbital electron configuration of the $[Fe(CN)_6]^{4-}$ ion when it absorbs a photon of visible light.

13.33 The complex $[Co(O_2C_2O_2)_3]^{3-}$ is diamagnetic. Sketch the *d*-orbital energy level diagram for this complex and indicate the electron occupancy of the orbitals.

13.34 Consider the complex $[MCl_4(OH_2)_2]^-$ illustrated in the centre below. Suppose the structure of this complex is distorted to give the structure on the right, where the water molecules along the *z*-axis have moved away from the metal somewhat and the four chloride ions along the *x*- and *y*-axes have moved closer. What effect will this distortion have on the splitting pattern of the *d* orbitals? Use a sketch of the splitting pattern to illustrate your answer.



TRANSITION METAL IONS IN BIOLOGICAL SYSTEMS

13.35 Summarise the differences between haemoglobin and myoglobin.

13.36 What features do myoglobin and the cytochromes have in common?

ISOLATION AND PURIFICATION OF TRANSITION METALS

13.37 Use your own words to define ‘metallurgy’.

13.38 What is gangue?

13.39 Why can gold be separated from impurities of rock and sand by panning?

13.40 Describe the flotation process.

13.41 Write chemical equations for the reactions that occur when Cu_2S and PbS are roasted in air. Write a chemical equation to show how SO_2 evolved from the roasting can be prevented from being released to the environment. Why might a sulfuric acid plant be located near a plant that roasts sulfide ores?

13.42 Why is reduction, rather than oxidation, necessary to extract metals from their compounds?

13.43 What is coke? How is it made?

13.44 Describe the chemical reactions involved in the reduction of Fe_2O_3 that take place in a blast furnace. What is the active reducing agent in the blast furnace?

13.45 What does ‘refining’ mean in metallurgy?

13.46 What is the difference between pig iron and steel?

APPLICATIONS OF TRANSITION METALS

13.47 Identify the coinage metals and describe some of their applications.

13.48 Identify the platinum metals and describe some of their applications.

13.49 What features of titanium account for its use as an engineering metal?

13.50 Explain why titanium(IV) oxide is used extensively as a white pigment.

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REVIEW PROBLEMS

13.51 The iron(III) ion forms a complex with six cyanide ions, called the ferricyanide ion. What is the net charge on this complex ion, and what is its formula?

13.52 Write the formula, including the correct charge, for a complex that contains Co(III), two Cl^- ligands and two ethylenediamine ligands.

13.53 Write the formula, including the correct charge, for a complex that contains Co(III), two NH_3 ligands and four NO_2^- ligands.

13.54 How would the following molecules or ions be named as ligands when writing the name of a complex ion?

(a) $C_2O_4^{2-}$

(b) S^{2-}

(c) Cl^-

(d) $(CH_3)_2NH$ (dimethylamine)

(e) NH_3

(f) N^{3-}

(g) SO_4^{2-}

(h) CH_3COO^-

13.55 Give IUPAC names for each of the following.

(a) $[Ni(NH_3)_6]^{2+}$

(b) $[CrCl_3(NH_3)_3]$

(c) $[Co(NO_2)_6]^{3-}$

(d) $[Mn(CN)_4(NH_3)_2]^{2-}$

(e) $[Fe(O_2C_2O_2)_3]^{3-}$

(f) $[AgI_2]^-$

(g) $[Co(en)_2(OH_2)_2]_2(SO_4)_3$

(h) $[CrCl(NH_3)_5]SO_4$

(i) $K_3[Co(O_2C_2O_2)_3]$

13.56 Write chemical formulae for each of the following.

(a) tetraaquadicyanidoiron(III) ion

(b) tetraammineoxalatonickel(II)

(c) diaquatetracyanidoferrate(III) ion

(d) potassium hexathiocyanatomanganate(III)

(e) tetrachloridocuprate(II) ion

(f) tetrachloridoaurate(III) ion

(g) bis(ethylenediamine) dinitroiron(III) ion

(h) tetraamminedicarbonatocobalt(III) nitrate

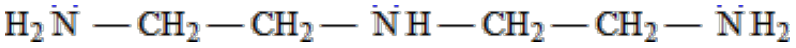
(i) ethylenediaminetetraacetatoferrate(II) ion

(j) diamminedichloridoplatinum(II)

13.57 In $[FeCl_2(en)(OH_2)_2]$, what is the coordination number of iron? What is its oxidation number in this complex?

13.58 What is the coordination number of nickel in $[Ni(NO_2)_2(O_2C_2O_2)_2]^{4-}$?

13.59 The compound shown below is commonly called diethylenetriamine (not its IUPAC name) and is abbreviated 'dien'.



It uses three donor atoms when it bonds to a transition metal ion.

(a) Identify the donor atoms.

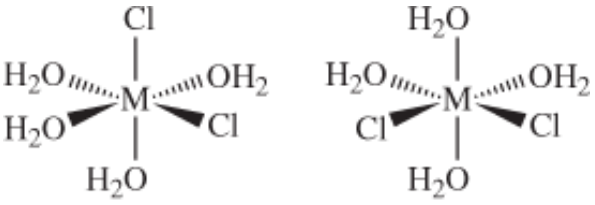
(b) What is the coordination number of cobalt in the complex $[Co(dien)_2]^{3+}$?

(c) Sketch the structure of the complex $[Co(dien)_2]^{3+}$.

(d) Which complex would be expected to have the larger β_n value, $[Co(dien)_2]^{3+}$ or $[Co(NH_3)_6]^{3+}$?

(e) Draw the structure of triethylenetetraamine.

13.60 The following are two structures for a complex. Are they different isomers, or are they identical? Explain your answer.



13.61 Sketch and label the isomers of the square planar complex $[PtBrCl(NH_3)_2]$.

13.62 The complex $[CoCl_3(NH_3)_3]$ can exist in two isomeric forms. Sketch them.

13.63 For each of the following pairs, in which complex do we expect to find the larger Δ_o?

(a) $[Cr(OH_2)_6]^{2+}$ or $[Cr(OH_2)_6]^{3+}$

(b) $[Cr(en)_3]^{3+}$ or $[CrCl_6]^{3-}$

13.64 Arrange the following complexes according to the wavelengths of their absorption maxima, from lowest to highest: $[Cr(OH_2)_6]^{3+}$, $[CrCl_6]^{3-}$, $[Cr(en)_3]^{3+}$, $[Cr(CN)_6]^{3-}$, $[Cr(NO_2)_6]^{3-}$, $[CrF_6]^{3-}$, $[Cr(NH_3)_6]^{3+}$.

13.65 Which complex is expected to absorb light of the highest frequency: $[Cr(OH_2)_6]^{3+}$, $[Cr(en)_3]^{3+}$ or $[Cr(CN)_6]^{3-}$?

13.66 In each of the following pairs, which complex should absorb light of the longer wavelength?

(a) $[Fe(OH_2)_6]^{2+}$ or $[Fe(CN)_6]^{4-}$

(b) $[Mn(CN)_6]^{3-}$ or $[Mn(CN)_6]^{4-}$

13.67 In each of the following pairs, which complex is expected to absorb the shorter wavelength of light? Justify your answers.

(a) $[RuCl(NH_3)_5]^{2+}$ or $[FeCl(NH_3)_5]^{2+}$

(b) $[Ru(NH_3)_6]^{2+}$ or $[Ru(NH_3)_6]^{3+}$

13.68 An octahedral complex [Co*A* o 6]$^{3+}$ is red. The complex $[CoB_6]^{3+}$ is green. Which ligand, *A* or *B*, produces the larger crystal field splitting energy, Δ_o? Explain your answer.

13.69 Referring to the two ligands, *A* and *B*, described in question 13.68, which complex is expected to be more easily oxidised, $[CoA_6]^{2+}$ or $[CoB_6]^{2+}$? Explain your answer.

13.70 Referring to the complexes in questions 13.68 and 13.69, is the colour of [Co*A* o 6]$^{2+}$ more likely to be red or blue?

13.71 Is the complex $[CoF_6]^{4}$ - more likely to be low-spin or highspin? Could it be diamagnetic?

13.72 Sketch the *d*-orbital energy levels for $[Fe(OH_2)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ and predict the number of unpaired electrons in each.

13.73 Determine the oxidation state and number of *d* electrons for the metal ion in each of the following coordination complexes.

(a) $[Ru(NH_3)_6]Cl_2$

(b) *trans*-$[Cr(en)_2I_2]I$

(c) *cis*-$[PdCl_2(P(CH_3)_3)_2]$

(d) *fac*-$[IrCl_3(NH_3)_3]$

(e) $[Ni(CO)_4]$

(f) $[Rh(en)_3]Cl_3$

(g) *cis*-$[MoBr_2(CO)_4]$

(h) $Na_3[IrCl_6]$

(i) *mer*-$[IrCl_3(NH_3)_3]$

(j) $[Mn(CO)_5Cl]$

13.74 Name the compounds in question 13.73.

13.75 Draw structures of the metal complexes in question 13.73.

13.76 Write the formulae of the following complexes.

(a) *cis*-tetraamminechloridonitrocobalt(III)

(b) amminetrichloridoplatinate(II)

(c) *trans*-diaquabis(ethylenediamine) copper(II)

(d) tetrachloridoferrate(III).

(e) potassium tetrachloridoplatinate(II)

(f) pentaammineaquachromium(III) iodide

(g) tris(ethylenediamine) manganese(II) chloride

(h) pentaammineiodidocobalt(III) nitrate.

13.77 Draw the structure of each complex ion in question 13.76.

13.78 For an octahedral complex of each of the following metal ions, draw a crystal field energy diagram that shows the electron occupancy of the various *d* orbitals:

(a) Ti(II),

(b) Cr(III),

(c) Mn(II),

(d) Fe(III),

(e) Zn(II),

(f) Cr(II),

(g) Co(II),

(h) Rh(III).

Where appropriate, show both the high-spin and low-spin configurations.

13.79 Predict whether each of the following complexes is diamagnetic or paramagnetic. If the complex is paramagnetic, state the number of unpaired electrons it has and estimate its magnetic moment.

(a) $[Ir(NH_3)_6]^{3+}$

(b) $[Cr(OH_2)_6]^{2+}$

(c) $[PtCl_4]^{2-}$ (square planar)

(d) $[Pd(P(CH_3)_3)_4]$ (square planar)

(e) $[Ru(CN)_6]^{4}$ -

(f) $[Co(NH_3)_6]^{3+}$

(g) $[CoBr_4]^{2-}$ (tetrahedral)

(h) $[PtCl_2(en)]$ (square planar)

13.80 Compounds of Zr(II) are dark purple, but most Zr(IV) compounds are colourless. Explain.

13.81 One of the coordination complexes $[Cr(OH_2)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ is violet and the other is orange. Decide which is which and explain your reasoning.

13.82 The complex $[Fe(en)_3]Cl_3$ is low-spin. State:

(a) the coordination number of the metal

(b) the oxidation number and number of *d* electrons of the metal

(c) the geometry of the complex

(d) whether the complex is diamagnetic or paramagnetic

(e) the number of unpaired electrons in the complex

(f) the magnetic moment of the complex.

13.83 The complex $[Mn(OH_2)_6]SO_4$ is high-spin. State:

(a) the coordination number of the metal

(b) the oxidation number and number of *d* electrons of the metal

(c) the geometry of the complex

(d) whether the complex is diamagnetic or paramagnetic

(e) the number of unpaired electrons in the complex

(f) the magnetic moment of the complex.

13.84 A solution containing Fe(II)(aq) is paramagnetic. Addition of sodium cyanide makes the solution diamagnetic. Use crystal field energy diagrams to explain why the magnetic properties of the solutions are different.

13.85 The complex $[Cr(NH_3)_6]^{3+}$ has its maximum absorbance at 465 nm. Calculate the crystal field splitting energy for the compound and predict its colour.

13.86 The complex $[Fe(OH_2)_6]^{3+}$ has its maximum absorbance at 724 nm. Calculate the crystal field splitting energy for the compound and predict its colour.

13.87 Draw all possible isomers of the following compounds:

(a) $[IrCl_3(NH_3)_3]$,

(b) $[PdCl_2(PMe_3)_2]$,

(c) $[CrBr_2(CO)_4]$,

(d) $[Cr(en)I_2(NH_3)_2]$.

13.88 Draw the structures of all possible isomers of each of the following coordination compounds.

(a) tetraamminedibromidocobalt(III) bromide

(b) triamminetrichloridochromium(III)

(c) dicarbonylbis(trimethylphosphane) platinum(0)

13.89 The carbonate ion can be either a monodentate or a bidentate ligand. Make sketches that show the ligand binding to a metal cation in both modes.

13.90 Write electron configurations for the following:

(a) Cr, Cr(II) and Cr(III),

(b) V, V(II), V(III), V(IV) and V(V),

(c) Ti, Ti(II) and Ti(IV),

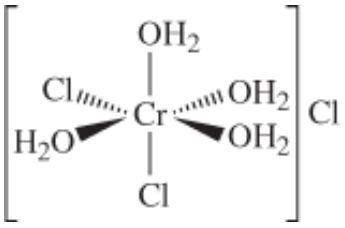
(d) Au, Au(I) and Au(II),

(e) Ni, Ni(II) and Ni(III),

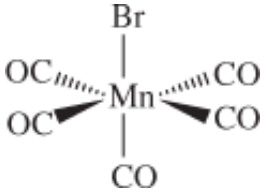
(f) Mn, Mn(II), Mn(IV) and Mn(VII).

13.91 Name the following coordination compounds.

(a)



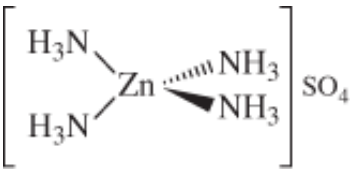
(b)



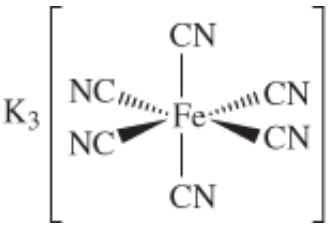
(c)



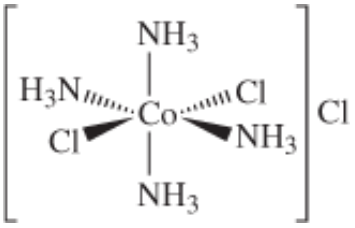
(d)



(e)



(f)



13.92 The Cu(II) ion forms tetrahedral complexes with some anionic ligands. When $CuSO_4 \cdot 5H_2O$ dissolves in water, a blue solution results. The addition of aqueous KF solution results in a green precipitate, but the addition of aqueous KCl results in a bright green solution. Identify each green species and write chemical reactions for these processes.

13.93 The Cu(II) ion forms tetrahedral complexes with some anionic ligands. When $CuSO_4 \cdot 5H_2O$ dissolves in water, a blue solution results. The addition of aqueous KCN solution results in a white precipitate at first, but the addition of more KCN causes the precipitate to dissolve. Identify the precipitate and the dissolved species and write chemical reactions for these processes.

13.94 Draw a ball-and-stick model of the *mer* isomer of *r* $[NiCl_3F_3]^{4-}$, oriented so that the fluoride ions are in the top, bottom and left forward positions.

13.95 Draw a ball-and-stick model of the *fac* isomer of $[NiCl_3F_3]^{4-}$, oriented so that the fluoride ions are in the top and two rear positions.

13.96 As ligands, chloride and cyanide are at opposite ends of the spectrochemical series. Nevertheless, experiments show that $[CrCl_6]^{3-}$ and $[Cr(CN)_6]^{3-}$ display similar magnetic behaviour. Explain how this can be so.

13.97 In octahedral geometry, the magnetism in d^4 - d^7 coordination compounds of the 3*d* transition metals depends on the ligands and the oxidation state of the metal. On the other hand, d^1 - d^3 and d^8 - d^9 compounds always display similar magnetic behaviour. Explain.

13.98 The $d_{x^2-y^2}$ and d_{z2} orbitals are degenerate in an octahedral complex. However, in a square planar complex, the $d_{x^2-y^2}$ orbital is of higher energy than the d_{z2} orbital. Use orbital sketches to explain the difference.

13.99 Use orbital sketches to explain why the d_{xz} and $d_{x^2-y^2}$ orbitals have different energies in octahedral coordination complexes.

13.100 Determine the Lewis structure of the dichromate anion, $[Cr_2O_7]^{2-}$, which contains one bridging oxygen atom, and draw a model showing its geometry.

13.101 Write a balanced equation for the reaction catalysed by the enzyme superoxide dismutase. Make a sketch of the coordination environment around the two metal atoms.

13.102 Some researchers use the term ‘the brass enzyme’ to describe superoxide dismutase. Can you suggest a reason for this nickname?

13.103 Blue copper proteins are blue when they contain Cu(II) but colourless as Cu(I) compounds. The colour comes from an interaction in which a photon causes an electron to transfer from a sulfur lone pair on a cysteine ligand to the copper centre. Why does this charge transfer interaction

occur for Cu(II) but not Cu(I)?

13.104 Solutions containing $Cu^{2+}(aq)$ ions are blue, whereas solutions containing $Zn^{2+}(aq)$ ions are colourless. Explain this observation.

13.105 One of the most common approaches to the investigation of metalloproteins is to replace the naturally occurring metal ion with a different one that has a property advantageous for chemical studies. For example, zinc proteins are often studied by visible spectroscopy after Co(II) has been substituted for Zn(II). Explain, using crystal field energy diagrams, why Co(II) is a better metal than Zn(II) for visible spectroscopy.

13.106 Explain how liquid mercury can be used to purify metals such as gold and silver.

13.107 Write balanced chemical equations for each of the following metallurgical processes:

(a) roasting of $CuFeS_2$,

(b) removal of silicon from steel in a converter,

(c) reduction of titanium tetrachloride using sodium metal.

13.108 A copper ore contains 2.37% Cu_2S by mass. If 5.60×10^4 kg of this ore is heated in air, calculate the mass of copper metal that is obtained and the volume of SO_2 gas produced in ambient conditions (9.93×10^4 Pa and 23.5 °C).

13.109 What mass of limestone, in kilograms, should be added to every kilogram of iron ore processed in a blast furnace if the limestone is 95.5% $CaCO_3$ and the iron ore contains 9.75% SiO_2?

13.110 Both vanadium and silver are lustrous silvery metals. Suggest why silver is widely used for jewellery but vanadium is not.

13.111 Titanium is nearly 100 times more abundant in the Earth's crust than copper. However, copper was exploited as a metal in antiquity, but titanium has found applications only in recent times. Explain.

13.112 What is the chemical name and the formula of the black tarnish that accumulates on objects made of silver? Write a balanced equation to show how this black tarnish forms.

13.113 What is the chemical name and the composition of the green tarnish that accumulates on objects made of copper? Write balanced equations to show how this green tarnish forms.

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ADDITIONAL EXERCISES

13.114 The complex $[PtCl_2(NH_3)_2]$ can be obtained as two distinct isomeric forms. Show that this means the complex cannot be tetrahedral.

13.115 A solution was prepared by dissolving 0.500 g of $CrCl_3 \cdot 6H_2O$ in 100 mL of water. Excess silver nitrate solution was added. This produced a precipitate of AgCl, which was filtered from the mixture, washed, dried and weighed. The AgCl had a mass of 0.538 g.

(a) What is the formula of the complex ion of chromium in this compound?

(b) What is the correct formula for the compound?

(c) Sketch the structure of the complex ion in this compound.

(d) How many different isomers of the complex can be drawn?

13.116 The octahedral chromium complexes $[Cr(NH_3)_5L]^{n+}$, where L is Cl^-, H_2O or NH_3, have absorption maxima at 515 nm, 480 nm and 465 nm, respectively.

(a) What is the value of *n* for each of the complexes?

(b) Predict the colours of the three complexes.

(c) Calculate the crystal field splitting energy in kJ mol^{-1} for each of the complexes and explain the trend in values.

13.117 The complex ion $[Ag(NH_3)_2]^+$ has a linear geometry. Predict the crystal field splitting diagram for this complex, placing the ligands along the *z*-axis.

13.118 Tetracarbonylnickel(0) is $[Ni(CO)_4]$, and tetracyanidozinc(II) is $[Zn(CN)_4]^{2-}$. Predict the geometry and colour of each complex.

13.119 Carbon monoxide and tungsten form a colourless octahedral complex. Sketch the *d*-orbital splitting field diagram for hexacarbonyltungsten(0), and suggest why the complex is colourless.

13.120 The complex $[Ni(CN)_4]^{2-}$ is diamagnetic, but $[NiCl_4]^{2-}$ is paramagnetic. Propose structures for the two complexes and explain why they have different magnetic properties.

13.121 Predict whether each of the following complexes is highspin or low-spin:

(a) $[Fe(CN)_6]^4$,

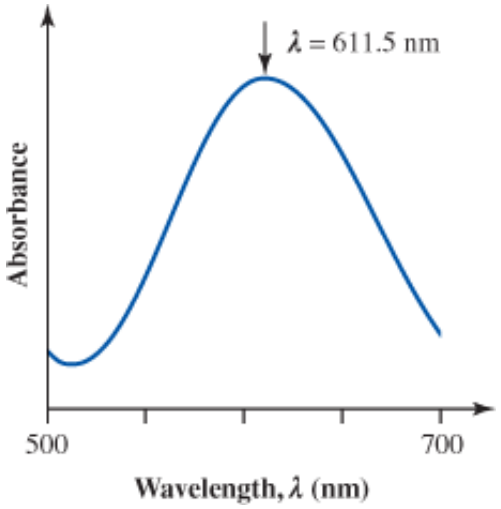
(b) $[MnCl_4]^2$,

(c) $[Rh(NH_3)_6]^{3+}$,

(d) $[Co(OH_2)_6]^{2+}$.

Estimate their magnetic moments.

13.122 A portion of the absorption spectrum of the octahedral complex ion $[CrCl_2(OH_2)_4]^+$ is shown above right.



(a) Estimate the crystal field splitting energy, Δ_o, in kJ mol^{-1}.

(b) What colour is the complex?

(c) Name the complex cation.

(d) Draw all possible isomers of the complex.

(e) Draw the *d*-orbital splitting diagram and show the electronic transition that gives the complex its colour.

13.123 In the 1890s, the Swiss chemist Alfred Werner prepared several platinum complexes that contained both ammonia and chlorine. He determined the formulae of these species by precipitating the chloride ions with Ag^+. The following table shows the empirical formulae and number of chloride ions that precipitate per formula unit.

Empirical formula	**Number of Cl^- ions**
$PtCl_4 \cdot 2NH_3$	0
$PtCl_4 \cdot 3NH_3$	1
$PtCl_4 \cdot 4NH_3$	2
$PtCl_4 \cdot 5NH_3$	3
$PtCl_4 \cdot 6NH_3$	4

Determine the molecular formulae of these platinum complexes, name them and draw their structures.

13.124 Silverplating processes often use $Ag(CN)^{2-}$ as the source of Ag^+ in solution. To make a solution of this ion, a chemist used 4.0 L of 3.00 m NaCN and 50 L of 0.2 m $AgNO_3$. What is the concentration of free Ag^+ ions in this solution? Why is AgCl not used in this process?

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KEY TERMS

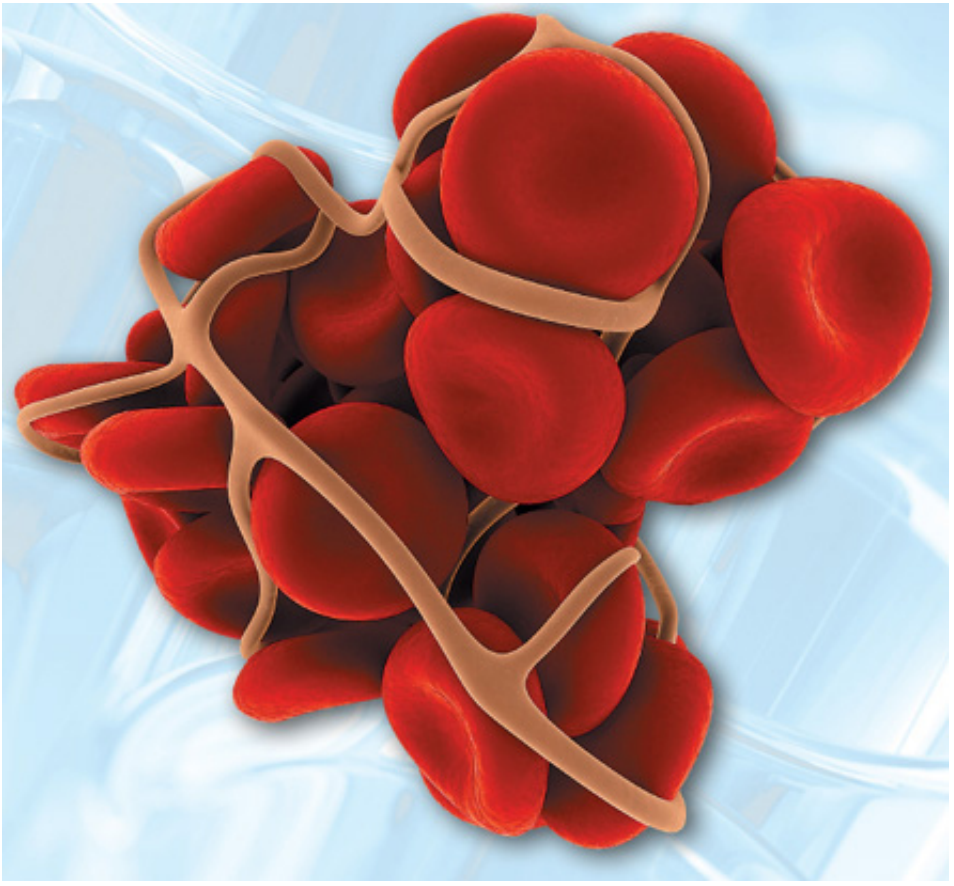
absorbance (*A*)
ambidentate
axial
Beer's law
Beer-Lambert law
bidentate
chelate complexes
chelate effect
chelate rings
cis isomer
cis–trans isomers
complementary colour
complexes
coordinate bonds
coordination chemistry
coordination compounds
Coordination isomers
coordination number
counterions
crystal field splitting energy
crystal field theory
cumulative formation constant (β_n)
***d*-*d*transitions**
dative bonds
degenerate
diamagnetic
disproportionation
donor atom
donor covalent bonds
electronic transition
equatorial
facial (fac)
ferromagnetism
high-spin
hydrate isomers
inert
ionisation isomers
labile
ligand-to-metal charge transfer (LMCT) transitions
ligands
linkage isomers
low-spin
magnetic moment (μ)
main-group metals
meridional (mer)
metal-to-ligand charge transfer (MLCT) transitions
metallurgy
monodentate
octahedral
organometallic compounds
pairing energy (*P*)
paramagnetic
polydentate
spectrochemical series
square planar
square pyramidal
Stereoisomers
strong-field
Structural isomers
tetrahedral
trans isomer
transition metals
trigonal bipyramidal
weak-field

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CHAPTER

14 The *p*-block Elements

You might think that everything had long since been learned about a molecule as simple as nitric oxide (nitrogen monoxide), NO, first prepared by Joseph Priestley over 200 years ago. Yet, it is only recently that we have recognised the importance of NO in a number of biochemical processes. Many animals synthesise NO, as it plays roles in nerve function, regulation of blood pressure, blood clotting, and immune system responses. In many of these processes, NO is produced in one part of an organism and moves to another part, where its chemical properties trigger a biochemical reaction. NO helps to adjust the interactions between blood and blood vessels. One example is blood clotting, shown in the accompanying photo. When the wall of a blood vessel is cut, an enzyme in the cell wall sends chemical signals that interact with blood platelets, causing clotting. NO inhibits this process — an effect exploited by mosquitoes; the saliva of mosquitoes contains NO-generating chemicals that prevent their victim's blood from clotting while the mosquito feeds.



Another example is the dilation of blood vessels. Nitroglycerine, $C_3H_5N_3O_9$, has been prescribed for more than a century as a treatment of angina (chest pain) because it dilates blood vessels, thereby decreasing blood pressure and increasing blood flow. Only recently was it discovered that NO is involved in the mechanism of this process. Biochemists speculate that NO binds to iron in the enzyme that causes dilation, but detailed knowledge is still lacking. There is evidence that the neural processes leading to memory include the production and diffusion of NO. An enzyme in the brain produces NO from an amino acid. How does NO interact with more complex molecules as the brain functions? One possibility

is that, once a neural trigger fires, an adjacent neuron produces NO, which diffuses back to the original neuron and stimulates further activity. This could be how long-term memory develops.

The components of the NO molecule, nitrogen and oxygen, are *p*-block elements, a name given to elements belonging to groups 13 to 18 of the periodic table. These elements are characterised by the gradual filling of the *p* orbitals. In this chapter, we describe selected features of the diverse chemistry of the *p*-block elements.



KEY TOPICS

14.1 The *p*-block elements

14.2 Chemistry of the *p*-block elements

14.3 The biogeochemical cycles of nature

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14.1 The *p*-block Elements

In chapter 1 (figure 1.16, p. 15), we showed that all elements in the periodic table could be classified as one of three types: metals, nonmetals and metalloids. We also showed that the different groups of the periodic table (1 to 18) are defined by the valence electron configuration; for example, groups 1 and 2 are called *s*-block elements, owing to their ns^1 or ns^2 configurations, while groups 3 to 12 are called *d*-block elements, with valence electron configurations of $(n + 1)s^2nd^1$ to $(n + 1)s^2nd^{10}$. While the elements of groups 1 to 12, and the lanthanoid and actinoid elements are, with the exception of hydrogen, exclusively metals, groups 13 to 18 contain elements which are predominantly nonmetals or metalloids. The elements of groups 13 to 18 are collectively called **p-block elements** and they are characterised by the gradual filling of the *p* orbitals across each period. As can be seen in figure 14.1, the valence-shell electron configuration of these elements ranges from ns^2np^1 (group 13) to ns^2np^6 (group 18).

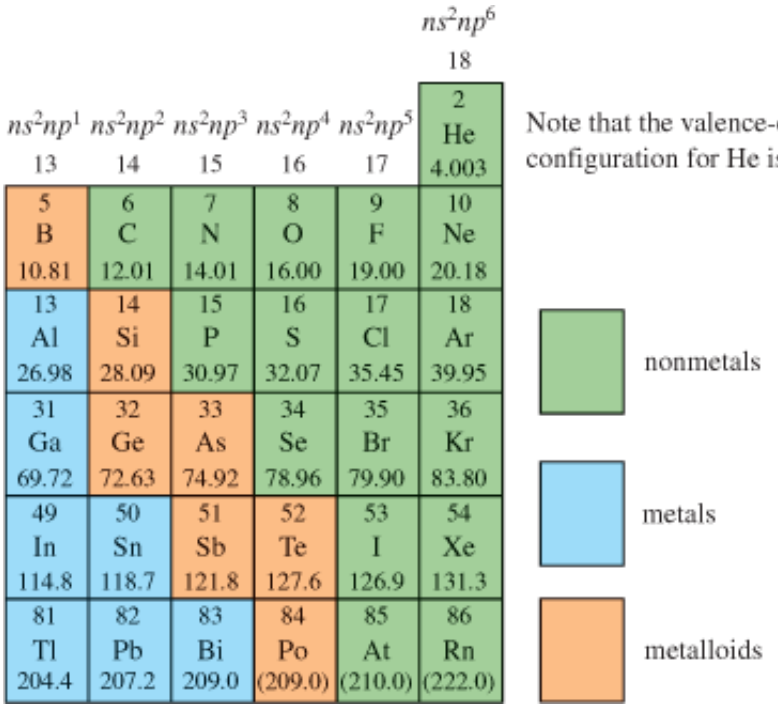


FIGURE 14.1 The *p*-block elements.

The chemistry exhibited by these elements is extraordinarily wide and varied, and a detailed description of all the *p*-block elements is beyond the scope of this text. We will therefore provide a brief introduction to each of the *p*-block elements before concentrating on representative elements which illustrate important concepts of structure, bonding and reactivity within the *p* block. We will also detail the importance of these elements in the biogeochemical cycles of nature.

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14.2 Chemistry of the p-block Elements

Group 13

13		
5 B 10.81	boron	[He] $2s^2 2p^1$
13 Al 26.98	aluminium	[Ne] $3s^2 3p^1$
31 Ga 69.72	gallium	[Ar] $4s^2 3d^{10} 4p^1$
49 In 114.8	indium	[Kr] $5s^2 4d^{10} 5p^1$
81 Tl 204.4	thallium	[Xe] $6s^2 5d^{10} 4f^{14} 6p^1$

The elements in group 13, with the exception of boron, are metals, and therefore display the expected characteristics outlined on p. 15 in chapter 1. The elements have the valence-electron configuration ns^2np^1, and tend to exhibit a formal oxidation number of +3 in their compounds. However, both indium and thallium have a significant chemistry in the +1 oxidation state owing to the fact that the valence ns^2 electrons experience a relatively high Z_{eff}, and are therefore held relatively tightly, due to the poor shielding characteristics of the inner *d* and *f* electrons.

Boron is a metalloid and, as befits its small size and consequent hard Lewis acidity, is found in combination with oxygen in nature, in a variety of borate minerals. The element itself is a shiny black solid, with a very high melting point (in fact, among the *p*-block elements the melting point of boron is exceeded only by that of carbon) which is attributable to its unusual solid state structure. The valence-electron configuration of boron, $2s^2 2p^1$, means that it is unable to complete an octet (p. 172) through the formation of three single bonds, and elemental boron therefore adopts a rather complex molecular structure that cannot be described by simple Lewis structures. Boron exists in several different crystalline forms (allotropes), each of which is characterised by clusters of 12 boron atoms located at the vertices of an icosahedron (a 20-sided geometric figure), as shown in figure 14.2.

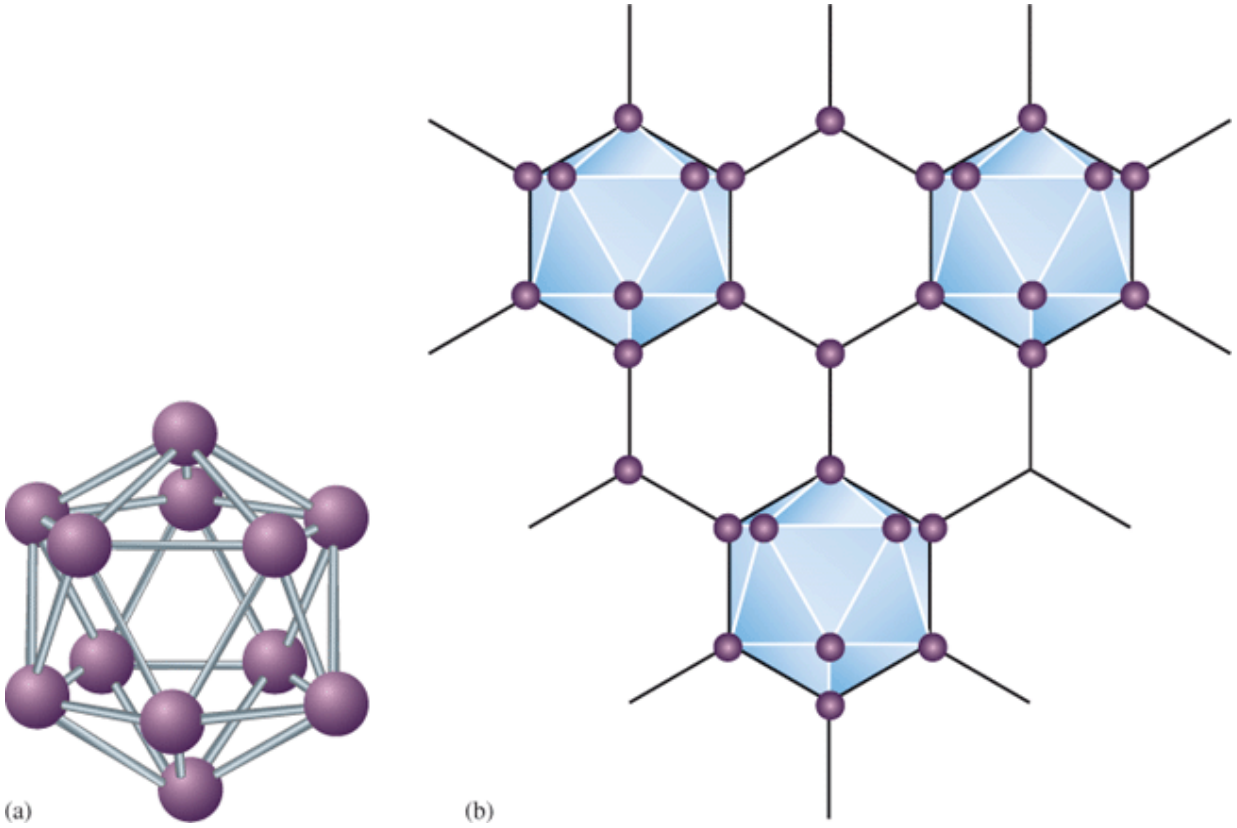


FIGURE 14.2 The structure of an allotrope of elemental boron.
(a) The arrangement of 12 boron atoms in a B_{12} cluster.
(b) The element boron consists of an interconnecting network of B_{12} clusters that produces a very hard and high-melting solid.

Each boron atom within a given cluster is equidistant from five others and, in the solid, each of these is also joined to yet another boron atom outside the cluster (figure 14.2b). The electrons available for bonding are therefore delocalised to a large extent over many boron atoms, and the simple Lewis idea of pairs of electrons in a covalent bond does not apply in this case. The linking together of B_{12} units produces a large, three-dimensional covalent solid that is very difficult to break down. As a result, boron is very hard (it is the second hardest element) and has a very high melting point (about 2200 °C). Boron atoms share with carbon atoms the ability to undergo catenation (p. 38), bonding to themselves to form moderately sized molecules. However, in contrast to carbon, such molecules generally adopt three-dimensional polyhedral structures, rather than chains or rings.

Aluminium is the only one of the four group 13 metals not to contain filled *d* orbitals; it therefore has a small atomic radius which renders it, like boron, a hard Lewis acid. It is found in nature as bauxite, Al(O)OH, a compound of which Australia is the world's largest producer, and in a variety of compounds called aluminosilicates which are composed of aluminium, silicon and oxygen; in all these compounds, aluminium exists as the 3+ cation. Reduction of bauxite, or indeed any aluminium compound, to metallic aluminium is difficult and, as a result, the pure element was first isolated only in 1825 from the reduction of $AlCl_3$ with potassium. Its rarity for a time following this meant that aluminium was more expensive than gold or platinum, and Emperor Napoleon III of France reputedly had aluminium dinnerware which was used for important guests. Nowadays, aluminium is produced from purified Al_2O_3 by electrolysis, using the Hall-Héroult process which was developed in the 1880s (see Chemical Connections on p. 601). Bauxite is first purified of insoluble impurities through conversion to the soluble complex ion $[Al(OH)_4]^-$ by dissolution in strong base:

$$Al(O)OH(s) + OH^-(aq) + H_2O \rightarrow [Al(OH)_4]^-(aq)$$

Dilution of this solution with water causes the precipitation of $Al(OH)_3$:

$$[Al(OH)_4]^-(aq) \xrightarrow{\text{added water}} Al(OH)_3(s) + OH^-(aq)$$

and dehydration of this gives pure Al_2O_3:

$$2Al(OH)_3(s) \xrightarrow{125\,^\circ C} Al_2O_3(s) + 3H_2O(g)$$

The melting point of Al_2O_3 is too high (2015 °C) and its electrical conductivity too low to make direct electrolysis commercially viable. Instead, Al_2O_3 is mixed with cryolite, Na_3AlF_6, containing about 10% CaF_2. This mixture has a melting point of 1000 °C, still a high temperature but not prohibitively so. Aluminium forms several complex ions with fluoride and oxide, so the molten mixture contains a variety of species, including AlF_4^-, AlF_6^{3-} and $AlOF_3^{2-}$. These and other ions move freely through the molten mixture as electrolysis occurs. Figure 14.3 shows a schematic representation of an electrolysis cell for aluminium production.

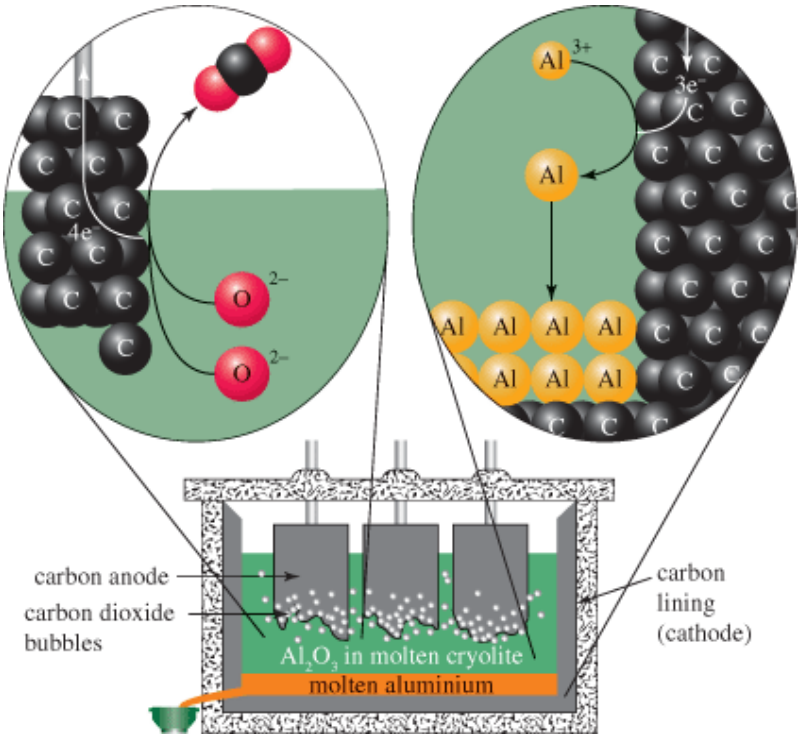


FIGURE 14.3 Aluminium metal is produced by electrolysis of aluminium oxide dissolved in molten cryolite. Al^{3+} is reduced to Al at the cathode, and C is oxidised to CO_2 at the anode.

An external electrical potential drives electrons into a graphite cathode, where Al^{3+} ions are reduced to Al metal:

$$Al^{3+}(melt) + 3e^- \longrightarrow Al(l) \quad (cathode)$$

The anode, which is also made of graphite, is oxidised during electrolysis. Carbon from the anode combines with oxide ions to form CO_2 gas:

$$2O^{2-}(melt) + C(s) \longrightarrow CO_2(g) + 4e^- \quad (anode)$$

Because of the variety of ionic species present in the melt, the reactions that take place at the electrodes are considerably more complex than the simple representations given here. Nevertheless, the overall reaction is the one given by the sum of these simplified reactions.

$$4Al^{3+}(melt) + 6O^{2-}(melt) + 3C(s) \rightarrow 3CO_2(g) + 4Al(l)$$

The electrolysis apparatus operates well above the melting point of aluminium (660 °C) and, as liquid aluminium has a higher density than the molten salt mixture, pure liquid metal settles to the bottom of the reactor. The pure metal is drained through a plug and cast into ingots (figure 14.4). Aluminium refining consumes huge amounts of electricity. In fact, the aluminium smelter at Tiwai Point in New Zealand consumes 15% of the country's entire energy output.



FIGURE 14.4 Aluminium refining uses very large amounts of electricity.

Connections Hall-Héroult process

A part from its obvious uses in cans (figure 14.5), foil, and windows and doors, aluminium's strength, lightness, high electrical and thermal conductivity, and resistance to corrosion make it useful in kitchen utensils, car, aircraft and rocket construction, electrical transmission lines and in coatings for high-precision mirrors such as those in telescopes.



FIGURE 14.5 Australia uses more than 3 million aluminium cans each year — just over half of these are for soft drinks; just over one-third are for beer.

Aluminium is the third most abundant element in the Earth's crust and the most abundant metal. Nevertheless, aluminium was not isolated until 1825 and was still a precious rarity 60 years later. The reason for this elusiveness is the high stability of Al^{3+}. The reduction of aluminium compounds to the free metal requires stronger reducing power than common chemical reducing agents can provide. The extraction of aluminium had to await the birth of electrochemistry and the development of electrolysis (see chapter 12).

Two 22-year-old scientists, the American chemist Charles Hall and the French metallurgist Paul Héroult, developed the same process independently in 1886, both becoming famous as founders of the aluminium industry, Hall in the United States and Heroult in Europe.

Hall was inspired by his chemistry professor, who observed that whoever perfected an inexpensive way of producing aluminium would become rich and famous. After his graduation, Hall set to work in his home laboratory trying to electrolyse various compounds of aluminium. Working with his sister Julia, who had also studied chemistry, Hall successfully produced globules of the metal within 8 months. Meanwhile, Heroult was developing the identical process in France. Hall founded a company for the manufacture of aluminium. That company became immensely successful, eventually growing into Alcoa.

Successful electrolysis of aluminium requires a liquid medium other than water that can conduct electricity. The key to the Hall-Heroult process is the use of molten cryolite, Na_3AlF_6, as a solvent. Cryolite melts at an accessible temperature, it dissolves Al_2O_3, and it is available in the necessary purity. A second important feature is the choice of graphite to serve as the anode. Graphite provides an easy oxidation process, the oxidation of carbon to CO_2.

The reasoning that led Hall and Heroult to the identical process was probably similar. Electrolysis was recognised as a powerful reducing method. All attempts to reduce aqueous aluminium cations failed, making it clear that some molten salt would have to be used. Experimenting with various salts, no doubt guided by the principle that 'like dissolves like', the two young men eventually tried Na_3AlF_6, a mineral whose constituent elements should not interfere with the reduction of aluminium. Graphite electrodes were already in use, so experimenting with them would have been a natural choice. All the ingredients for this invention may have been in place, but that does not detract from its brilliance.

In more than 100 years of growth in the aluminium industry, the only significant change to the Hall-Heroult process has been the addition of CaF_2 to the melt to lower the operating temperature.

Gallium is a silvery white metal that is obtained primarily as a by-product of the purification of bauxite, discussed on p. 600. Removal of $Al(OH)_3$ leads to concentration of gallium compounds in the remaining alkaline solution and electrolysis eventually yields the pure metal. Gallium was one of the 'missing' elements predicted by Mendeleev in his original periodic table (see figure 1.15, p. 14). Gallium is of interest, among other things, for its very low melting point (around 30 °C) and the extremely large temperature range over which it exists as a liquid (it boils around 2200 °C). Compounds of gallium find extensive use in light-emitting diodes (LEDs).

Indium is not found in nature in its elemental state. Its relatively large size means it behaves as a soft Lewis acid, and this is reflected in the fact that it is generally found in sulfide ore deposits along with zinc, copper and tin. The pure metal is obtained as a by-product of the electrolytic refining of zinc and is known for the fact that it emits a high-pitched 'cry' when it is bent. The major use of indium is in thin films of indium tin oxide (ITO) which are used in liquid crystal displays.

Thallium is a soft metal which exhibits a metallic lustre when freshly cut. However, it quickly develops a grey oxide layer on exposure to air and generally resembles lead in appearance. It is found in sulfide and selenium ore deposits, reflecting its soft Lewis acidic nature. Thallium and its compounds are highly toxic and were once poisons of choice for serial killers. In fact, Sydney woman Caroline Grills was sentenced to death in 1953 (later commuted to life in prison) for the attempted murder of two of her in-laws using thallium, and over the previous year there were some 46 reported cases of thallium poisoning, with 10 deaths, in Sydney. The toxicity of the element, which limits its usefulness, is thought to arise from both its similarity in size to potassium and its affinity for sulfur-containing amino acids. However, there has been some interest in thallium-containing materials as high-temperature superconductors.

Group 14

14		
6 C 12.01	carbon	[He] $2s^2 2p^2$
14 Si 28.09	silicon	[Ne] $3s^2 3p^2$
32 Ge 72.63	germanium	[Ar] $4s^2 3d^{10} 4p^2$
50 Sn 118.7	tin	[Kr] $5s^2 4d^{10} 5p^2$
82 Pb 207.2	lead	[Xe] $6s^2 5d^{10} 4f^{14} 6p^2$

Group 14 comprises a nonmetal, two metalloids and two metals. The elements have valence electron configurations ns^2np^2 and the predominant oxidation number of group 14 elements in their compounds is +4. However, as we also saw in group 13, the heavier elements can display an oxidation state two lower than that usually found in the group. Thus both tin and lead have significant chemistry in the +2 oxidation state, with compounds of the latter in the +4 oxidation state often being unstable with respect to reduction.

We have already briefly discussed the different allotropes of elemental carbon, and chapter 16 is devoted to the chemistry of carbon, so we will not concern ourselves further with this element here.

Silicon behaves as a hard Lewis acid, and occurs in nature as SiO_2 (silica) and various silicate anions. The element may be obtained by the high-temperature reduction of silica using coke in an electric arc furnace, according to the equation:

$$SiO_2 + 2C \rightarrow Si + 2CO$$

but this gives silicon with a purity of only 98% — not high enough for its most important use in silicon chips. High-purity silicon is obtained by reduction of $SiCl_4$, itself prepared by reaction of SiO_2 and coke in the presence of Cl_2 at high temperature:

$$SiO_2 + 2C + 2Cl_2 \rightarrow SiCl_4 + 2CO$$

The $SiCl_4$ is distilled and then reduced with magnesium to give silicon and $MgCl_2$, which is removed by washing with water:

$$SiCl_4 + 2Mg \rightarrow Si + 2MgCl_2$$

The silicon is purified further by zone refining, a process depicted in figure 14.6. A rod of impure silicon is melted and resolidified many times by a heating coil that passes back and forth along the rod. During this process, impurities remain preferentially in the liquid phase, which floats to the top, yielding solid silicon in the lower part of the rod containing less than 1 part per billion of impurities.

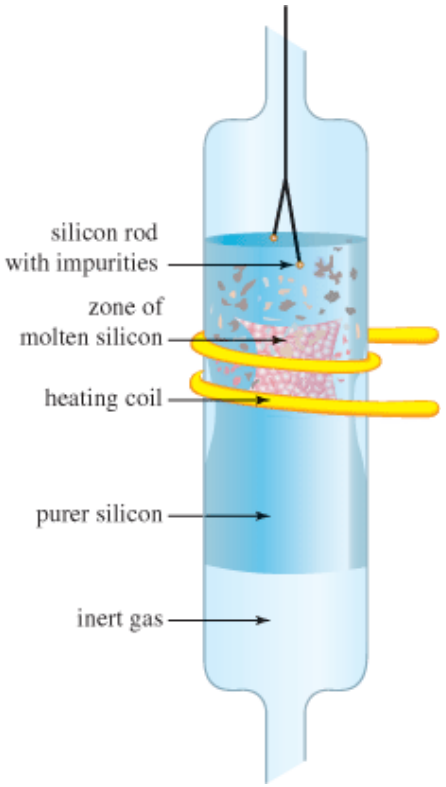


FIGURE 14.6 In zone refining, a rod of impure silicon passes along a heating coil. The impurities concentrate in the molten zone, leaving behind solid material that is of higher purity. Repeated passage through the coil moves the impurities to the end of the rod.

Germanium is found in some sulfide minerals and zinc ores, and in coal. Like silicon, germanium finds extensive use in semiconductors, and the ultrapure element is also prepared by zone refining. Germanium crystallises as grey-white crystals with the same structure as diamond, but these are brittle and nowhere near as hard. The main uses of germanium and its compounds are in fibre optics, infrared optics and solar cells. On reduction by sodium in liquid ammonia, germanium, like both tin and lead below it in the periodic table, forms interesting polyatomic anions; examples of these include Ge_4^{2-}, Ge_9^{4-} and Ge_9^{2-}.

Tin is found in nature as SnO_2 in the mineral cassiterite and this can be reduced to the metal using charcoal at high temperature. Historically, tin was used widely as a constituent of metal alloys, of which bronze, solder and pewter are common examples. Bronze (figure 14.7) is an alloy of copper containing approximately 20% tin and smaller amounts of zinc. Pewter (figure 14.8) is another Cu–Sn alloy that contains tin as the major component (=85%), with roughly

equal portions of copper, bismuth and antimony. Solder consists of 67% lead and 33% tin.



FIGURE 14.7 Bronze.



FIGURE 14.8 Pewter.

Because of its relatively low melting point (232 °C) and good resistance to oxidation, tin is used to provide protective coatings on metals such as iron that oxidise more readily. 'Tin cans' are actually iron cans dipped in molten tin to provide a thin surface film of tin. Metals that are soft Lewis acids, such as cadmium, mercury and lead, are extremely hazardous to living organisms. Tin, in contrast, is not. One reason is that tin oxide is highly insoluble, so tin is seldom found at measurable levels in aqueous solution. Perhaps more importantly, the toxic metals generally act by binding to sulfur in essential enzymes. Tin is a harder Lewis acid than the other heavy metals, so it has a lower affinity for sulfur, a relatively soft Lewis base.

Tin holds the record for the greatest number of stable isotopes of any element (10), and this is probably not unrelated to the fact that the tin nucleus contains 50 protons; as we will see in chapter 27 (p. 1163), 50 is a magic number.

Lead is one of the oldest known metals and was used extensively in pipes in the Roman Empire; in fact, our modern word 'plumbing' derives from the Latin word for lead, *plumbum*. It is found in nature primarily as PbS in the mineral galena, and this is converted to the element first by roasting in air to form PbO, and subsequent reduction with

charcoal:

$$2PbS + 3O_2 \xrightarrow{heat} 2Pbo + 2SO_2$$

$$PbO + C \xrightarrow{heat} Pb + CO$$

Lead is a soft blue-grey metal, and both it and its compounds are appreciably toxic to humans. Indeed, the extensive use of lead by the Romans in cooking and drinking vessels has led some to speculate that lead poisoning was a factor in the decline of the Roman Empire. Lead compounds were used in huge quantities in the twentieth century as additives in both petrol and paint; thankfully, the incredible folly of this has finally been appreciated and such applications are now rare. The major use of lead currently is in batteries.

Group 15

15		
7 N 14.01	nitrogen	[He] $2s^2 2p^3$
15 P 30.97	phosphorus	[Ne] $3s^2 3p^3$
33 As 74.92	arsenic	[Ar] $4s^2 3d^{10} 4p^3$
51 Sb 121.8	antimony	[Kr] $5s^2 4d^{10} 5p^3$
83 Bi 209.0	bismuth	[Xe] $6s^2 5d^{10} 4f^{14} 6p^3$

Group 15 comprises two nonmetals, two metalloids and a metal. Elemental nitrogen makes up 78% (by volume) of the air around us. It exists as the diatomic molecule N_2, in which the two nitrogen atoms are held together by a triple bond of considerable strength (942 kJ mol^{-1}, see worked example 5.10, p. 204). This makes the molecule unreactive under ambient conditions, a fact for which humankind can be extraordinarily grateful, given that this means it does not instantly react with the 21% by volume of oxygen in the atmosphere. However, its lack of reactivity also means that, in order for it to be converted into compounds that can be utilised by living systems, nature has had to develop an extremely complex enzyme called nitrogenase, generally found in legumes, to catalyse the conversion of N_2 to ammonia. Despite the best efforts of some of the finest scientists over many years, we have yet to be able to replicate this process usefully in the laboratory, and in order to prepare nitrogen-based fertilisers, we use the rather less elegant Haber–Bosch process, in which N_2 and H_2 are heated together at high pressure over an iron catalyst. The importance of this process is shown by the fact that it consumes an estimated 1-2% of the world's energy supply each year. Elemental nitrogen finds extensive use in its liquid form as a coolant; liquid nitrogen (figure 14.9) boils at -196 °C at atmospheric pressure.



FIGURE 14.9 Liquid nitrogen boils at -196 °C.

Phosphorus was isolated from the distillation of urine by Hennig Brand in 1669, making it the element having the earliest authenticated date of discovery. It exists as a number of different-coloured allotropes, the most common being white, red and black. It is, like nitrogen, essential to life, being a constituent of the biologically important molecules DNA, RNA, and adenosine mono-, di- and triphosphate. Perhaps surprisingly then, pure white phosphorus is highly toxic, with a dose of only 50 mg considered lethal. Modern production of elemental phosphorus uses a technique similar to the metallurgical processes described in chapter 13. Apatite is mixed with silica and coke and then heated strongly in the absence of oxygen. Under these conditions, coke reduces phosphate to elemental phosphorus, the silica forms liquid calcium silicate, and the fluoride ions in apatite dissolve in the liquid calcium silicate. The reactions are not fully understood, but the stoichiometry for the calcium phosphate part of apatite is as follows:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \xrightarrow{1450°C} P_4 + 6CaSiO_3 + 10CO$$

Elemental phosphorus is a gas at the temperature of the reaction, so the product distils off along with carbon monoxide. When cooled to room temperature, P_4 condenses as a waxy white solid.

White phosphorus consists of individual P_4 molecules with the four atoms at the corners of a tetrahedron. Each atom bonds to three others and has one lone pair of electrons, giving a total of four electron pairs around each P atom (chapter 5). However, the triangular geometry of the faces of the tetrahedron constrains the bond angles in the P_4 tetrahedron to 60°, far from the optimal 4-coordinate geometry of 109.5°. As a result, P_4 is highly reactive. Samples of white phosphorus are stored under water because P_4 burns spontaneously in the presence of oxygen (figure 14.10). The glow that emanates from P_4 as it burns in the dark led to its name (from the Greek *phos*, meaning ‘light’, and *phoros*, meaning ‘bringing’).

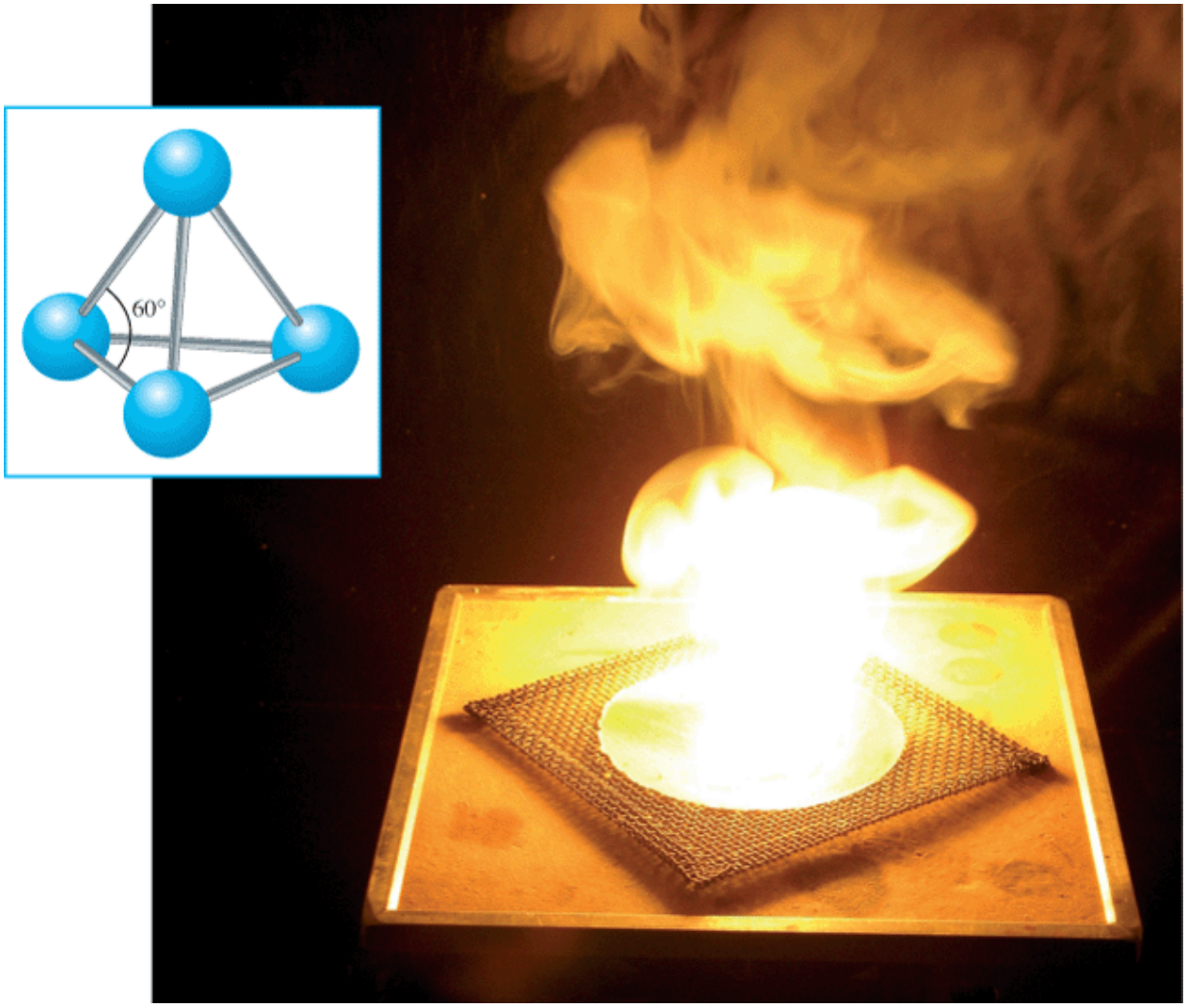


FIGURE 14.10 The strained 60° bond angles in tetrahedral P_4 make white phosphorus highly reactive. This form of the element must be kept out of contact with air, in which it burns spontaneously.

Heating white phosphorus in the absence of oxygen causes the discrete P_4 units to link together, giving a chemically distinct elemental form, red phosphorus. As figure 14.11 shows, one P—P bond of each tetrahedron breaks to allow formation of the bonds that link the P_4 fragments. The bond angles that involve the links are much closer to 109.5°, making red phosphorus less strained and less reactive than white phosphorus. Red phosphorus undergoes the same chemical reactions as the white form, but higher temperatures are required. In addition, red phosphorus is essentially nontoxic, so it is easier and safer to handle.

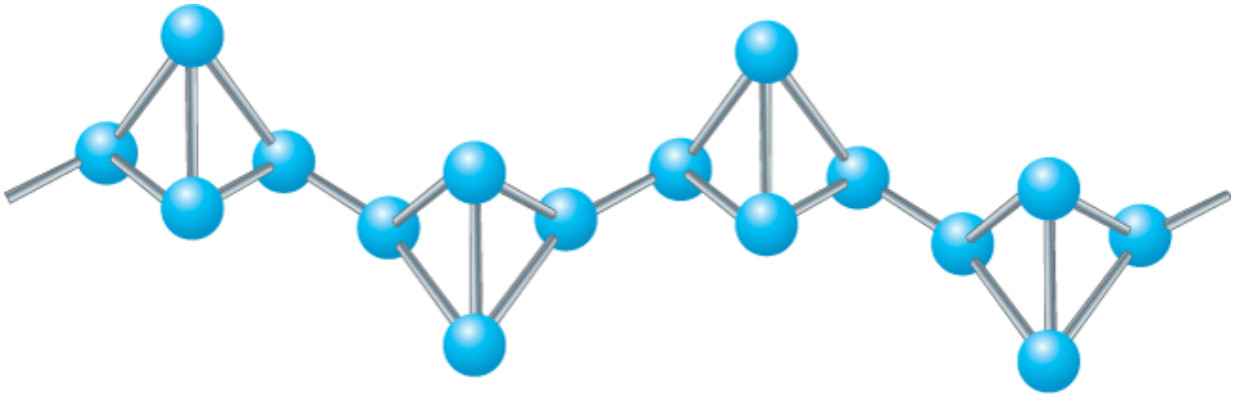


FIGURE 14.11 Red phosphorus consists of chains of P_4 tetrahedra linked through P—P bonds.

Another stable form of the element is black phosphorus, which can be prepared by heating red phosphorus under high pressure. The black form contains chains of P_4 units cross-linked by P—P bonds, making this form even more polymerised and less strained than red phosphorus. Worked example 14.1 explores another difference between the elemental forms of phosphorus.

WORKED EXAMPLE 14.1

Melting points of phosphorus

The melting point of white phosphorus is 44.1 °C. In contrast, red phosphorus remains a solid up to 400 °C. Account for this large difference in melting point.

Analysis

As described in chapter 7, melting points of solids may depend on both covalent bonds and intermolecular forces, so we must explain the melting point difference with reference to the bonding differences between the two forms.

Solution

White phosphorus consists of individual P_4 molecules. Because there are no polar bonds, the molecules are held in the solid state by dispersion forces only, and it would be expected that white phosphorus would have a relatively low melting point. Red phosphorus is made of long chains of P_4 groups, each of which is held together by covalent P—P bonds, as shown in figure 14.11 on the previous page. Thus, red phosphorus consists of macromolecules held together by dispersion forces. To melt, red phosphorus must break some chemical bonds. Bond breaking requires much more energy than the energy needed to overcome dispersion forces, giving red phosphorus the higher melting temperature.

Is our answer reasonable?

The molecular models in figures 14.10 and 14.11 show that white phosphorus is a molecular solid, whereas red phosphorus is intermediate between molecular and network. This correlates well with the melting points.

PRACTICE EXERCISE 14.1

Predict whether black phosphorus melts at a higher or lower temperature than the white and red forms, and rank the three forms of elemental phosphorus in order of increasing density, giving a reason for your ranking.

Arsenic is possibly best known among the general public for being a poison. In addition to its many human victims, it also has been recently found to have accounted for the early demise of Phar Lap, the famous New Zealand-born and Australia-raised racehorse; analysis of hairs from Phar Lap's mane using sophisticated X-ray based spectroscopic techniques showed the ingestion of arsenic while the horse was still alive. Elemental arsenic exists as the grey

allotropic form at room temperature and pressure, while at least two other allotropes are known. It is often found in combination with sulfur in a variety of minerals, with FeSAs (arsenopyrite) being the most common; heating this in the absence of air gives the pure element. Arguably the most important use of arsenic is in the semiconductor gallium arsenide (GaAs), which shows properties similar, and in some cases superior, to silicon in diodes and solar cells.

Antimony compounds have been known for over 2000 years, with Sb_2S_3 (stibnite) being used as both a medicine and a black eye makeup in ancient Egypt. The element is a grey metallic solid at ambient temperatures and at least four other allotropes are known. Stibnite is the most important ore of antimony, and the pure element is obtained from either roasting in air and subsequent reduction of the resulting Sb_2O_3 with coke, or direct reduction by Fe. Antimony is used primarily to harden the lead used in car batteries, while some antimony compounds have been found to be effective against parasite-borne tropical diseases.

Bismuth is primarily obtained as a by-product of the smelting of lead and copper. The element is a soft grey metal having a relatively low melting point (271 °C) and a high boiling point (1564 °C). These properties, coupled with the low neutron absorption cross-section of the element, make it useful as a coolant in nuclear reactors. Bismuth is one of the few substances (water being the best known) that expands on freezing. The element is finding increasing use as a nontoxic substitute for lead, most notably in shotgun pellets and lead-free solders. The biological importance of bismuth compounds has long been known, particularly in the treatment of gastrointestinal problems; Pepto-Bismol contains the bismuth compound bismuth subsalicylate (figure 14.12) as its active ingredient.

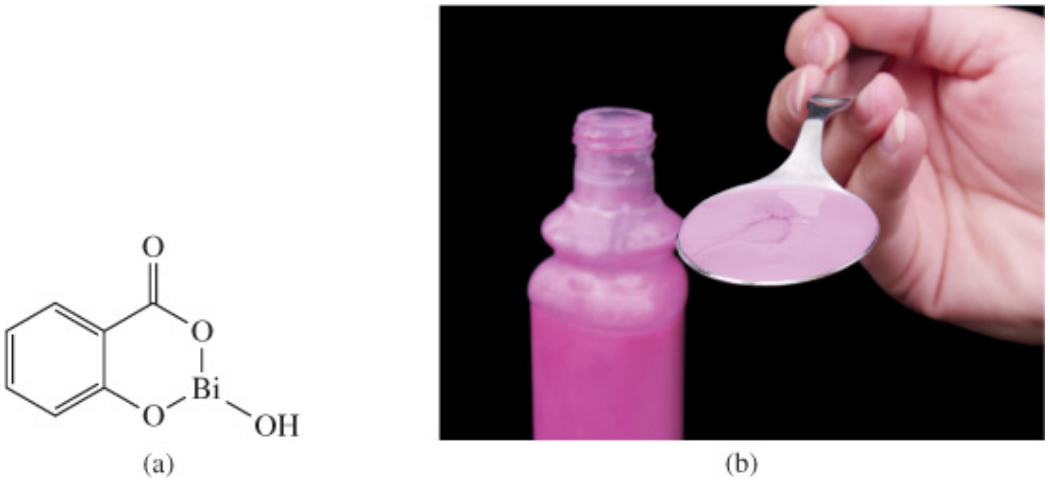


FIGURE 14.12 (a) The structure of bismuth subsalicylate, the active ingredient in (b) Pepto-Bismol.

Group 16

16		
8 O 16.00	oxygen	[He] $2s^2 2p^4$
16 S 32.07	sulfur	[Ne] $3s^2 3p^4$
34 Se 78.96	selenium	[Ar] $4s^2 3d^{10} 4p^4$
52 Te 127.6	tellurium	[Kr] $5s^2 4d^{10} 5p^4$
84 Po (209.0)	polonium	[Xe] $6s^2 5d^{10} 4f^{14} 6p^4$

The ability of photosynthetic bacteria over two billion years ago to produce elemental oxygen is responsible for life on Earth evolving as we now know it. Oxygen and its compounds are ubiquitous throughout the Earth's atmosphere, crust and biosphere, and it is the third most abundant element in the universe, after hydrogen and helium. It forms stable

compounds with the majority of elements in the periodic table, the only exceptions being some of the elements in group 18. The pure gaseous element is colourless, odourless and tasteless, while the liquid form exhibits a pale blue colour. The first person to isolate and study oxygen gas was the Swedish pharmacist Carl Wilhelm Scheele over the period 1771–73, but the English part-time scientist Joseph Priestley, who isolated oxygen in 1774, is usually credited as the discoverer of oxygen. This is because Scheele did not publish his work until 1777 and was thus beaten into print by Priestley by some two years. Antoine Lavoisier (chapter 1, p. 3) was also instrumental in early work on oxygen, especially in recognising its importance in combustion reactions. Ozone, O_3, is an allotrope of oxygen; it occurs in the atmosphere, and a layer in the stratosphere acts as a shield for potentially damaging ultraviolet radiation from the Sun (pp. 666-7). It is also an excellent oxidising agent and is increasingly being used in place of chlorine-based oxidants in the pulp and paper industry, as well as for the treatment of drinking water.

Sulfur is encountered most often in sulfide minerals such as pyrite, FeS_2, molybdenite, MoS_2, chalcocite, Cu_2S, cinnabar, HgS, and galena, PbS. It is also present in huge amounts as H_2S in natural gas and in sulfur-containing organic compounds in crude oil and coal. In addition, sulfur is found in abundance as the pure element, particularly around hot springs and volcanoes and in capping layers over natural salt deposits. References to sulfur occur throughout recorded history, dating back more than 3500 years. Under ambient conditions elemental sulfur is a yellow crystalline solid that consists of individual S_8 molecules. As shown in figure 14.13, the eight atoms in each molecule form a ring that puckers in such a way that four atoms lie in one plane and the other four atoms lie in a second plane. There are a large number of sulfur allotropes having cyclic structures, ranging from S_6 to S_{20}, while some catenated forms are also known.

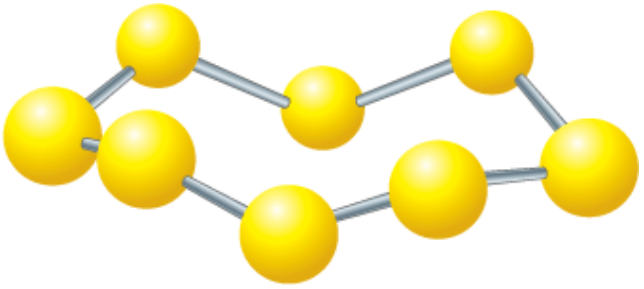


FIGURE 14.13 Under normal conditions, sulfur forms yellow crystals. The crystals consist of individual S_8 molecules, with the eight sulfur atoms of each molecule arranged in a puckered ring.

The major present-day source of the element is from hydrogen sulfide produced as a by-product of oil and gas refining. Many petroleum and natural gas supplies contain some sulfur — up to 25% in some cases. Besides being undesirable in the final products, sulfur poisons many of the catalysts used in oil refining; hence, it must be removed from crude petroleum as a first step in the refining process. About 90% of world output of sulfur is converted to sulfuric acid, the most produced industrial chemical worldwide, and more than 60% of that sulfuric acid is used to extract phosphoric acid from phosphate minerals to prepare fertilisers. This major use exploits the fact that sulfuric acid is the least expensive strong Brønsted–Lowry acid. In addition to protonating the phosphate anions, sulfuric acid sequesters Ca^{2+} as $CaSO_4$, a waste by-product of the process.

Selenium is a rare element, and mining it directly is not economic. It is therefore obtained as a by-product from the electrolytic purification of copper (pp. 587-8). At least six allotropes are known, four of which are red, one metallic grey (the stable form under ambient conditions), and one black. Three of the red allotropes consist of Se_8 rings, thus mirroring the structure of elemental sulfur. Selenium is a trace element but is toxic in high doses. It is incorporated into proteins via selenocysteine (figure 14.14), a modified amino acid in which the sulfur atom of cysteine (p. 1057) has been replaced by a selenium atom. The resulting proteins act, among other things, to reduce reactive oxygen species and to regulate thyroid hormones. The glass industry is the major user of selenium; it is used to remove the green tint in glass, caused by iron, and also to absorb solar radiation in plate glass. Selenium also finds uses in photocopiers; being a semiconductor, it can be used as a photoreceptor to obtain the latent image, which is then developed by the toner.

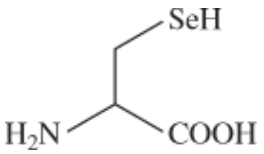


FIGURE 14.14 Structure of the amino acid selenocysteine.

Tellurium, like selenium, is obtained predominantly from the electrolytic purification of copper. The pure element is silver-white with a metallic lustre and is rather brittle. In contrast to the two elements directly above it in the periodic table, the stable form under ambient conditions does not consist of eight-atom rings; rather, it comprises helical chains. The major use of tellurium is as an additive to a number of metals to improve their machining characteristics. It is also starting to find extensive use in CdTe (cadmium telluride) solar cells, and also in high-speed rewriteable phase-change memory (PCM) chips. Compounds of tellurium are considered moderately toxic, and ingestion of even tiny amounts leads to garlic-smelling 'tellurium breath' from the formation of dimethyltellurium (Me_2Te) in the body. The element forms a remarkable variety of polyatomic cations and anions; examples include Te_n^{2-} (π = 2-5, 7, 8), Te_6^{3-}, Te_4^{2+}, Te_6^{2+}, Te_6^{4+}, Te_8^{4+} and Te_{10}^{2+}.

Polonium was discovered by the Curies in 1898 and was named after Marie's home country of Poland. All isotopes of polonium are radioactive and this, coupled with its very low abundance (estimated at 0.1 mg per tonne of pitchblende, an ore of uranium), therefore limits the usefulness of the element. In addition to its radioactivity, polonium is toxic in the same way that other heavy metals such as lead and mercury are toxic. In 2006, the Russian journalist Alexander Litvinenko was murdered using what was thought to be as little as 1 mg of the isotope ^{210}Po. The intense energy of the radiation emitted by polonium can be appreciated by the observation that a sample of around 0.5 g of the pure metal will heat itself to over 500 °C.

Group 17

17		
9 F 19.00	fluorine	[He] $2s^2 2p^5$
17 Cl 35.45	chlorine	[Ne] $3s^2 3p^5$
35 Br 79.90	bromine	[Ar] $4s^2 3d^{10} 4p^5$
53 I 126.9	iodine	[Kr] $5s^2 4d^{10} 5p^5$
85 At (210.0)	astatine	[Xe] $6s^2 5d^{10} 4f^{14} 6p^5$

Elemental fluorine, F_2, is a pale green gas of extraordinary reactivity. It reacts directly with all elements except O_2, N_2, He, Ne, Kr and Ar. Compounds of fluorine with all elements except He and Ne are known. It does not exist in nature as the gaseous element, but as the fluoride ion, predominantly in minerals such as fluorspar, CaF_2, and cryolite, Na_3AlF_6. Because F_2 is an extremely powerful oxidising agent ($E^{\ominus} = +2.87\,V$, table 12.1, p. 510), the element cannot be prepared by chemical oxidation of F^- and is therefore obtained by electrolysis of KF2·HF, as depicted in figure 14.15; here, KF acts as an electrolyte.

$$2F^- \rightarrow F_2 + 2e^- \quad \text{(anode)}$$
$$2HF + 2e^- \rightarrow H_2 + 2F^- \quad \text{(cathode)}$$
$$2HF \rightarrow F_2 + H_2 \quad \text{(cell reaction)}$$

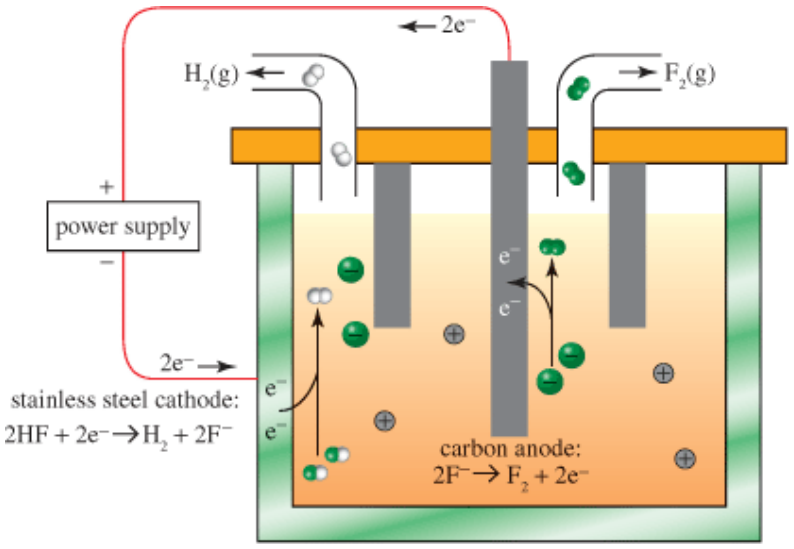


FIGURE 14.15 Schematic view of an electrolytic cell used for the production of molecular fluorine, showing the molecular species involved in the redox reactions.

Over half of the F_2 produced annually is used to prepare uranium hexafluoride (UF_6), a compound used in the separation of the fissile isotope ^{235}U (p. 1176) from the predominant ^{238}U isotope for use in nuclear power stations. As we will see on pp. 798-9, the introduction of fluorine atoms into organic molecules gives them interesting and unusual properties, the most notable example of this being Teflon, the non-stick polymer derived from tetrafluoroethene, and such molecules represent an important use of fluorine.

The stable form of chlorine that exists under ambient conditions is the diatomic, pale green gas Cl_2, but, like the other members of group 17, it is found in nature predominantly as the halide ion, in this case Cl^-. Chlorine is an important industrial chemical, and some industrial applications of chlorine derivatives are outlined in table 14.1.

TABLE 14.1 Major uses of chlorine

Reactant	Intermediate	Final products
Organic reagents		
benzene	chlorobenzenes	plastics, dyestuffs
butadiene	chloroprene	neoprene (chlorinated rubber)
ethene	chloroethenes	plastics (PVC), solvents
methane	chloromethanes	silicones
Inorganic reagents		
CO	$COCl_2$	plastics (polycarbonate)
NaOH	NaOCl	bleaches, disinfectants
phosphorus	PCl_3, $POCl_3$	pesticides, flame retardants
rutile (TiO_2 ore)	$TiCl_4$	paint pigment (pure TiO_2)

The starting material for all industrial chlorine chemistry is sodium chloride, obtained primarily by evaporation of sea water. Like fluorine, chemical oxidation of this is not feasible because of the strongly oxidising nature of the parent halogen, and so chloride must be oxidised electrolytically to produce chlorine gas. This is carried out on an industrial

scale using the chlor-alkali process, which is shown schematically in figure 14.16. As with all electrolytic processes, the energy costs are very high, but the process is economically feasible because it generates three commercially valuable products: H_2 gas, aqueous NaOH and Cl_2 gas.

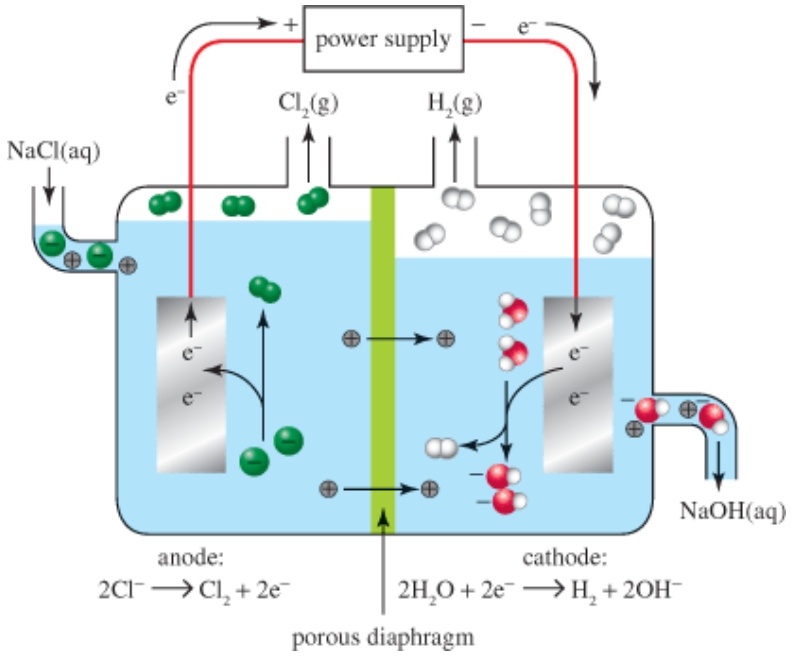


FIGURE 14.16 Schematic view of the electrolytic chlor-alkali process showing the molecular species involved in the redox reactions.

The major use of chlorine is in the production of chlorine-containing organic compounds such as 1,2-dichloroethane and chloroethene (vinyl chloride) for the production of PVC (polyvinylchloride). It is also widely used in the paper industry, as an oxidising agent to bleach both pulp and paper, and also as a bleaching agent for textiles. Molecular chlorine is used extensively as a purifying agent for water supplies because it destroys harmful bacteria, producing Cl^- in the process. Dissolution of Cl_2 in water results in formation of hypochlorous acid, HOCl, according to the equation:

$$Cl_2(aq) + H_2O(l) \rightarrow HOCl(aq) + Cl^-(aq) + H^+(aq)$$

The hypochlorite ion, OCl^-, the conjugate base of hypochlorous acid, is the active ingredient in most bleaches. This ion oxidises many organic materials that are coloured, breaking them into smaller, colourless substances that are easily removed by detergents. Like all the other halogens, molecular chlorine is toxic, and it holds the dubious distinction of being the first chemical warfare agent to be used on a large scale. During World War I, nearly 6000 cylinders of chlorine were used at the Second Battle of Ypres, on 22 April 1915.

WORKED EXAMPLE 14.2

Disproportionation

Show, by assigning oxidation numbers to all chlorine-containing species in the equation:

$$Cl_2(aq) + H_2O(l) \rightarrow HOCl(aq) + Cl^-(aq) + H^+(aq)$$

that this is an example of a disproportionation reaction. Use electrochemical data from chapter 12 to determine $E^\ominus$ for this process, and comment on its spontaneity under standard conditions in both acidic ($[H^+]$ = 1.0 M) and basic ([OH] = 1.0 M) solution.

Analysis

As we saw in chapter 13, disproportionation is the simultaneous oxidation and reduction of a single chemical species. In this case, molecular chlorine, Cl_2, is the species undergoing disproportionation. Assign oxidation

numbers using the rules from chapter 12 (p. 491), and calculate $E^{\ominus}$ using $E^{\ominus} = E_R - E_L$, as outlined in chapter 12.

Solution

The oxidation number of chlorine in Cl_2 is 0, as is the case for any free element.

The oxidation number of chlorine in HOCl is +1. The compound is neutral, H has an oxidation number of +1, and O has an oxidation number of -2. Therefore, Cl must have an oxidation number of +1 so that the sum of all oxidation numbers in the molecule is zero.

The oxidation number of chlorine in Cl^- is -1, the same as the charge on the ion.

Thus we can see that Cl_2, in which the oxidation number of chlorine is zero, is being converted to species with a lower (Cl^-) and higher (HOCl) oxidation number for chlorine; this, therefore, is an example of disproportionation.

If we assume that reduction occurs at the right-hand electrode of a galvanic cell, then we calculate $E^{\ominus}$ as follows (data from table 12.1, p. 510):

$$\begin{aligned} Cl_2(aq) + 2e^- &\rightarrow 2Cl^-(aq) && \text{(reduction)} \\ Cl_2(aq) + 2H_2O(l) &\rightarrow 2HOCl(aq) + 2H^+(aq) + 2e^- && \text{(oxidation)} \\ \hline 2Cl_2(aq) + 2H_2O(l) &\rightarrow 2HOCl(aq) + 2Cl(aq) + 2H^+(aq) \end{aligned}$$

Dividing this by 2 gives:

$$Cl_2(aq) + H_2O(l) \longrightarrow HOCl(aq) + Cl^-(aq) + H^+(aq)$$

$$E^{\ominus} = E_R - E_L = +1.36\,V - (+1.63\,V) = -0.27\,V$$

Thus, under standard conditions in acidic solution, this reaction is not spontaneous.

In basic solution, the reactions are as follows:

$$\begin{aligned} Cl_2(aq) + 2e &\rightarrow 2Cl(aq) && \text{(reduction)} \\ Cl_2(aq) + 4OH^-(aq) &\rightarrow 2OCl^-(aq) + 2H_2O(l) + 2e^- && \text{(oxidation)} \\ \hline 2Cl_2(aq) + 4OH^-(aq) &\rightarrow 2OCl^-(aq) + 2Cl^-(aq) + 2H_2O(l) \end{aligned}$$

Dividing this by 2 gives:

$$Cl_2(aq) + 2OH^-(aq) \rightarrow OCl(aq) + Cl^-(aq) + H_2O(1)$$

Knowing that $E^{\ominus}_{OCl^-/Cl_2} = +0.32\,V$, we can then calculate $E^{\ominus}$ as:

$$E^{o} = E_R - E_L = +1.36\,V - (+0.32\,V) = +1.04\,V$$

Thus under standard conditions in basic solution, this reaction is spontaneous.

Recall from our discussion on pp. 359-60 that a positive value of $\Delta G^{\ominus}$ (which corresponds to a negative value of $E^{\ominus}$) does not mean the forward reaction does not occur at all; it merely means that it never proceeds to such an extent that all products will be present at $c^{\ominus}$. Thus, dissolution of Cl_2 in 1.0 M H_3O^+ will result in the formation of small amounts of HOCl and Cl^-. However, the forward reaction is much more favoured in basic solution, as evidenced by its large positive value of $E^{\ominus}$.

Bromine is a dense deep red liquid, one of only two elements on the periodic table which exist as a liquid under ambient conditions (the other is mercury). As Br_2 is a weaker oxidising agent than Cl_2, chemical oxidation of Br^- is

feasible and, indeed, Br_2 is prepared on an industrial scale by the oxidation of Br^- with Cl_2. Br^- is found primarily in sea water, salt lakes and brine deposits. The most well-known source is probably the Dead Sea, on the border of Israel and Jordan. Bromine finds its major use in flame retardants, accounting for over 50% of the world's annual production. Like chlorine, it is also used in water purification. Before the advent of digital cameras, silver bromide was used extensively as the lightsensitive material in photographic film. Bromomethane (methyl bromide) is used in large quantities as a pesticide; however, its use is decreasing as it is recognised to be an ozone-depleting chemical.

Iodine, like bromine, is prepared by oxidation of the halide ion by Cl_2. It is a deep purple solid with a significant vapour pressure, and a sample of I_2 in a closed container will be seen to have a purple vapour above it (see figure 14.17). There are no major industrial uses of iodine, but it is increasingly being used as an alternative to chlorine in water treatment, especially in Australia. Iodine is a trace element, being a constituent of thyroxine (p. 1058), a hormone which regulates the rate of cellular use of oxygen. Iodine deficiency was historically manifested by a goitre, a swollen thyroid gland, but the compulsory addition of small amounts of NaI to table salt (in 1924, New Zealand was one of the first countries in the world to do this) has all but eliminated this in developed countries. However, it is also now known that iodine deficiency can lead to developmental disabilities and ironically the current fad for using ‘natural’ salt containing no iodine appears to have contributed to iodine deficiency again being a problem in both Australia and New Zealand. For this reason, bakers in both countries have been required to use iodised salt in their products since 2009.



FIGURE 14.17 Iodine sublimes at atmospheric pressure, and purple iodine vapour can be seen above a sample of solid iodine.

Astatine occurs in tiny amounts on Earth owing to its presence in three radioactive disintegration series (p. 1170) and the extremely short lifetime (8.3 h) of its longest lived isotope. All of its isotopes are radioactive. It competes with francium for the distinction of being the rarest element in the Earth's crust.

Group 18

18		
2 He 4.003	helium	$1s^2$
10 Ne 20.18	neon	[He] $2s^2 2p^6$
18 Ar 39.95	argon	[Ne] $3s^2 3p^6$
36 Kr 83.80	krypton	[Ar] $4s^2 3d^{10} 4p^6$
54 Xe 131.3	xenon	[Kr] $5s^2 4d^{10} 5p^6$
86 Rn (222.0)	radon	[Xe] $6s^2 5d^{10} 4f^{14} 6p^6$

There was no place in Mendeleev's original periodic table (chapter 1, p. 14) for the elements of group 18, simply because none of them had been discovered at that time. They were originally called the noble gases, as they were thought to be chemically nonreactive, but the isolation of the first noble gas compound in 1962 showed them to have significant reactivity under the correct conditions. They all exist as monatomic gases under ambient conditions.

Although helium is the second most abundant element in the universe, it is present on Earth in very low concentrations, owing to the fact that it is light enough to escape the Earth's gravitational pull. Helium is obtained primarily from natural gas deposits, having been formed as a result of radioactive decay of ^{238}U (p. 1170), and is used extensively in cryogenic (very low temperature) applications. Helium has the lowest boiling point of any element; it condenses to a liquid at 4.2 K. Several materials become superconducting at very low temperatures and liquid helium is used to obtain these conditions. Of particular interest to chemists is the use of liquid helium to cool the superconducting magnets used in NMR spectrometers (p. 885). Helium is unusual in that it cannot be solidified at atmospheric pressure. It also exhibits a phenomenon called superfluidity when it is cooled below 2.17 K; this means the liquid has zero viscosity and will coat the entire surface of any container in which it is placed. The superfluid also shows extraordinarily high thermal conductivity, greater than that of copper.

Neon is found in the atmosphere at concentrations of 1 part in 65 000, and it is usually obtained from the fractional distillation of liquid air. The passage of an electric discharge through the gas causes a beautiful orange-red glow (figure 14.18), due to a large number of electronic transitions that give rise to many atomic emission lines around 600 nm (figure 4.20, p. 120). This effect was used by Georges Claude in the construction of the first neon light in 1910. The emission properties of neon are also used in helium-neon (HeNe) lasers; these emit red light of wavelength 632.8 nm.



FIGURE 14.18 Emission of photons from excited neon atoms gives a brilliant red light.

Argon is the most abundant of the group 18 elements. It is the third most abundant component of air (0.934% by volume) after nitrogen and oxygen, and is obtained from this source. Its relative profusion and lack of chemical reactivity make it the inert gas of choice in applications which require exclusion of oxygen that are carried out under conditions where nitrogen might react. As we will see in chapter 27 (p. 1172), the argon isotope ^{40}Ar is important in the dating of rocks. Although it is considered chemically inert, the compound HArF has been recently reported; however, it is stable only in a matrix of frozen argon below 27 K.

chemical Connections

Chemical Connections Compounds of group 18 elements

Prior to 1962, most chemists thought that the group 18 elements were chemically nonreactive and would not form compounds with any element on the periodic table. However, the work of Neil Bartlett, a young British chemist working at the University of British Columbia in Vancouver in the early 1960s, changed this misconception forever.

Bartlett's original interest was not in the group 18 elements but, rather, in compounds formed between fluorine and platinum. As a graduate student in England, he had isolated an unusual red solid with the formula PtF_6O_2 while studying the reactions of both metallic platinum and some platinum compounds with elemental fluorine in the presence of small amounts of oxygen. When he moved to Vancouver he set about trying to characterise this further. He eventually showed, using a variety of techniques, that the correct formula of this solid was $O_2^+PtF_6^-$. This was the first example of a compound containing an oxidised O_2 molecule; we usually think of O_2 as being an excellent oxidising agent, and therefore it is easily reduced. Oxidising O_2 should be extremely difficult and would require an oxidising agent of enormous strength. As one of the ways in which he had prepared the solid involved the reaction of the gas PtF_6 with O_2, Bartlett realised that PtF_6 must be an exceptionally good oxidising agent. Isolation of $O_2^+PtF_6$ from this reaction was an achievement in itself, but even more remarkable results lay in store.

While preparing for an undergraduate lecture, Bartlett happened to look at a table of ionisation potentials and found that the energy required to remove an electron from Xe(g) (1170 kJ mol^{-1}) was essentially equal to that required for O_2(g) (1177 kJ mol^{-1}). To put these numbers in perspective, recall from chapter 5 that the N≡N triple bond, one of the strongest known covalent bonds, has a bond energy of 942 kJ mol^{-1}; removing an electron from either O_2 or Xe is *really* difficult! Bartlett therefore reasoned that if PtF_6 was a strong enough oxidising agent to oxidise O_2, it should also be able to oxidise Xe and possibly form a compound with this group 18 element. Such reasoning went against all perceived chemical wisdom of the

time but, nevertheless, Bartlett set up a simple apparatus in which deep red gaseous PtF_6 and colourless Xe at room temperature were separated by a seal; when the seal was broken, a yellow solid formed immediately, and chemical history was made (figure 14.19).

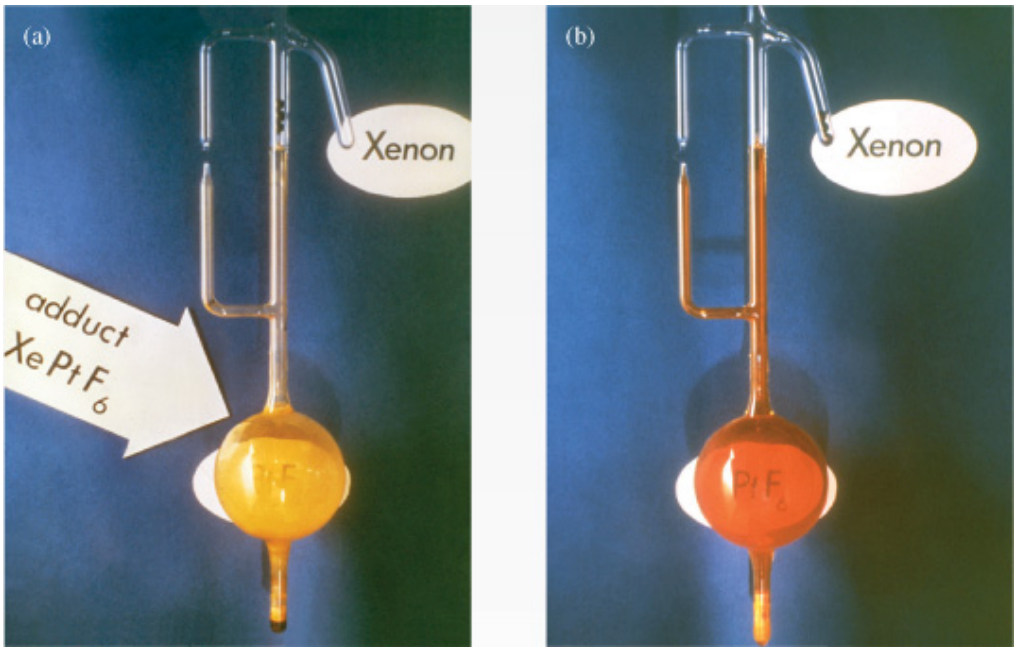


FIGURE 14.19 When

(a) platinum hexafluoride, a red gas, is allowed to mix with a large molar excess of xenon, the immediately formed product is

(b) a yellow solid with the composition $XePtF_6$,the first recognised compound of a noble gas

Even today, the exact identity of the yellow solid is not certain. Originally, it was thought to be $Xe^+PtF_6^-$, by analogy with the O_2^+ compound. However, it now appears that the compound is better described as $[XeF]^+[PtF_5]^-$. Regardless, Bartlett's experiment inspired chemists around the world to study the reactivity of the group 18 elements with strong oxidising agents. The first krypton compound was reported in 1963, while the first xenon oxide, XeO_3, was also prepared that year. Bartlett was possibly the first person to experience the highly unstable nature of xenon oxides when what was thought to be a sample of XeO_2 exploded in a quartz tube while he was not wearing eye protection; 27 years later, a piece of glass was removed from his eye.

There are now several hundred known compounds containing group 18 elements, and research into their synthesis and properties continues to this day. Bartlett's extraordinary discovery changed chemistry overnight and forced chemists to fundamentally alter their ideas concerning reactivity; we now no longer think of group 18 elements as being chemically inert. Surprisingly, Bartlett, who died in 2008, was not awarded the Nobel Prize for his achievement; however, his name is immortalised in every inorganic chemistry textbook as the man who showed that the noble gases are not quite so noble.

Krypton has an abundance in air around one-fifth that of helium. Its emission properties make it ideal for use in high-speed photographic flash bulbs, as it gives a high-intensity white light, while it also finds use in krypton–fluoride (KrF) lasers, which give ultraviolet light of wavelength 248 nm. Krypton is the first of the group 18 elements that show appreciable chemical reactivity; the compound KrF_2 was prepared in 1963 by low temperature (20 K) photolysis of a mixture of krypton and fluorine, and it is stable up to 250 K. Since this time, over 30 Kr compounds, all containing Kr in the +2 oxidation state and all of which have krypton bonded to fluorine, have been prepared.

Xenon is the least abundant of the group 18 elements found in the atmosphere (around 0.09 parts per million) but the most chemically interesting. The first xenon compounds were prepared in 1962, thereby demonstrating the potential reactivity of the so-called ‘noble’ gases. The fluorides XeF_2, XeF_4 and XeF_6 are all known, as are the oxides XeO_3 and XeO_4; the last two are both excellent oxidising agents as evidenced by the following reduction potentials:

$$XeO_3 + 6H^+ + 6e^- \rightarrow Xe + 3H_2O \quad E^\ominus = +2.10\,V$$
$$H_4XeO_6 + 8H^+ + 8e^- \rightarrow Xe + 6H_2O \quad E^\ominus = +2.18\,V$$

but both are dangerously explosive. Several mixed oxofluorides have been prepared, while compounds containing Xe bonded to C, N, Cl and some transition metals are also known. The element itself is used in xenon lamps, lasers and as an anaesthetic.

Radon is formed from the radioactive decay of radium, which is in turn formed from both uranium and thorium. All isotopes of radon are radioactive, and the longest lived has a half-life of less than four days. This means that radon occurs in miniscule amounts on Earth. However, houses constructed of stone, or built in areas containing high levels of uranium or thorium minerals, can accumulate potentially dangerous concentrations of radon in their basements owing to its weight — it is around eight times the density of air — and kits which test radon concentrations in air are commercially available. Although some controversy exists, recent research has proposed Ernest Rutherford as the original discoverer of radon.

WORKED EXAMPLE 14.3

Lewis structure of a group 18 compound

Draw the Lewis structure of XeO_3, and deduce the most probable geometry of this molecule.

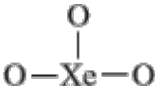
Analysis

We obtain the Lewis structure of the molecules using the rules in chapter 5, and we then use these, in conjunction with VSEPR theory (chapter 5) to propose the geometry of the molecules.

Solution

Step 1: Count the valence electrons; Xe has 8 valence electrons and each O atom has 6. Therefore, there is a total of 26 valence electrons.

Step 2: Draw the bonding framework using single bonds.



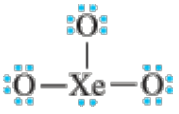
Electrons used = 6. Therefore, there are 20 electrons still to be allocated.

Step 3: Place three nonbonding pairs on each outer atom.



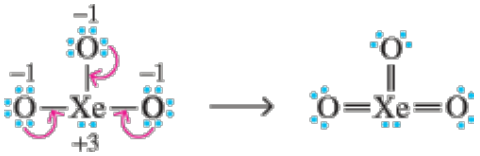
Electrons used = 18. Therefore, there are 2 electrons still to be allocated.

Step 4: Assign the remaining electrons to the inner atom.



Electrons used = 2. All electrons are now assigned.

Step 5: Minimise formal charges on all atoms.
The formal charges on each atom are as shown below. Moving electron pairs to make three Xe≡O double bonds will result in each atom having a formal charge of zero.



There are four sets of electron pairs around the central Xe atom, so the structure of XeO_3 will be based on a tetrahedron. As only three of the sets are equivalent, the molecule will adopt a trigonal pyramidal geometry.

PRACTICE EXERCISE 14.2

Draw the Lewis structures of XeO_4 and KrF_2, and determine their most probable geometries.

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14.3 The Biogeochemical Cycles of Nature

Having introduced the *p*-block elements, we will now concentrate on what are arguably the most important of these: oxygen, sulfur, nitrogen, phosphorus and carbon, which all lie in the second and third periods of the periodic table. We choose these elements because of their importance in the Earth's biochemical and geochemical systems.

Bonding in the *p*-block Elements

As we have already seen, the elements of the *p* block adopt a wide variety of structures, and these can be related to the valence-electron configuration of each element and the bonding which results as a consequence of this. We first introduced the concept of an octet in chapter 5 (p. 172). From what we have learned about the lack of reactivity of the group 18 elements in this chapter and their valence-electron configurations (ns^2np^6), we can see that the presence of eight electrons in the valence shell appears to confer some stability to an atom. The group 18 elements are reluctant to undergo reaction with any but the most reactive chemical reagents and exist as monatomic gases. We also often find that an octet of electrons about an atom in a molecule appears to be a particularly stable energetic situation, particularly for elements in the second period, and that the structures adopted by elements can be rationalised on the basis of this. For example, if we start at Ne (group 18) and go across the periodic table to C (group 14), we find the number of valence electrons decreases by one for each group we traverse. Therefore, in order to obtain an octet, atoms must share one or more electrons. This is illustrated in table 14.2.

TABLE 14.2 Single and multiple covalent bonding in second period p-block elements

Element	Valence-electron configuration	Electrons required for octet	Structure
neon	$2s^2 2p^6$	0	:Ne:
fluorine	$2s^2 2p^5$	1	:F—F:
oxygen	$2s^2 2p^4$	2	:O=O:
nitrogen	$2s^2 2p^3$	3	:N≡N:
carbon	$2s^2 2p^2$	4	—C—C— C=C —C≡C—

A fluorine atom can obtain the single electron required for an octet by sharing a single electron with another fluorine atom; this gives both atoms a share of an octet, and so elemental fluorine exists as F_2, with a single two-electron bond between the atoms. An oxygen atom requires two electrons for an octet and will therefore share two electrons with another oxygen atom. This results in O_2 molecules, which contain a double bond between the atoms. The triple bond in elemental nitrogen results from each atom sharing three electrons with the other, to give N_2. If this trend were to be continued, we might expect carbon to exist as C_2 molecules with a quadruple bond between the atoms. However, this is not energetically favourable, and a carbon atom instead obtains an octet by sharing four electrons with four, three or two neighbouring atoms to give alkanes, alkenes and alkynes, respectively. Inspection of the final column of table 14.2 in fact shows the relationship between the structures of F_2, O_2 and N_2, and C_2H_6, C_2H_4 and C_2H_2, respectively. We say that F_2 and C_2H_6 are isoelectronic (they contain the same number of electrons), as are O_2 and C_2H_4, and N_2 and C_2H_2. The multiple bonds that hold the latter molecules together are formed from overlap of *p* orbitals in a π-type fashion (chapter 5, p. 196); this is favourable for elements from the second period owing to their relatively small sizes, which allow close approach of the atoms and correspondingly efficient orbital overlap. However, this is not the case for elements from the third period as their atomic radii are larger, and π bonding between these is therefore significantly weaker. Therefore, these elements tend to adopt structures based on *σ* bonding only between neighbouring atoms. Thus the structure of elemental silicon is the same as that of diamond (pp. 258–9), with each Si atom connected to four other Si atoms; phosphorus exists as σ-bonded P_4 tetrahedra with each P atom bonded to three others (p. 605), and sulfur is composed of S_8 rings with single S—S bonds (p. 607).

While there are significant differences between the structures of the second and third period elements, the compounds that these elements form with hydrogen unanimously reflect the group to which they belong. As can be seen below, the number of H atoms in each compound corresponds to the number of electrons required by the *p*-block element to obtain an octet.

Group 14	Group 15	Group 16	Group 17	Group 18
CH_4	NH_3	OH_2 (H_2O)	FH (HF)	Ne
SiH_4	PH_3	SH_2 (H_2S)	ClH (HCl)	Ar

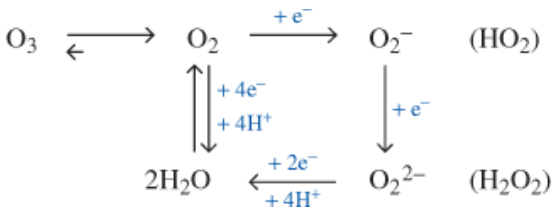
All of these compounds contain 4 sets of electron pairs and therefore, according to VSEPR theory (p. 176), their structures are based

on the tetrahedron, with 0, 1, 2 or 3 lone pairs.

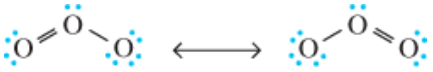
The Group 16 Cycles

The Oxygen Cycle

We have seen earlier in this chapter that there are two allotropes of elemental oxygen: the O_2 molecule and the O_3 (ozone) molecule. Both are vital to life on Earth. There are also three reduced forms of oxygen, O_2^- (superoxide), O_2^{2-} (peroxide) and O^{2-}(oxide), all of which are important in living systems. These species are related as shown in the oxygen cycle below:



The ozone molecule can be written as two resonance forms (p. 174):



with the true structure being the average of these. This is reflected by the fact that the oxygen-oxygen bond lengths in O_3 are identical (128 pm) and lie between the lengths of the O—O single bond in H_2O_2 (148 pm) and the O═O double bond in O_2 (121 pm), thereby attesting to their partial double bond character. The presence of a lone pair on the central O atom results in the molecule adopting a bent geometry, with an O—O—O angle of 117°. Ozone is prepared in the laboratory by the passage of an electric discharge through O_2, and the pungent odour of ozone can often be detected in the vicinity of high-voltage electrical equipment. In nature, it is formed in the upper atmosphere by the action of ultraviolet radiation from the Sun on O_2. It is also formed at lower altitudes in photochemical smog, owing to the presence of nitrogen oxides (NO_x) originating from vehicle and industrial emissions. These are converted to NO_2, which releases an oxygen atom on photolysis, and this then reacts with O_2 to give O_3. The ozone molecule is highly reactive, as might be expected from its positive Gibbs energy of formation:

$$\tfrac{3}{2}O_2(g) \rightarrow O_3(g) \quad \Delta_f G^{\ominus} = +163\,\text{kJ mol}^{-1}$$

and its large positive standard reduction potential:

$$O_3(g) + 2H^+(aq) + 2e^- \rightarrow O_2(g) + H_2O(l) \quad E^{\ominus} = +2.08\,\text{V}$$

Oxygen, O_2, is involved in what are arguably the two most important chemical reactions in the biosphere: photosynthesis and respiration. In photosynthesis (p. 494), green plants use the Sun's energy to convert CO_2 and H_2O to carbohydrates and O_2. The oxidation half-equation in this redox process involves the oxidation of H_2O to O_2:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

and the electrons released are then used to reduce CO_2 to (in this case) glucose:

$$6CO_2(g) + 24H^+(aq) + 24e^- \rightarrow C_6H_{12}O_6(s) + 6H_2O(l)$$

The overall reaction then becomes:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

Given that $\Delta_f G^{\ominus}$ for $C_6H_{12}O_6(s)$ is -911 kJ mol^{-1}, we can use the data in table 8.6 (p. 329) to show that, for the overall reaction, $\Delta G^{\ominus} = +2879\,\text{kJ}$. This corresponds to $K = 2 \times 10^{-505}$ at 298 K and, in the absence of energy from sunlight, we would expect this reaction not to proceed at all.

Respiration is essentially the opposite of photosynthesis. In this, glucose reacts with O_2 to give CO_2 and H_2O, plus a large amount of energy which can be used by the organism. The overall reaction involves the four-electron reduction of O_2 to H_2O, which does not occur as a single process but in a series of steps involving stepwise reduction to O_2^- and O_2^{2-}. Of these, superoxide, O_2^-, is toxic to cells, and nature uses the enzyme superoxide dismutase (pp. 579–80) to control the amount of this potentially dangerous ion within an organism.

WORKED EXAMPLE 14.4

Electronic structures of reduced oxygen species

What are the bond orders in the superoxide, O_2^-, and peroxide, O_2^{2-}, anions? Order the three species O_2^-, O_2^{2-} and O_2 in order of decreasing O—O bond length.

Analysis

We will use the MO diagram we derived for the O_2 molecule in chapter 5 (figure 5.49), add the appropriate number of electrons, and determine the bond order using the equation:

$$\text{bond order} = \frac{1}{2}(\text{number of electrons in bonding molecular orbitals} - \text{number of electrons in antibonding molecular orbitals})$$

introduced on p. 199.

Solution

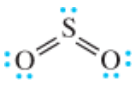
Using figure 5.49 (p. 202), we find that the electronic configuration of the formally double-bonded O_2 molecule is $(\sigma_s)^2 (\sigma_s^*)^2 (\sigma_p)^2 (\pi_x)^2 (\pi_y)^2 (\pi_x^*)^1 (\pi_y^*)^1$. One electron reduction to give O_2^- requires the added electron to be placed in either of the degenerate antibonding π_x^* or π_y^* orbitals. This gives the electronic configuration $(\sigma_s)^2 (\sigma_s^*)^2 (\sigma_p)^2 (\pi_x)^2 (\pi_y)^2 (\pi_x^*)^2 (\pi_y^*)^1$. The bond order in O_2^- is therefore $\frac{1}{2}(8-5) = 1.5$.

Addition of a further electron to give O_2^{2-} results in the electronic configuration $(\sigma_s)^2 (\sigma_s^*)^2 (\sigma_p)^2 (\pi_x)^2 (\pi_y)^2 (\pi_x^*)^2 (\pi_y^*)^2$, in which the π^* orbitals are full. The bond order of O_2^{2-} is therefore $\frac{1}{2}(8-6) = 1$.

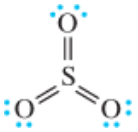
On the basis of bond orders, we would predict O_2^{2-} to have the longest O—O bond, followed by O_2^- and O_2. The respective O—O bond lengths of 149 pm, 128 pm and 121 pm are consistent with this molecular orbital electronic description.

The Sulfur Cycle

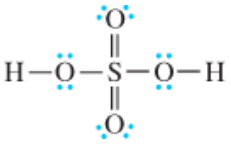
Sulfur is a nutrient that is essential for life. It is found in the amino acids cysteine (Cys) and methionine (Met) (table 24.1, p. 1057) in which the sulfur-containing functional group is a thiol and thioether, respectively. In these compounds, sulfur exhibits its lowest possible formal oxidation number of -2. Sulfur as S^{2-} is also found coordinated to metal ions in a variety of metalloproteins and metalloenzymes. However, the presence of O_2 in Earth's atmosphere and its thermodynamically favourable reactions with many sulfur-containing species mean that oxidation is generally a facile process, resulting ultimately in compounds such as SO_2, SO_3 and H_2SO_4. The thermodynamic stability of these molecules is reflected in their values of $\Delta_f G^\circ$; these are -300.4 kJ mol^{-1}, -370.4 kJ mol^{-1} and -689.9 kJ mol^{-1} for $SO_2(g)$, $SO_3(g)$ and $H_2SO_4(l)$, respectively, at 25 °C (appendix A). Investigation of the Lewis structures of these molecules shows that an octet of electrons about the central sulfur atom is not necessarily the most energetically favourable arrangement, as is often found with elements from the third period. The SO_2 molecule adopts a bent geometry, with two S═O double bonds and a lone pair on the sulfur atom.



The S═O double bonds arise from the necessity to minimise the formal charges on the oxygen and sulfur atoms, and doing this therefore results in 10, rather than 8, electrons surrounding the central sulfur atom. A similar situation arises for SO_3, where the Lewis structure in which the formal charges are minimised has 12 electrons surrounding the S atom:

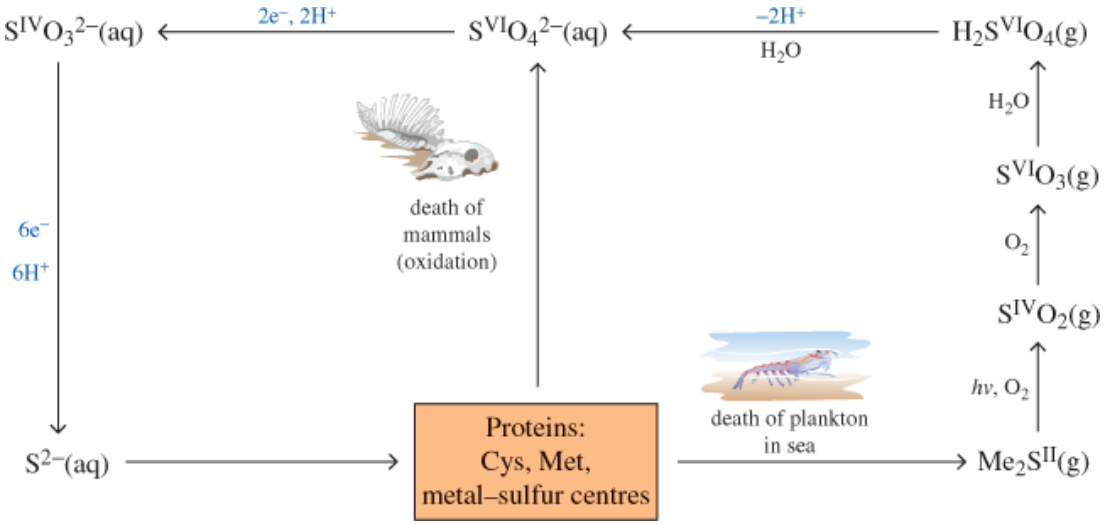


while the optimal Lewis structure for H_2SO_4 also places 12 electrons around the sulfur atom:



The ability of third period elements and below to be surrounded by more than eight electrons (sometimes called expanding the octet) is attributed by some to participation of *d* orbitals on the central atom in bonding. However, it should be noted that this interpretation is controversial and other explanations have been advanced.

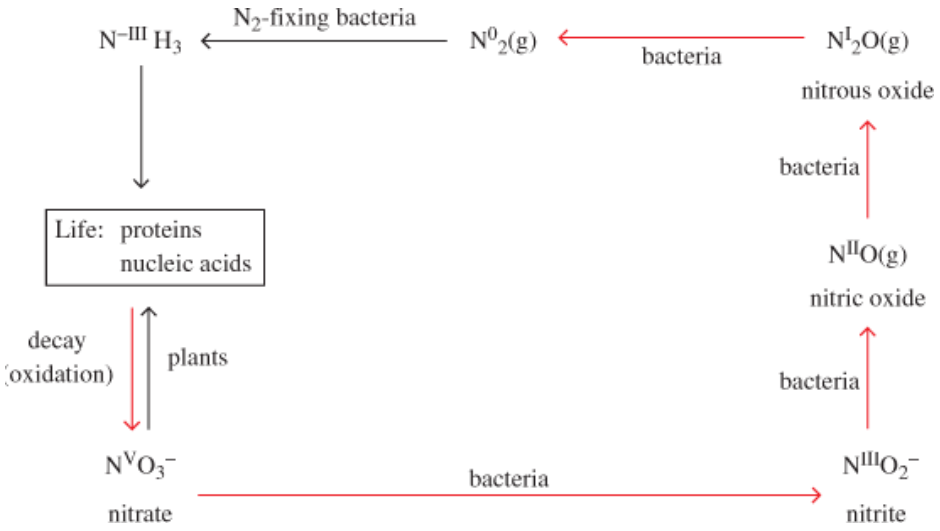
The biological sulfur cycle is shown below. As can be seen, those sulfur compounds important to life tend to contain the element in the thermodynamically disfavourable (in the presence of O_2) -2 oxidation state, and nature therefore requires a method by which both sulfur and sulfur-oxygen compounds can be reduced. This is achieved by a variety of micro-organisms under anaerobic (absence of oxygen) conditions. When mammals die, their reduced sulfur species are oxidised to sulfate by biological oxidants, and this is either incorporated in sulfate minerals or dissolved in aqueous solution. The same result can be achieved chemically through the oxidation of sulfur species in the atmosphere; the decomposition of plankton results in the formation of volatile dimethyl sulfide, Me_2S, which escapes into the atmosphere and is photochemically oxidised to SO_2. This then reacts further with O_2 to give SO_3, and reaction of this with water gives sulfuric acid, H_2SO_4, the most important component of acid rain. While this process occurs naturally in the atmosphere, industrial production of SO_2 over the last century has increased the amount of H_2SO_4 in the atmosphere to the point where acid rain has led to significant environmental damage, mainly in the Northern Hemisphere. The sulfur impurities in both coal and fossil fuels initially form SO_2 on combustion, and this is then converted into H_2SO_4 in the atmosphere via the above route. The reduction of sulfate to sulfite and eventually sulfide takes place in plants and bacteria, which use a number of enzymes to effect this conversion. The resulting sulfide is then incorporated into cysteine and methionine, and the cycle starts again. It should also be noted that sulfide itself occurs as a ligand in the M—S (M = a metal ion) centres of a number of metalloproteins, most importantly iron-sulfur proteins, and appears to derive from breakdown of organic sulfur species, rather than being directly incorporated as S^{2-}.



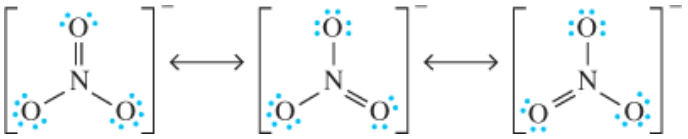
The Group 15 Cycles

The Nitrogen Cycle

Earlier in this chapter, we discussed the extraordinary stability of the N_2 molecule, a consequence of the strong N≡N triple bond, and how nature uses the nitrogenase enzyme to allow conversion of N_2 to NH_3. As with sulfur, the reduced states of the element are important in living systems, and incorporation of nitrogen into biological molecules such as amino acids and the nucleic acid bases (p. 1088) generally occurs through NH_3.



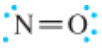
Decomposition of living matter ultimately results in oxidation of N-containing molecules to NO_3^- in which N displays its highest oxidation state of +5. Remembering that N is a second period element, it prefers to be surrounded by an octet of electrons, and this is shown in the three possible resonance structures of the NO_3^- ion in which the formal charges on the atoms are minimised.



Nitrate can be reduced by anaerobic bacteria to various nitrogen oxides, and ultimately to molecular N_2. Such bacteria essentially 'respire' using these N-containing species and are actually poisoned by O_2! The initial reduction step involves formation of nitrite ion, NO_2^-; this is often used as a preservative in bacon, ham and corned beef, although there have been some recent health concerns regarding its use. The ion adopts a bent geometry, and two resonance structures can be drawn.



Subsequent reduction gives nitric oxide, NO(g), a molecule of considerable biological importance as discussed in the introduction to this chapter. This is one of eight known neutral compounds containing only N and O (the others are N_2O, NO_2, NO_3, N_2O_2, N_2O_3, N_2O_4 and N_2O_5). The Lewis structure of NO is interesting, as, owing to the odd number of electrons in a nitrogen atom ($1s^22s^22p^3$) and the even number of electrons in an oxygen atom ($1s^22s^22p^4$), the molecule contains an odd number of electrons. The structure can be drawn such that there is a formal double bond between the nitrogen and oxygen atoms, and an unpaired electron on the N atom:



although it appears that, in reality, the unpaired electron is involved in N—O bonding to give an N—O bond order of 2.5. Reduction of NO yields nitrous oxide, N_2O, commonly referred to as laughing gas. This name came about as a result of an experiment in 1799 by the English chemist Humphry Davy, who wished to show that the recently prepared (1793) molecule was, in fact, not toxic. In a procedure that would be frowned upon today, he simply inhaled small amounts of the gas mixed with air and reported no ill effects. When he eventually breathed the pure gas, he reported 'a highly pleasurable thrilling, particularly in the chest and extremities' and stated that 'trains of vivid visible images rapidly passed through my mind and were connected with words in such a manner as to produce perceptions perfectly novel' — he had indirectly discovered the anaesthetic properties of nitrous oxide, although it was not used as such until 1844. The molecule is linear and, as we saw on pp. 175-6, three resonance structures can be drawn, two of which are the major contributors to the actual structure:

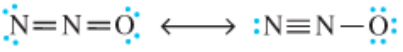


Figure 14.20 shows the electron distributions in NO_3^-, NO_2, NO and N_2O.

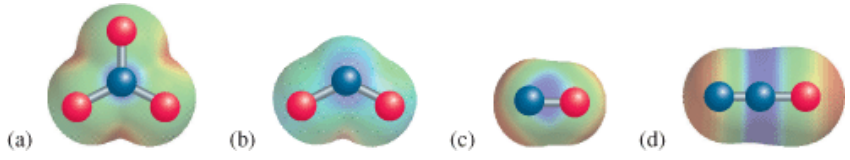
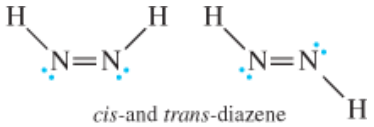


FIGURE 14.20 The electron density distributions for
(a) NO_3^-,
(b) NO_2^-,
(c) NO and
(d) N_2O.
Red indicates the highest electron density and blue indicates the lowest.

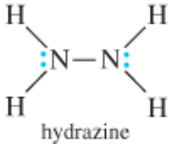
Reduction of N_2O gives $N_2(g)$, which is then used as a feedstock in N_2-fixing bacteria to form ammonia. The overall reaction for this process is:

$$N_2 + 8H^+ + 16MgATP + 8e^- \rightarrow 2NH_3 + H_2 + 16MgADP + 16P_i$$

where P_i is inorganic phosphate, and MgATP and MgADP are the magnesium salts of adenosine triphosphate (p. 623) and adenosine diphosphate, respectively. This reaction is catalysed by a variety of nitrogenase enzymes, which are metalloenzymes containing Fe, Fe and Mo, or Fe and V, at the active sites, and which generally operate under anaerobic conditions. Although the exact mechanism of the reduction process has yet to be determined, it appears plausible that the reaction proceeds via two intermediate compounds of nitrogen and hydrogen, diazene, N_2H_2, and hydrazine, N_2H_4.



cis-and *trans*-diazene



hydrazine

Diazene is unstable, with a lifetime of only minutes at room temperature, and can exist as *cis* and *trans* isomers owing to the relative orientations of the hydrogen atoms. Pure hydrazine, although much more stable than diazene at room temperature, can undergo violent decomposition at higher temperatures and this property has led to its use as a rocket fuel. In the chemical laboratory (where it is usually handled as an aqueous solution!), it is an excellent reducing agent, especially in basic aqueous solution:

$$NH_3 + \frac{1}{2}N_2 + H_2O + e^- \rightarrow N_2H_4 + OH^- \quad E^\circ = -2.42\,V$$

Table 14.3 shows how the N—O and N—N bond lengths in the nitrogen compounds discussed thus far correlate with the structures we have drawn. Both NO_3^- and NO_2^- have N—O bond orders greater than 1 and less than 2, and this is reflected in their N—O bond lengths of 124 pm, significantly shorter than the N—O single bond in gaseous HNO_3 (141 pm). The neutral N_2O molecule has a slightly shorter N—O bond length (119 pm), again consistent with a bond order between 1 and 2, whereas the 115 pm N—O bond length in NO reflects a bond order of at least 2.

TABLE 14.3 N—O and N—N bond lengths in selected nitrogen compounds

Compound	N—O length (pm)	N—N length (pm)
NO_3^-	124	–
NO_2^-	124	–
NO	115	–
N_2O	119	113
N_2	–	110
N_2H_2	–	125
N_2H_4	–	145

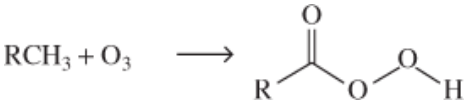
Similar trends are seen in the N—N bond lengths of the compounds in table 14.3. N_2H_4, with a formal N—N single bond, displays the longest N—N distance (145 pm), which shortens to 125 pm in double-bonded diazene. The resonance structures of N_2O predict an N—N bond order between 2 and 3, which is consistent with the still shorter bond length (113 pm), while triple-bonded N_2 displays the shortest N—N distance (110 pm).

Nitrogen oxides (NO_x) resulting from the combination of nitrogen and oxygen at high temperature in internal combustion engines have been implicated in atmospheric pollution. Of these species, both colourless NO and dark brown NO_2 cause particular problems

involving ozone; NO destroys O_3 molecules while NO_2, somewhat ironically, catalyses formation of O_3 molecules. In the lower atmosphere, NO_2 can undergo photochemical dissociation to give reactive oxygen atoms and NO; the former can combine with O_2 molecules to form O_3 while the latter react with oxygen to regenerate NO_2. The overall process is as follows:

$$\begin{aligned} NO_2 &\xrightarrow{h\nu} NO + O \\ O + O_2 &\rightarrow O_3 \\ NO + \tfrac{1}{2}O_2 &\rightarrow NO_2 \\ \tfrac{3}{2}O_2 &\rightarrow O_3 \end{aligned}$$

NO_2 is a catalyst in this process, and hence a single molecule of NO_2 can potentially generate an enormous number of O_3 molecules. While O_3 in the upper atmosphere is beneficial in that it absorbs damaging ultraviolet radiation from the Sun, at lower altitudes O_3 reacts with hydrocarbons in the atmosphere to form toxic peroxy acids, inhalation of which can lead to respiratory problems.



This combination of atmospheric pollutants is called photochemical smog.

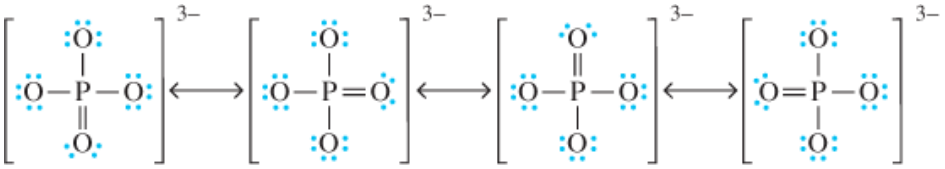
In the upper atmosphere, the NO formed from photolysis of NO_2 reacts with O_3, causing its depletion. Again, this is a catalytic process, as NO is regenerated from the reaction of NO_2 with an oxygen atom.

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ O + NO_2 &\rightarrow NO + O_2 \\ O + O_3 &\rightarrow 2O_2 \end{aligned}$$

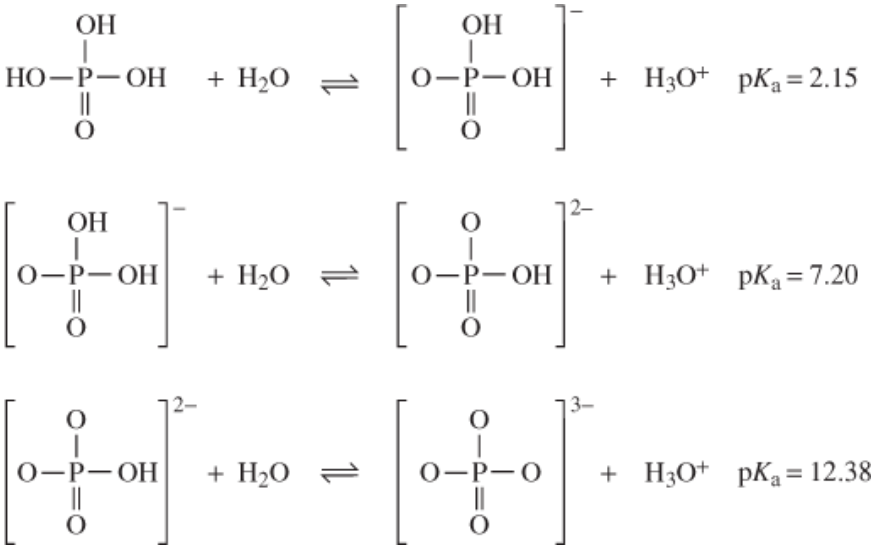
Catalytic converters in the exhaust systems of cars have been used since the mid 1970s to minimise the amount of NO_x species emitted; these generally use catalysts containing precious metals such as platinum and rhodium to convert NO_x species to N_2 and O_2.

The Phosphorus Cycle

The phosphorus cycle differs from those we have investigated so far, in that there is essentially no redox chemistry involved. In contrast to both sulfur and nitrogen, where nature uses the reduced states of the elements, phosphorus in nature exists nearly exclusively in the +5 oxidation state as phosphate, or a phosphate derivative. (It should be noted that the term ‘phosphate’ technically refers only to the PO_4^{3-} ion, but it is often used to denote any phosphorus-containing species in which there are four phosphorus-oxygen bonds. In order to distinguish PO_4^{3-}, and any of its protonated derivatives, from other phosphates, it is often referred to as ‘inorganic’ phosphate, abbreviated P_i.) Being a third period element, phosphorus is able to accommodate more than eight electrons around it and, as we saw on p. 175, there are four resonance structures that can be drawn for the PO_4^{3-} ion.



The PO_4^{3-} ion can be thought of as deriving from complete deprotonation of phosphoric acid, H_3PO_4. This is a rare example of a triprotic acid, with pK_a values of 2.15, 7.20 and 12.38 corresponding to the three deprotonations.



The first pK_a of 2.15 shows phosphoric acid to be of significant strength, but it is far from being a strong acid, as is often incorrectly stated.

Phosphoric acid consistently ranks among the top 10 industrial chemicals produced, owing to its subsequent conversion to fertilisers. Almost all phosphoric acid is produced directly from fluoroapatite. The ore is partially purified, crushed and then slurried with aqueous sulfuric acid.

$$Ca_5(PO_4)_3F(s) + 5H_2SO_4(aq) \rightarrow 3H_3PO_4(aq) + 5CaSO_4(s) + HF(aq)$$

The dilute phosphoric acid obtained from this process is concentrated by evaporation and is often highly coloured because of the presence of many metal ion impurities in the phosphate rock. However, this impure acid is suitable for the manufacture of phosphate fertilisers, which accounts for almost 90% of phosphoric acid production. High-purity H_3PO_4 is obtained using a more expensive redox process that starts from the pure element. Controlled combustion of white phosphorus gives phosphorus(V) oxide, P_4O_{10} (figure 14.21) and addition of water to this generates high-purity phosphoric acid:

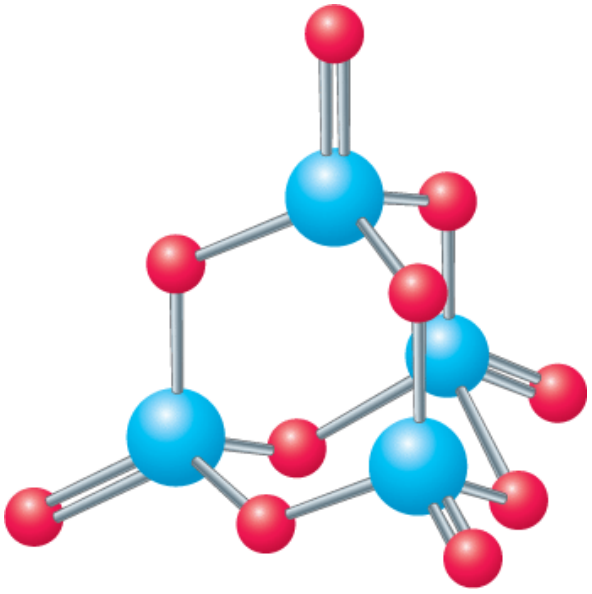


FIGURE 14.21 Phosphorus(V) oxide, P_4O_{10}, contains the same tetrahedral arrangement of phosphorus atoms as in P_4 (see figure 14.11), but an oxygen atom is inserted into each P—P bond. An additional terminal O atom is double-bonded to each P atom.

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

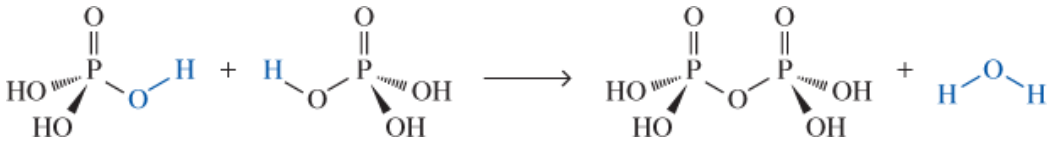
This highly pure product, which constitutes about 10% of the total industrial output of phosphoric acid, is the starting material for making food additives, pharmaceuticals and detergents.

Plants typically contain about 0.2% phosphorus by weight, but the element is easily depleted from soils. For this reason, the major commercial application of phosphorus is in fertilisers. There are several common phosphorus fertilisers, but the most important one is ammonium hydrogen phosphate, $(NH_4)_2HPO_4$. This phosphate compound is particularly valuable because it is highly soluble and provides both phosphorus and nitrogen. The compound can be made by treating phosphoric acid with ammonia:

$$H_3PO_4 + 2NH_3 \rightarrow (NH_4)_2HPO_4$$

This is the predominant industrial route to $(NH_4)_2$ HPO_4, accounting for the single largest use of phosphoric acid.

An important reaction of phosphoric acid (and its derivatives) is phosphate condensation, a process that is similar to the condensation reactions of other species that contain O—H bonds.



The product, $H_4P_2O_7$, is pyrophosphoric acid, a tetraprotic acid. A second condensation leads to triphosphoric acid, which can lose five protons.

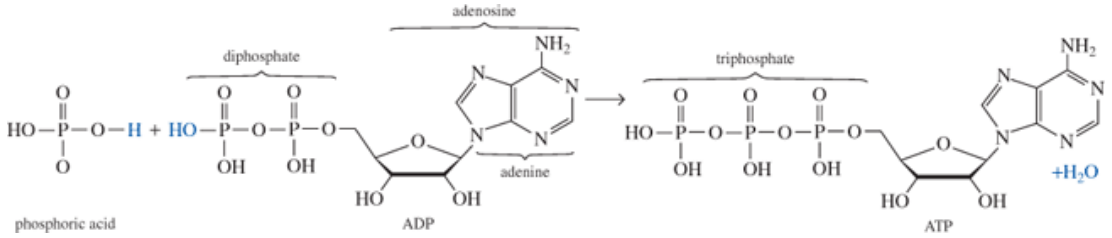
$$H_4P_2O_7 + H_3PO_4 \rightarrow H_5P_3O_{10} + H_2O$$

The sodium salts of these acids, sodium pyrophosphate, $Na_4P_2O_7$, and sodium triphosphate, $Na_5P_3O_{10}$, have been used widely in detergents. The polyphosphate anions are good additives for cleaning agents because they form complexes with metal ions, including those that make water 'hard' (Ca^{2+}, Mg^{2+}) and those that can cause colour stains (Fe^{3+}, Mn^{2+}). Moreover, polyphosphates are nontoxic, nonflammable and noncorrosive; they do not attack dyes or fabrics, and they are readily decomposed during wastewater treatment. These advantages appear to make polyphosphates ideal for use in cleaning agents. Unfortunately, adding phosphates to water leads to an imbalance in aquatic biosystems, particularly in lakes. Inorganic phosphate is rapidly incorporated as a nutrient by algae, leading to excess algal growth, which can overwhelm a lake with decaying organic matter. Organic decay consumes oxygen, depleting the lake of this life-sustaining substance and leading to the death of fish and other aquatic life forms. This contributes more organic decay with a corresponding increase in oxygen depletion, until eventually the lake supports no animal life.

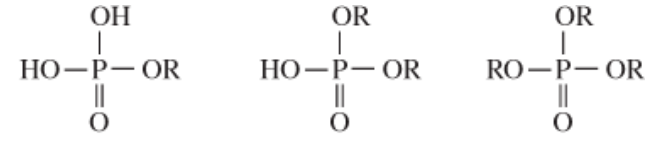
Phosphate condensation reactions play an essential role in metabolism. The conversion of adenosine diphosphate (ADP) to adenosine triphosphate (ATP) requires an input of Gibbs energy.

$$ADP + H_3PO_4 \rightarrow ATP + H_2O \quad \Delta G^{\ominus} = +30.6\,kJ$$

ATP serves as a major biochemical energy source, releasing energy in the reverse, hydrolysis, reaction. The ease of interchanging O—H and O—P bonds probably accounts for the fact that nature chose a phosphate condensation–hydrolysis reaction for energy storage and transport.



In ADP and ATP, one end of the polyphosphate chain links to adenosine through an O—C bond. These bonds form in condensation reactions between hydrogen phosphate and alcohols. Other biochemical substances contain P—O—C linkages, and these are generally referred to as phosphate esters, by analogy with 'organic' esters (chapter 23). However, while it is possible to replace only a single proton in a carboxylic acid with an alkyl group, replacement of one, two or three protons in phosphoric acid by an alkyl group gives phosphate mono-, di- and triesters, respectively.



Both ADP and ATP are phosphate monoesters, while the most important biological phosphate diesters are DNA and RNA (see figure 25.5, p. 1090).

The major repository for phosphorus on Earth is in phosphate minerals, the most important of which are apatites. These have the general formula $Ca_5(PO_4)_3X$, where X = F (fluoroapatite), Cl (chloroapatite) and OH (hydroxyapatite), all of which are sparingly soluble under neutral conditions. Tooth enamel is essentially pure hydroxyapatite, and this is also an important component of bones. Use of fluoridated toothpaste is thought to result in conversion of hydroxyapatite to the less soluble fluoroapatite, thereby slowing the rate of tooth decay. Important phosphate deposits are found across the world, perhaps most interestingly on the tiny (21 km^2) Pacific island of Nauru. At one time in the twentieth century, Nauru had one of the highest per capita incomes in the world solely because of its phosphate exports. Today, however, extensive strip mining has exhausted the phosphate deposits and, with these providing the only source of foreign income, the island's future is uncertain.

The phosphorus cycle (figure 14.22) essentially involves the interconversion between inorganic and organic phosphate (here, organic phosphate refers to biological molecules such as DNA, RNA, ADP and ATP). Inorganic phosphate, from the weathering of rocks, is assimilated by plants and converted to organic phosphate. The plants are consumed by animals and, when both die, bacterial action converts the organic phosphate back to inorganic phosphate.

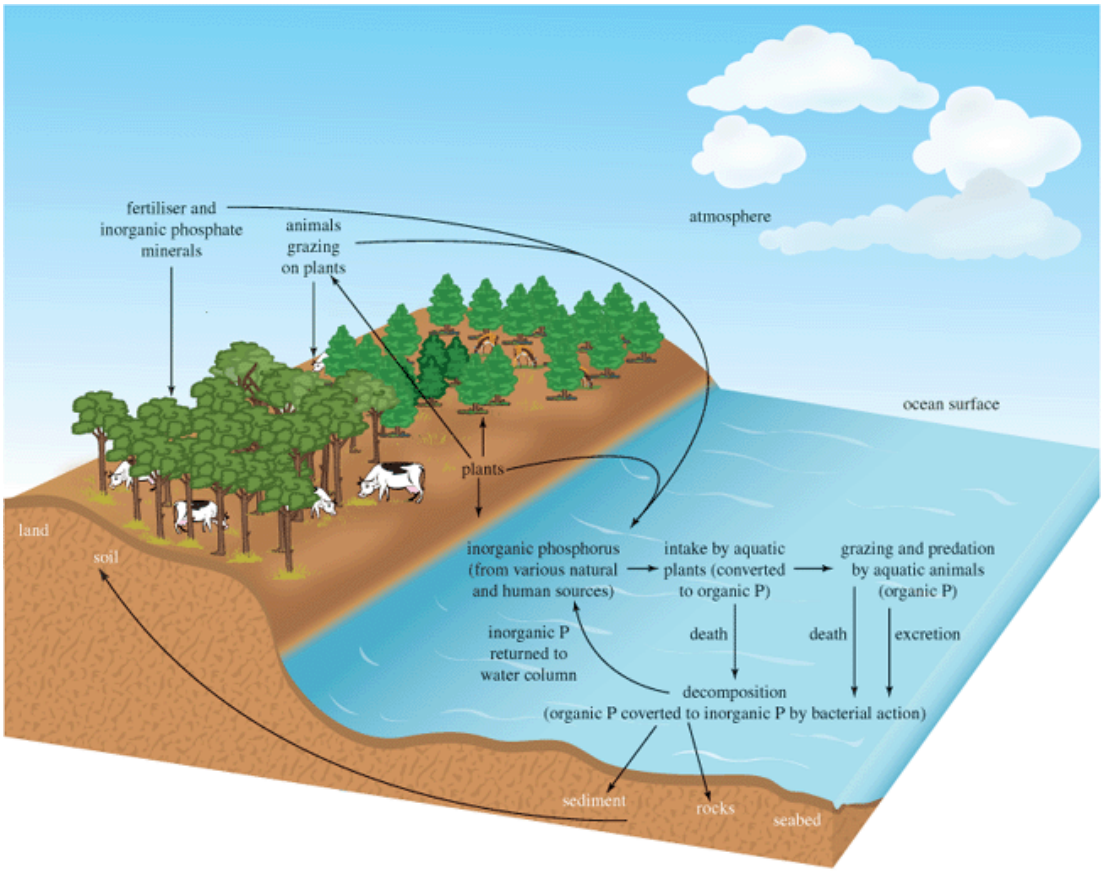


FIGURE 14.22 The phosphorus cycle.

The Carbon Cycle

Carbon accounts for only 0.08% of the mass of Earth; yet all life on this planet is based on carbon. While we will discuss the organic chemistry of carbon in detail over the second half of this book, we have as yet only touched upon the inorganic chemistry of carbon in detailing how CO_2 can act as a greenhouse gas. Carbon appears in nature in oxidation states ranging from -4 to +4, and its cycling between compounds exhibiting these oxidation states is extremely complex. We will therefore restrict ourselves to the way in which CO_2 travels between the atmosphere, aquatic systems and the Earth's crust. This simplified cycle (figure 14.23) does not therefore involve any redox chemistry.

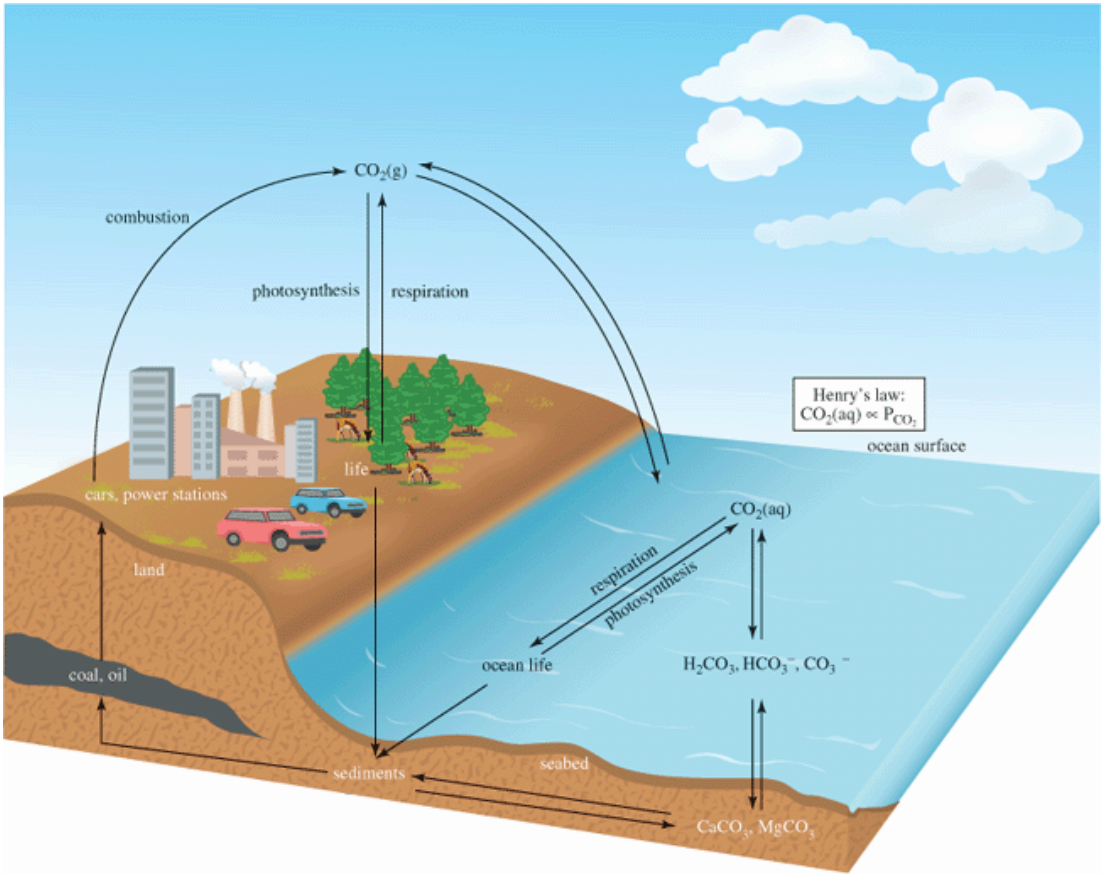


FIGURE 14.23 The simplified carbon cycle.

Carbon dioxide is the ultimate product of the combustion of any carbon-containing compound. It is a linear molecule, with formal double bonds between the C and O atoms.

$$\ddot{O}=C=\ddot{O}$$

CO_2 currently comprises over 380 parts per million of the Earth's atmosphere and this amount is steadily increasing owing to burning of fossil fuels. It is slightly soluble in water, with a solubility of 0.145 g L^{-1} at 25 °C. The resulting solution is measurably acidic and this is ascribed to the formation of carbonic acid, H_2CO_3.

$$H_2O(l) + CO_2(g) \rightarrow H_2CO_3(aq)$$

Given the importance of this molecule, it is surprising that conclusive evidence for its existence was obtained only in 1987, on the basis of mass spectrometric measurements.

H_2CO_3 is a diprotic acid which can undergo two dissociations:

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \quad pK_a = 6.35$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \quad pK_a = 10.33$$

However, the first of these equilibria is complicated by the fact that only a small fraction of dissolved CO_2 actually exists as H_2CO_3; the majority is present simply as hydrated carbon dioxide, $CO_2(aq)$. When this is taken into account, the first pK_a drops to around 3.7. It is the presence of dissolved CO_2, which makes natural fresh water slightly acidic, and this can easily be shown (on a small scale) by measuring the pH of tap water, bottled water or water in the laboratory — provided it is not freshly distilled, it will have a pH close to 5.

Inspection of the two equilibria above shows that they provide a mechanism for the formation of both hydrogen carbonate (HCO_3^-, also called bicarbonate) and carbonate (CO_3^{2-}) ions which can then be incorporated into minerals in the Earth's crust by precipitation as metal salts. The two most important carbonate salts in this respect are $MgCO_3$ and $CaCO_3$, both of which are only slightly soluble (K_{sp} values of 2×10^{-5} and 3.3×10^{-9}, respectively) and precipitate readily.

Nature has provided a method by which carbon dioxide can be used as a chemical feedstock by plants. The process of photosynthesis takes carbon dioxide and water as reactants and turns them into carbohydrates and oxygen, as we outlined in the oxygen cycle earlier. Therefore, carbon in the atmosphere is found primarily as CO_2; in the biosphere it is found mainly as carbohydrates, and in the lithosphere it is found as carbonate minerals and sediments. Until recently, the distribution of carbon

between these terrestrial spheres was stable. However, with the advent of the industrial revolution and burning of fossil fuels, the atmospheric concentration of CO_2 has steadily increased over the last century. Increasing CO_2 in the atmosphere may contribute to global warming that could have catastrophic consequences. In a warmer climate, for example, much of the polar ice caps would melt, and the oceans would expand as their temperatures increased. Sea levels could rise by several metres and inundate many of the world's most populous regions, such as Bangladesh, the Netherlands, and the East and Gulf Coasts of the United States. In addition, even small temperature fluctuations may alter global weather patterns and perhaps lead to serious droughts.

Our planet is such a complicated, dynamic set of interconnected systems that scientists do not know with certainty the result of increasing the concentration of atmospheric CO_2. They are studying the carbon cycle in hopes of learning what lies ahead for the planet. There is some urgency to such studies because recent global weather patterns show some of the characteristics predicted from computer models of global warming: average temperatures higher than those in previous years and an increased incidence of extreme weather such as cyclones and heavy rainfall.

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SUMMARY

The P-block Elements

Groups 13 to 18 of the periodic table contain elements which are predominantly nonmetals or metalloids. The elements of groups 13 to 18 are collectively called *p*-block elements and are characterised by the gradual filling of the *p* orbitals across each period. The valence-shell electron configuration of these elements ranges from ns^2np^1 (group 13) to ns^2np^6 (group 18).

Chemistry of the *P*-block Elements

Group 13: boron (B), aluminium (Al), gallium (Ga), indium (In), thallium (Tl)

Group 14: carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb)

Group 15: nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), bismuth (Bi)

Group 16: oxygen (O), sulfur (S), selenium (Se), tellurium (Te), polonium (Po)

Group 17: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At)

Group 18: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), radon (Rn)

The Biogeochemical Cycles of Nature

The oxygen cycle involves O_2, O_3, O_2^-, O_2^{2-} and H_2O, which interconvert through redox processes. Photosynthesis involves the formation of O_2 from H_2O, while respiration is essentially the reverse reaction, the formation of H_2O from O_2 via reaction with glucose. Ozone is formed in the upper atmosphere through the action of ultraviolet light on oxygen, while in the lower atmosphere it is produced from photochemical smog.

The sulfur cycle involves S^{2-}, Me_2S, SO_2, SO_3, H_2SO_4, SO_4^{2-}, SO_3^{2-} and sulfur-containing amino acids and M-S centres. Formation of compounds containing sulfur in a high oxidation state (+4 or +6) is thermodynamically favourable. To be useful to living organisms, these are reduced by micro-organisms under anaerobic conditions. Acid rain results from the burning of fossil fuels containing sulfur impurities.

The nitrogen cycle involves N_2, NH_3, NO_3^-, NO_2^-, NO, N_2O and amino and nucleic acids. The N_2 molecule, while usually chemically nonreactive, is converted to ammonia by the nitrogenase enzyme, and this then acts as the source of nitrogen in amino acids and nucleic acids. NO_3^- is formed as the end result of decomposition of living matter, and this is reduced to the other nitrogen oxides by anaerobic bacteria. Various nitrogen oxides are involved in atmospheric pollution.

The phosphorus cycle involves the interconversion of organic and inorganic phosphate, and differs from the other cycles of importance in that no redox chemistry is involved. Inorganic phosphate includes various metal salts of phosphate in varying states of protonation, along with phosphate minerals such as apatites. Molecules such as ATP, ADP, DNA and RNA constitute organic phosphate; these molecules are important in energy storage and the transfer of genetic information.

CO_2 travels between the Earth's atmosphere, oceans and crust. Dissolution of CO_2 in water gives small amounts of carbonic acid, H_2CO_3, with the majority of CO_2 existing simply as hydrated CO_2.

Deprotonation reactions give both HCO_3^- (hydrogen carbonate) and CO_3^{2-} (carbonate) which are incorporated into the Earth's crust by precipitation as slightly soluble metal salts such as $MgCO_3$ and $CaCO_3$.

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KEY CONCEPTS AND EQUATIONS

The Biogeochemical Cycles of Nature *(section 14.3)*

The *p*-block elements oxygen, sulfur, nitrogen, phosphorus and carbon are important in nature and, with the exception of phosphorus, form compounds containing the elements in a variety of oxidation states. These compounds are involved in chemical cycles in nature.

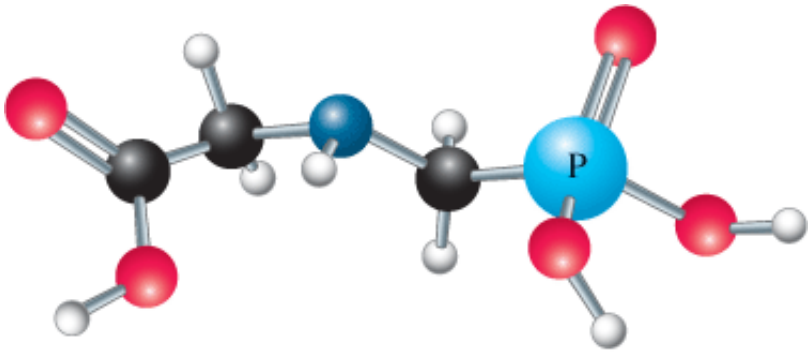
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REVIEW QUESTIONS

The biogeochemical cycles of nature

14.1 Figure 14.21 highlights the triangular arrangement of phosphorus atoms in P_4O_{10}. As every phosphorus atom bonds to four oxygen atoms, however, the geometry around each phosphorus atom is tetrahedral, just as in the phosphate anion. Redraw figure 14.21 in a way that highlights one of the tetrahedral PO_4 units.

14.2 Shown below is a ball-and-stick model of the active ingredient (glyphosate) in Roundup®, a commercial herbicide. Draw the Lewis structure of Roundup and describe its functional groups.



glyphosate, the active ingredient in Roundup

14.3 Determine the changes in oxidation states for the sulfur atoms in the following reactions that convert H_2S into S_8.

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$16H_2S + 8SO_2 \xrightarrow{Fe_2O_3} 3S_8 + 16H_2O$$

14.4 Determine the Lewis structures and describe the bonding and geometry of the following compounds:

(a) SF_4,

(b) BrF_5 and

(c) $F_2C{=}CF_2$.

14.5 Which of the following statements about species involved in the biogeochemical sulfur cycle and the chemical transformations in this cycle is *incorrect?*

A. The transformation of $(CH_3)_2S$ to SO_2 is an oxidation reaction.

B. SO_2 is best described as being V-shaped.

C. H_2SO_4 is a stronger acid than H_2SO_3.

D. The sulfite ion is trigonal planar in shape.

E. The reaction of SO_3 with water to form H_2SO_4 is a non-redox process.

14.6 Which one of the following statements about species present in the biogeochemical carbon cycle and the chemical transformations in this cycle is *incorrect?*

A. The transformation of coal into CO_2 is an oxidation reaction.

B. The shape of the CO_3^{2-} ion is best described as trigonal planar.

C. HCO_3^- is a weaker acid than H_2CO_3.

D. CO_2 reacts completely with water to form H_2CO_3.

E. The reaction of CO_2 with water is a non-redox process.

14.7 Which one of the following statements about species involved in the biogeochemical oxygen cycle is *correct?*

A. Photosynthesis leads to production of carbon dioxide.

B. Anaerobic organisms use dioxygen to eliminate electrons produced by oxidation of food molecules.

C. O_2 is evolved as a by-product of respiration.

D. H_2O_2 is the neutral form of the peroxide anion.

E. Two electrons are required to reduce dioxygen to the superoxide anion.

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REVIEW PROBLEMS

14.8 Write Lewis structures for the following three species found in the solution that is electrolysed to form aluminium metal: $[AlF_4]^-$, $[AlF_6]^{3-}$ and $[AlOF_3]^{2-}$.

14.9 Although Cl_2 can be manufactured by electrolysis of aqueous brine, the analogous reaction cannot be used to make F_2. Explain why anhydrous HF must be used for production of F_2.

14.10 Pyrophosphate, $P_2O_7^{4-}$, and triphosphate, $P_3O_{10}^{5-}$, are the two smallest polyphosphate anions. What is the chemical formula of the next largest polyphosphate anion? Draw a ball-and-stick model of this anion.

14.11 Three phosphate anions can condense to form a ring with the chemical formula $P_3O_9^{3-}$. Determine the Lewis structure and draw a ball-and-stick model of this anion.

14.12 Describe the reactions that convert fluoroapatite to phosphoric acid. Identify Brønsted-Lowry acid-base reactions and redox reactions, if any.

14.13 Describe the reactions that convert calcium phosphate to phosphoric acid. Identify Brønsted-Lowry acid-base reactions and redox reactions, if any.

14.14 Write structural formulae showing the conversion of white phosphorus into red phosphorus. Use curved arrows to show how electrons move during this conversion.

14.15 Write structural formulae showing the reaction of ATP with water to form ADP. What is the other product?

14.16 Identify the oxidising agent, reducing agent and changes of oxidation state that occur in the reaction forming $SiCl_4$ from SiO_2.

14.17 Each of the following molecules or ions plays a crucial role in the biogeochemical cycle for sulfur. For each of these species draw a Lewis structure, and predict the electron pair geometry, molecular shape and bond angles. Show formal charges where required.

(a) S_8

(b) SO_3^{2-}

(c) SO_4^{2-}

(d) Me_2S

Which of these species has a non-zero dipole moment?

14.18 Denitrifying bacteria respire on the different oxides of nitrogen and carry out (reductive) chemical changes such as:

$$NO_3^- \rightarrow NO_2^- \quad NO_2^- \rightarrow NO \quad NO \rightarrow N_2O \quad N_2O \rightarrow N_2$$

Write balanced half-equations for each of these steps in acidic solution.

On the other hand, nitrogen-fixing bacteria carry out (oxidative) changes such as:

$$N_2 \rightarrow NH_4^+ \quad NH_4^+ \rightarrow NO_3^-$$

Write balanced half-equations for each of these steps in acidic solution.

14.19 (a) Carbonate buffers are important in regulating the pH of blood at 7.40. What is the concentration ratio of $CO_2(aq)$ (usually written H_2CO_3) to $HCO_3^-(aq)$ in blood at pH = 7.40?

$$CO_2(aq) + 2H_2O(l) \rightleftharpoons H_2CO_3(aq) + H_2O(l)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \quad pK_a = 6.35$$

(b) Phosphate buffers are important in regulating the pH of intracellular fluids at pH values generally between 7.1 and 7.2. What is the concentration ratio of $H_2PO_4^-$ to HPO_4^{2-} in intracellular fluid at pH = 7.15?

$$H_2OPO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq) \quad pK_a = 7.20$$

(c) Why is a buffer composed of H_3PO_4 and $H_2PO_4^-$ ineffective in buffering the pH of intracellular fluid?

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq) \quad pK_a = 2.15$$

14.20

(a) Draw the biological nitrogen cycle, giving the formula of each of the molecules and ions present in the cycle.

(b) Write equations to demonstrate that the presence of nitrogen dioxide in the lower atmosphere leads to the production of ozone in the lower atmosphere.

(c) Write equations to demonstrate that diffusion of nitrogen dioxide to the upper atmosphere leads to the loss of ozone in the upper atmosphere.

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ADDITIONAL EXERCISES

14.21 Water in thermal hot springs is often unpalatable due to dissolved H_2S. Treatment with Cl_2 oxidises the sulfur to S_8, which precipitates (the other product is HCl). Balance this reaction and calculate the mass of Cl_2 required to purify 6.0×10^3 L of water containing 25 parts per million (by mass) of dissolved H_2S.

14.22 Calcium dihydrogen phosphate is a common phosphorus fertiliser that is made by treating fluoroapatite with phosphoric acid. Hydrogen fluoride is a by-product of the synthesis. Write a balanced equation for the production of this fertiliser and calculate the mass percentage of phosphorus in the fertiliser.

14.23 The black tarnish that forms on pure silver metal is the sulfide Ag_2S, which is formed by reaction with H_2S in the atmosphere.

$$4Ag + 2H_2S + O_2 \rightarrow 2Ag_2S + 2H_2O$$

The sulfide forms in preference to Ag_2O, even though the atmosphere is 20% O_2 with just a trace of H_2S. Use Lewis acid-base arguments to explain this behaviour.

14.24 Thionyl chloride, $SOCl_2$, is used to remove water of hydration from metal halide hydrates. Besides the anhydrous metal halide, the products are SO_2 and HCl.

(a) Draw the Lewis structure of $SOCl_2$.

(b) Write the balanced equation for the reaction of iron(III) chloride hexahydrate with $SOCl_2$.

14.25 Ammonium dihydrogen phosphate and ammonium hydrogen phosphate are common fertilisers that provide both nitrogen and phosphorus to growing plants. In contrast, ammonium phosphate is rarely used as a fertiliser because this compound has a high vapour pressure of toxic ammonia gas. Write balanced equations showing how each of these solid phosphates could generate ammonia gas. Why does ammonium phosphate have the highest vapour pressure of NH_3 of these three compounds?

14.26 Boron trichloride is a gas, boron tribromide is a liquid, and boron triiodide is a solid. Explain this trend in terms of intermolecular forces and polarisability.

14.27 Aluminium refining requires large amounts of electricity. Calculate the masses of Al and Na that are produced per mole of charge by electrolytic refining of Al_2O_3 and NaCl.

14.28 Trisodium phosphate forms strongly basic solutions that are used as cleaning agents. Write balanced equations that show why Na_3PO_4 solutions are strongly basic. Include pK_a values to support your equations.

14.29 The first commercially successful method for the production of aluminium metal was developed in 1854 by Henri Deville. The process relied on earlier work by the Danish scientist Hans Oersted, who discovered that aluminium chloride is produced when chlorine gas is passed over hot aluminium oxide. Deville found that aluminium chloride reacts with sodium metal to give aluminium metal. Write balanced equations for these two reactions.

14.30 Metal oxides and sulfide ores are usually contaminated with silica, SiO_2. This impurity must be removed when the ore is reduced to the pure element. Silica can be removed by adding calcium oxide to the reactor. Silica reacts with CaO to give $CaSiO_3$. Write a balanced equation for this reaction, and describe the reaction in terms of Lewis acids and bases.

14.31 Phosphorus(V) oxide has a very strong affinity for water; hence, it is often used as a drying agent in laboratory desiccators. One mole of P_4O_{10} reacts with 6 moles of water. Based on this stoichiometry, identify the product of the reaction and balance the equation.

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KEY TERM

p-block elements

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CHAPTER

15 Reaction Kinetics

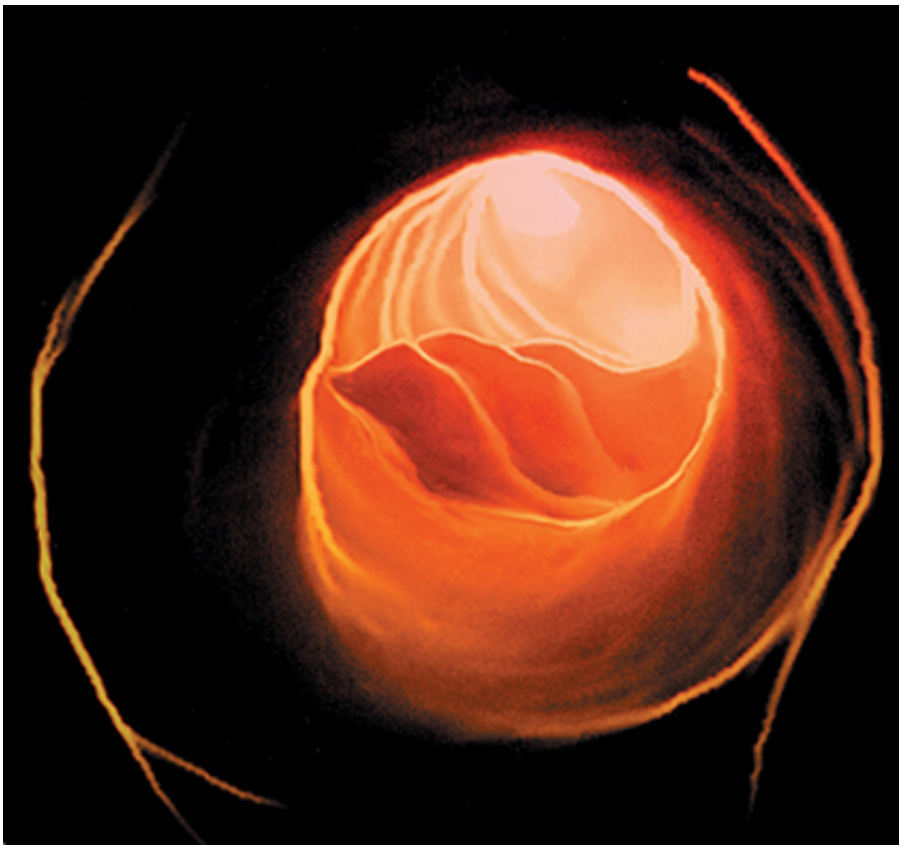
Chemical reactions occur at many different speeds. Reactions like the rusting of iron, ripening of fruit, weathering of stone, spoiling of milk and breakdown of plastics take place very slowly. Other reactions, like the combustion of petrol and explosion of gunpowder, occur very quickly. Understanding the mechanism of chemical reactions and why some reactions are fast and others are not is an important field in chemical research. Indeed, the 1999 Nobel Prize in chemistry was awarded to Ahmed H Zewail for developing ultrafast laser techniques that can record the motion of atoms in a molecule during a chemical reaction. This enables the study of reaction mechanisms, including the detailed steps involved in transforming reactants into products.



Marie Schmitt

The area of chemistry that deals with reaction rates and mechanisms is called chemical kinetics. Reaction speeds are influenced by many variables, such as tempera ture, pressure and concentration.

The images on this page show cross-sectional views of coronary arteries with atherosclerotic plaque. Arterosclerosis is a condition in which an artery wall thickens as the result of a build-up of fatty materials such as cholesterol. In recent years it has become clear that the strong oxidant hypochlorite (HOCl), which is made by white blood cells in our body in a reaction that involves the enzyme myeloperoxidase, can damage the body's own cells and structures. Myeloperoxidase is present and active within the artery wall and may contribute to the development of atherosclerotic lesions and heart disease plaques. Understanding the chemical mechanism by which this enzyme generates damage to the artery wall, and more importantly how this might be prevented, is of fundamental importance to human health.



SPL/Zephyr

KEY TOPICS

15.1 Reaction rates
15.2 Factors that affect reaction rates
15.3 Overview of rate laws
15.4 Types of rate laws: differential and integrated
15.5 Theory of chemical kinetics
15.6 Reaction mechanisms
15.7 Catalysts

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15.1 Reaction Rates

In chapter 8 we learned about the definition of a spontaneous reaction. While the value and sign of ΔG indicate the spontaneity of a chemical reaction, they do not tell us anything about how fast the reaction might be. For example, the thermodynamic data for the conversion of diamond to graphite (figure 15.1) tell us that this is a spontaneous process under standard conditions $\left(\Delta G^{\ominus} = -2.9\ \text{kJ mol}^{-1}\right)$, but everybody — not just those lucky enough to own precious diamond jewellery — knows that this reaction is very, very slow! The formation of ammonia from gaseous hydrogen and nitrogen through the process:

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$$

also has a thermodynamic tendency to occur, but no products are observed to form at room temperature and atmospheric pressure. There are many other examples of spontaneous reactions that occur so slowly that we cannot observe any change over long periods of time (in some cases, years).

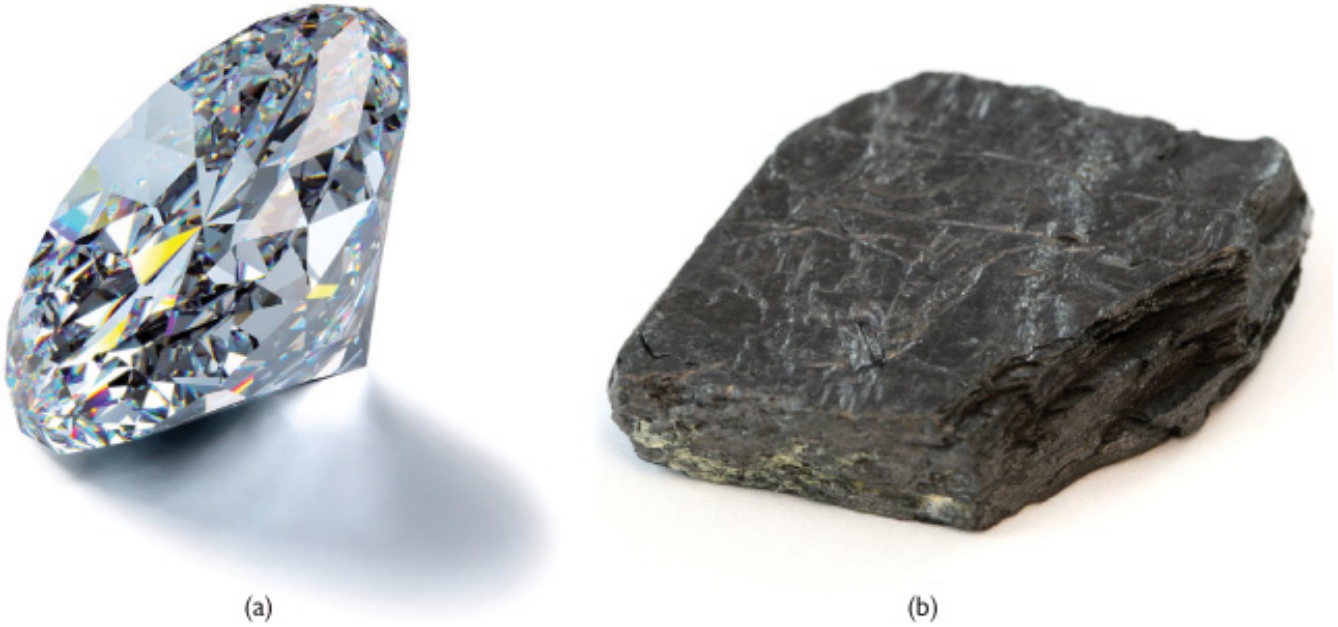


FIGURE 15.1 (a) Diamond and (b) graphite are two different allotropes of carbon. Although $\Delta G^{\ominus}$ for the conversion of diamond into carbon is negative, a diamond will not revert into graphite at a measurable rate under normal conditions.
Tyler Boyes

Chemical kinetics can help us understand why reactions proceed in a particular way. It is the study of the rates of change of the concentrations of reactants and products in a chemical reaction. Figure 12.9 on p. 501 shows a copper wire being dipped into a solution of silver nitrate. With increasing reaction time, the blue colour of the aqueous solution intensifies, indicating formation of Cu^{2+} ions, whereas elemental silver continuously deposits on the wire. The rates of chemical reactions are studied by monitoring the concentrations of reactants and/or products over time. There are many different ways to observe concentration changes as the reaction proceeds. Figure 15.2 shows a *concentration–time* profile for the hypothetical reaction $A \rightarrow 2B$.

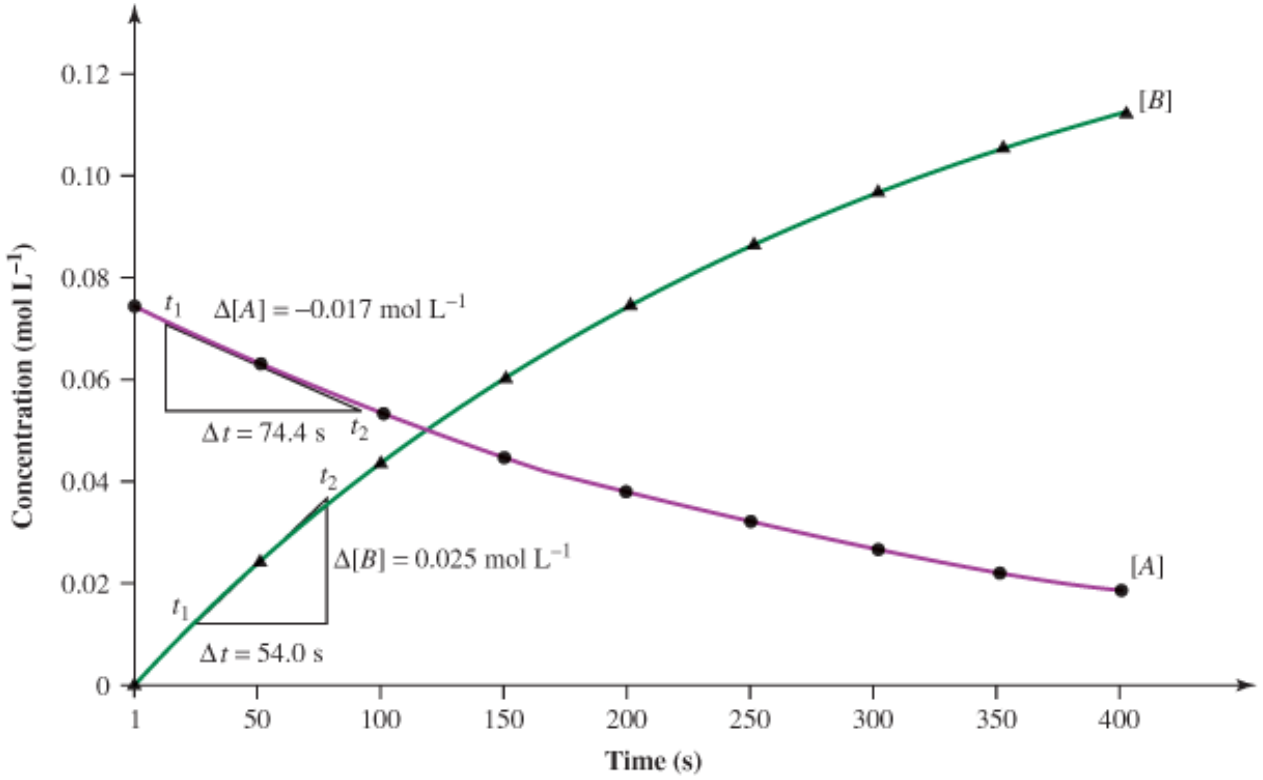


FIGURE 15.2 The progress (concentration–time profile) of the reaction $A \rightarrow 2B$, showing the concentrations of *A* and *B* over time.

Figure 15.2 shows that the concentration of the reactant, *A*, decreases with time, while the concentration of the product, *B*, increases with time, and we usually talk of the rate of consumption of a reactant and the rate of formation of a product. We can determine the rate of consumption of *A* and the rate of formation of *B* by measuring the concentrations of *A* and *B* at two different times, t_1 (early in the reaction) and t_2 (later in the reaction).

$$\text{rate of consumption of } A = \frac{\text{concentration of } A \text{ at time } t_2 - \text{concentration of } A \text{ at time } t_1}{t_2 - t_1} = \frac{\Delta[A]}{\Delta t}$$

The square brackets indicate concentration in mol L^{-1}, and the symbol Δ indicates a change in a given quantity (final volume–initial volume). Similarly, the rate of formation of *B* is:

$$\text{rate of formation of } B = \frac{\text{concentration of } B \text{ at time } t_2 - \text{concentration of } B \text{ at time } t_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}$$

By convention, rates of formation and consumption are always reported as a positive value, irrespective of whether something increases or decreases in concentration. (This can be compared with the speed of a car; it may drive to or away from a particular spot, but the speed is always a positive number.)

The second and third columns of table 15.1 show measurements of the concentrations of *A* and *B*, respectively, over time as our hypothetical reaction proceeds.

TABLE 15.1 Concentration of *A* and *B* and average rates as a function of time for the reaction $A \rightarrow 2B$, as shown in figure 15.1

Time (s)	[*A*] (mol L^{-1})	[*B*] (mol L^{-1})	Time period (s)	$-\frac{\Delta[A]}{\Delta t}$ (mol L^{-1} s^{-1})
0	0.0750	0.0		
50	0.0629	0.0242	0 → 50	2.4×10^{-4}
100	0.0529	0.0442	50 → 100	2.0×10^{-4}

150	0.0444	0.0612	100 → 150	1.8×10^{-4}
200	0.0372	0.0756	150 → 200	1.4×10^{-4}
250	0.0313	0.0874	200 → 250	1.2×10^{-4}
300	0.0262	0.0976	250 → 300	1.0×10^{-4}
350	0.0220	0.106	300 → 350	8.0×10^{-5}
400	0.0185	0.113	350 → 400	7.0×10^{-5}

We can use the data in table 15.1 to calculate the **average rate** of consumption of *A* in the first 50 seconds of the reaction.

$$\begin{aligned}\text{rate of consumption of } A &= \frac{\Delta[A]}{\Delta t} \\ &= \frac{[A]_{t=50} - [A]_{t=0}}{50\text{ s} - 0\text{ s}} \\ &= \frac{0.0629\text{ mol L}^{-1} - 0.0750\text{ mol L}^{-1}}{50\text{ s}} \\ &= -2.4 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}\end{aligned}$$

As you can see, $\Delta[A]$ is a negative quantity, because the concentration of *A* decreases with time. Since rates of change of concentration are always positive numbers, the rate of consumption of a reactant is defined as:

$$\text{rate of consumption} = -\frac{\Delta[\text{reactant}]}{\Delta t}$$

The average rate of consumption of *A* in the first 50 seconds of the reaction is therefore:

$$\begin{aligned}\text{rate of consumption of } A &= \frac{\Delta[A]}{\Delta t} \\ &= -\left(-2.4 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}\right) \\ &= 2.4 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}\end{aligned}$$

The last column of table 15.1 gives average rates of consumption of *A* for this reaction during some other 50-second time intervals. The data show that average rates of consumption of *A* decrease with time as *A* is used up. This is because these rates usually depend on the concentration of *A*, which changes as the reaction proceeds. Therefore, to minimise errors it is better to determine reaction rates over short periods of time.

The rate of change of concentration at a particular time is called the **instantaneous rate of change of concentration**. Looking back to figure 15.2, we see that the instantaneous rate of consumption of *A* or formation of *B* can be determined from the slope of the tangent to the curve. For example, in figure 15.2 a tangent is drawn at $t = 50$ seconds on the *A* curve. The slope of this line, as calculated from the values of $\Delta[A]$ and Δt given in figure 15.2, gives the instantaneous rate of consumption of *A* at $t = 50$ seconds (remember that we are looking at the consumption of a reaction and that the slope will, therefore, be negative).

$$\begin{aligned}\text{rate of consumption of } A &= -(\text{slope of tangent}) = -\frac{\mathrm{d}[A]}{\mathrm{d}t} \\ &= \frac{-0.017\text{ mol L}^{-1}}{74.4\text{ s}} \\ &= 2.3 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}\end{aligned}$$

In this equation, 'd' indicates an infinitesimally small change. Remember that the rate of a reaction has the unit *concentration per unit time* or (concentration) $(\text{time})^{-1}$ and this is usually mol L^{-1} s^{-1}.

Now, look at the rate of formation of the product, *B*. For this, the coefficients in the balanced equation for the reaction have to be taken into account, because the stoichiometry determines the relative rates at which reactants are consumed and products formed. In the case of our hypothetical reaction, $A \rightarrow 2B$, *B* is produced twice as fast as *A* is consumed, which can be verified from figure 15.2. The slope of the tangent to the *B* curve at $t = 50$ seconds gives the instantaneous rate of formation of *B* at 50 seconds, which is:

$$\begin{aligned} \text{rate of formation of } B &= (\text{slope of tangent}) = \frac{\mathrm{d}[B]}{\mathrm{d}t} \\ &= \frac{0.025\ \text{mol}\,\text{L}^{-1}}{54.0\ \text{s}} \\ &= 4.6 \times 10^{-4}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1} \end{aligned}$$

This shows that the rate of formation of *B* is indeed twice that of consumption of *A*. Note that the slope of the tangent is positive.

As you can see, the rates of consumption of reactants and rates of formation of products in a particular reaction are not necessarily the same. It is much more meaningful for us to define the **rate of reaction** whose value is the same regardless of whether we are monitoring rates of consumption of reactants or rates of formation of products. For the general reaction:

$$aA + bB \rightarrow cC + dD$$

where *a* to *d* are the stoichiometric coefficients of the reactants *A* and *B* and the products *C* and *D* respectively, we define the rate of reaction as:

$$\text{rate of reaction} = -\frac{1}{a}\frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{1}{c}\frac{\mathrm{d}[C]}{\mathrm{d}t} = \frac{1}{d}\frac{\mathrm{d}[D]}{\mathrm{d}t}$$

Therefore, for our reaction $A \rightarrow 2B$, we would write:

$$\begin{aligned} \text{rate of reation} &= -\frac{\mathrm{d}[A]}{\mathrm{d}t} = \frac{1}{2}\frac{d[B]}{\mathrm{d}t} \\ &= 2.3 \times 10^{-4}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1} \end{aligned}$$

The rate of a reaction has units of (concentration) $(\text{time})^{-1}$. It is important that you appreciate the difference between the rate of reaction and the rates of consumption of reactants and rates of formation of products. The rate of reaction has only one value for any particular reaction and is independent of the reaction stoichiometry, whereas the rates of reactant consumption and product formation are different if the stoichiometric coefficients differ.

WORKED EXAMPLE 15.1

Estimating the Initial Rate of a Reaction

The following data have been measured at 508 °C for the reaction $2HI(g) \rightarrow H_2(g) + I_2(g)$.

Time (s)	[HI] (mol L^{-1})
0	0.100
50	0.0716
100	0.0558
150	0.0457

200	0.0387
250	0.0336
300	0.0296
350	0.0265

What is the initial rate of consumption of HI, and what is the initial rate of reaction at this temperature?

Analysis

The initial rate of consumption of HI is the instantaneous rate of consumption of HI at time zero. Once we plot the data, we can draw a tangent to the curve showing [HI] as a function of time at time zero. The instantaneous rate of consumption of HI is the slope of the tangent. The slope of the line can be calculated from the coordinates of any two points (x_1, y_1) and (x_2, y_2) using the equation:

$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\text{d[HI]}}{\text{d}t}$$

The initial rate of reaction can be calculated using the stoichiometry of the reaction.

$$\text{rate of reaction} = -\frac{1}{2}\frac{\text{d[HI]}}{\text{d}t}$$

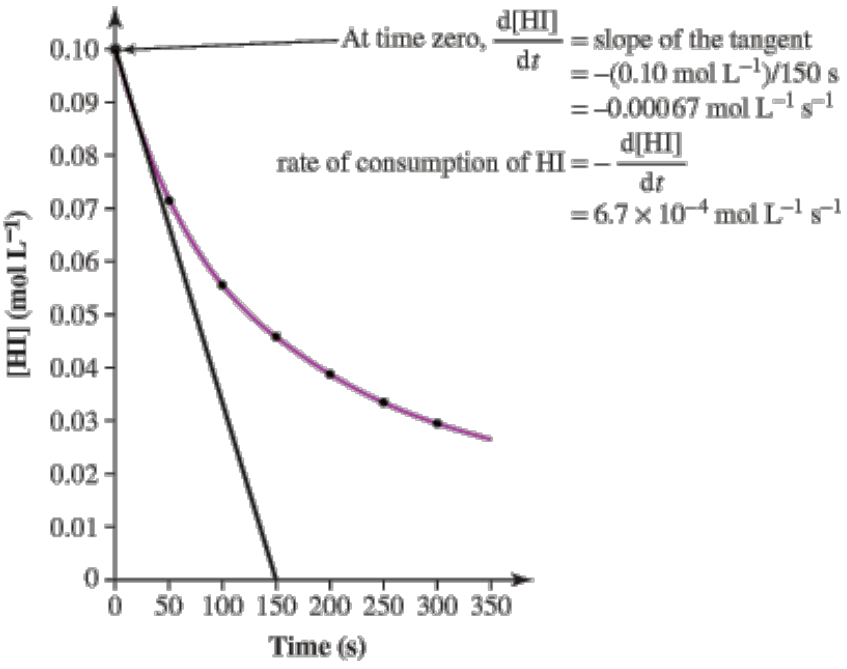
Solution

Because we want to study the rates at which concentrations change, we have to use differential calculus. Thus, since a tangent to a curve touches the curve at only one point, we can draw the line as shown in the diagram below.

To determine the slope of the tangent precisely, we should choose two points that are as far apart as possible. We could use, for example, the point on the curve (0 s, 0.10 mol L^{-1}) and the intersection of the tangent with the time axis (150 s, 0 mol L^{-1}), which are widely separated.

$$\text{slope} = \frac{\text{d[HI]}}{\text{d}t} = \frac{0.10\ \text{mol L}^{-1} - 0.00\ \text{mol L}^{-1}}{0\ \text{s} - 150\ \text{s}} = -6.7 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

(There is no requirement to restrict the extrapolation to concentration = 0 to find the slope.)



The slope is negative because the concentration of HI is decreasing as time increases. Reaction rates are positive quantities, so we report the initial rate of consumption of HI as 6.7×10^{-4} mol L^{-1} s^{-1}. To do this calculation, we rely on accurately drawing by hand a tangent to the curve at $t = 0$. Because of this, there is a degree of uncertainty in the accuracy of our answer. The initial rate of reaction is defined by the equation:

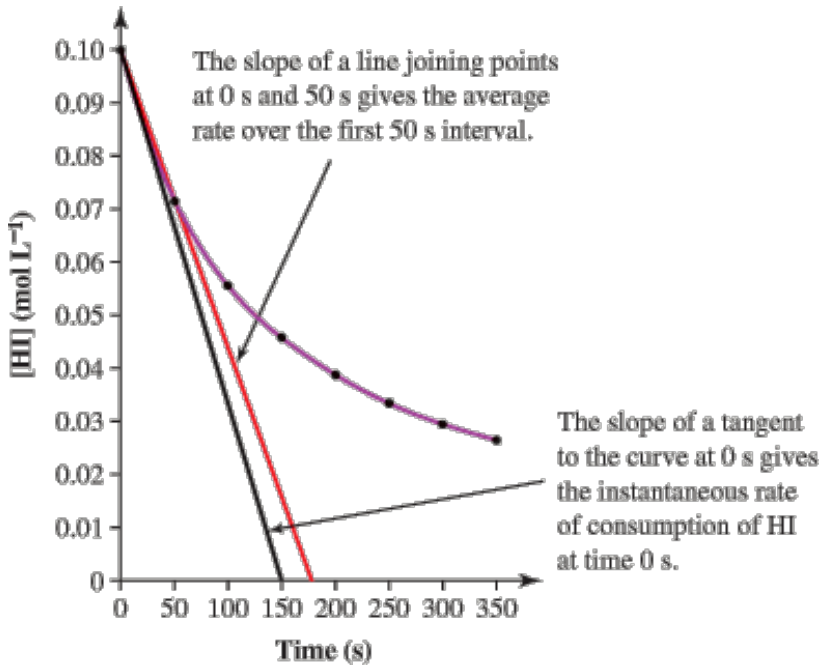
$$\text{rate of reaction} = -\frac{1}{2}\frac{d[HI]}{dt}$$

We have already calculated the initial $\frac{d[HI]}{dt}$ at time zero as being -6.7×10^{-4} mol L^{-1} s^{-1}, so the initial rate of reaction is:

$$-\frac{1}{2}\left(-6.7 \times 10^{-4}\right) = 3.4 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Is our answer reasonable?

As noted previously, drawing a tangent to a curve by eye is not precise. There may be considerable variation in the determined time difference, which affects the accuracy of our calculated rate. One way of checking our answer is to realise by inspection of the graph that the instantaneous rate of consumption of HI at time zero should be close to, but slightly greater than, the average rate of consumption of HI between 0 s and 50 s.



We can calculate the average rate of consumption of HI directly from the data in the table on p. 632, which have been accurately measured.

$$\text{slope} = \frac{0.0716\ \text{mol L}^{-1} - 0.100\ \text{mol L}^{-1}}{50\ \text{s} - 0\ \text{s}} = -5.7 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

So the average rate of consumption of HI from 0 s to 50 s is 5.7×10^{-4} mol L^{-1} s^{-1}. As expected, this is close to but slightly less than the instantaneous rate of consumption of HI at time zero, 6.7×10^{-4} mol L^{-1} s^{-1}.

A concept related to reaction rate is the **half-life** $\left(t_{\frac{1}{2}}\right)$ of a reaction. This is the time taken for the concentration of a specified reactant to fall to half of its initial concentration. We will learn more about half-lives later in this chapter.

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15.2 Factors that Affect Reaction Rates

Five principal factors influence reaction rates: the chemical nature of the reactants, the physical nature of the reactants, the concentrations of the reactants, the temperature, and the availability of rate-accelerating agents called catalysts.

Chemical Nature of the Reactants

During reactions, bonds break and new bonds form. The most fundamental differences between reaction rates, therefore, lie in the reactants themselves, in the inherent tendencies of their atoms, molecules or ions to undergo bond-breaking and/or bond-making processes. Some reactions are fast by nature and others are slow. As you have seen in chapter 4 (figure 4.50), alkali metals can be easily ionised, which leads to a high reactivity of these compounds towards oxidation. Thus, a freshly exposed surface of metallic sodium tarnishes almost instantly when exposed to air and moisture. Under identical conditions, potassium also reacts with air and moisture, but the reaction is much faster because the ionisation energy of potassium is even lower than that of sodium (figure 15.3). Compared with these fast reactions, the reaction of silver with water is very slow, which you can check by putting a silver ring into a glass of water and observing that nothing happens.

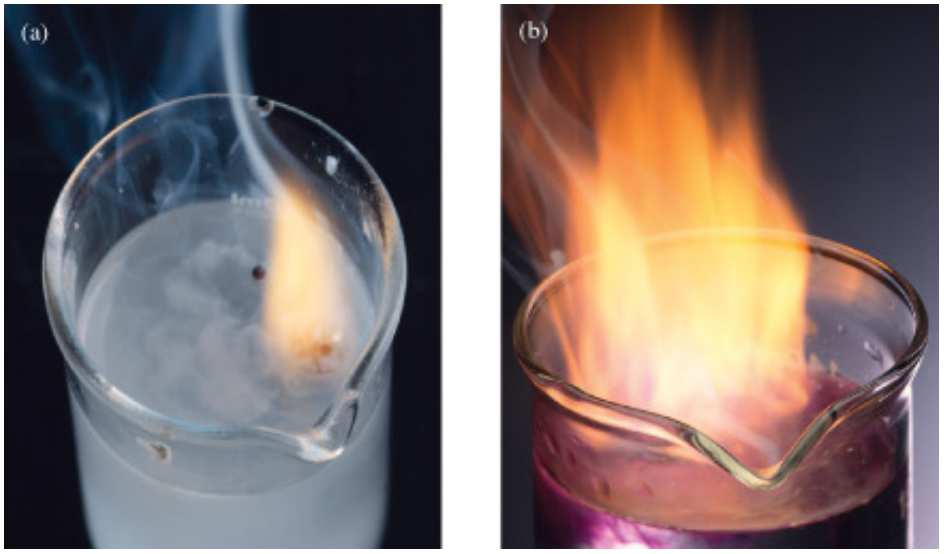


FIGURE 15.3 The chemical nature of the reactants affects reaction rates.
(a) Sodium is easily oxidised, so it reacts quickly with water.
(b) Potassium is even more easily oxidised than sodium, so its reaction with water is explosively fast.

Physical Nature of the Reactants

Most reactions involve two or more reactants whose constituent atoms, ions or molecules must collide for the reaction to occur. This is why reactions are rarely carried out in the solid state, but often occur in liquid solutions or in the gas phase where the reactants are able to intermingle and their constituent atoms, molecules or ions can collide with each other easily.

Consider, for example, that, although liquid petrol burns rapidly, petrol vapour explodes when mixed with air in the right proportions and ignited. (An explosion is an extremely rapid reaction that generates hot expanding gases.) The combustion of vaporised petrol illustrates a **homogeneous reaction**, because

all of the reactants are in the same phase.

When the reactants are present in different phases, for example, if one is a gas and the other is a liquid or a solid, the reaction is called a **heterogeneous reaction**. In a heterogeneous reaction, the reactants are able to meet only at the interface between the phases, *so the area of contact between the phases affects the reaction rate*. This area is controlled by the sizes of the particles of the reactant constituents. By pulverising a solid, the total surface area can be significantly increased (figure 15.4). This maximises contact between the atoms, ions or molecules in the solid state with those in a different phase.

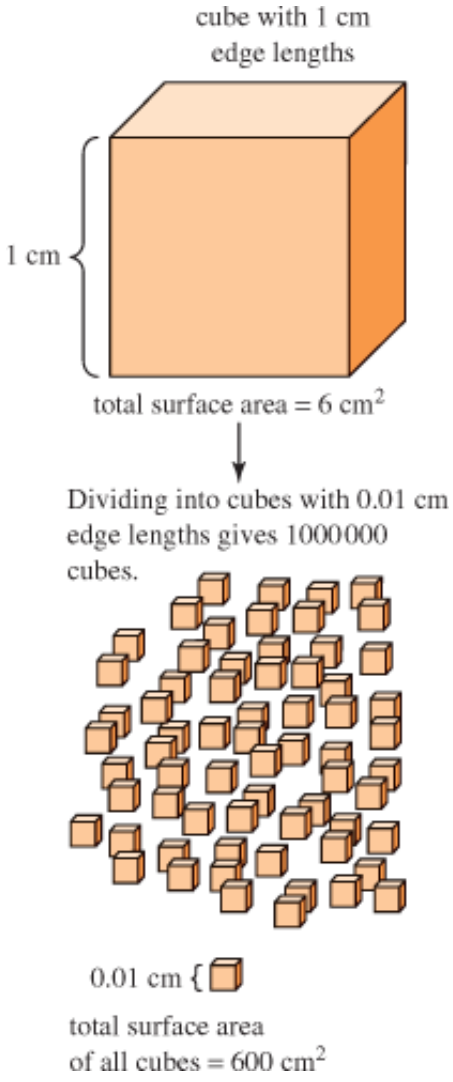


FIGURE 15.4 Effect of crushing a solid. When a single solid is subdivided into much smaller pieces, the total surface area of all of the pieces becomes very large.

Although heterogeneous reactions are obviously important, they are very complex and difficult to analyse. In this chapter, therefore, we will focus mostly on homogeneous systems.

Concentrations of the Reactants

The rates of both homogeneous and heterogeneous reactions are affected by the concentrations of the reactants. For example, wood burns relatively quickly in air but extremely rapidly in pure oxygen. Even red-hot steel wool, which only sputters and glows in air, bursts into flame when thrust into pure oxygen. Studies have shown that the Earth's atmosphere has had an oxygen content as high as 35% in the past (nowadays, it is only 21%). This higher oxygen concentration had some negative consequences, such as fires burning hotter and faster.

Temperature of the System

Almost all chemical reactions occur faster at higher temperatures. Milk doesn't spoil as quickly when it is cold. It takes longer to cook an egg at 80 °C than at 100 °C. You may also have noticed that insects move more slowly when the air is cool. Insects are cold-blooded creatures, which means that their body temperature is determined by the temperature of their surroundings. As the air cools, insects cool, and so the rates of their chemical metabolism slow down, making them sluggish.

Presence of Catalysts

Catalysts are substances that increase the rate of chemical reactions without being used up. Catalysts affect every moment of our lives because the enzymes that direct our body chemistry are all catalysts. Many of the substances used by the chemical industry to make petrol, plastics, fertilisers and other everyday products are also catalysts. We will discuss how catalysts affect reaction rates in section 15.7.

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15.3 Overview of Rate Laws

In worked example 15.1, we discussed the decomposition of hydrogen iodide.

$$2HI(g) \rightarrow H_2(g) + I_2(g) \quad \text{(forward reaction)}$$

We have seen in chapter 9 that chemical reactions are reversible. As the decomposition proceeds, H_2 and I_2 are formed and can themselves react to form HI (see figure 15.5).

$$H_2(g) + I_2(g) \rightarrow 2HI(g) \quad \text{(reverse reaction)}$$

When hydrogen iodide gas is first placed in an empty container, the forward reaction is dominant and the rate of change of concentration of HI depends only on the rate of the forward reaction. When sufficient products have formed, the rate of the reverse reaction becomes important too, and the rate of change of concentration of HI then depends on the difference in the rates of the forward and reverse reactions.

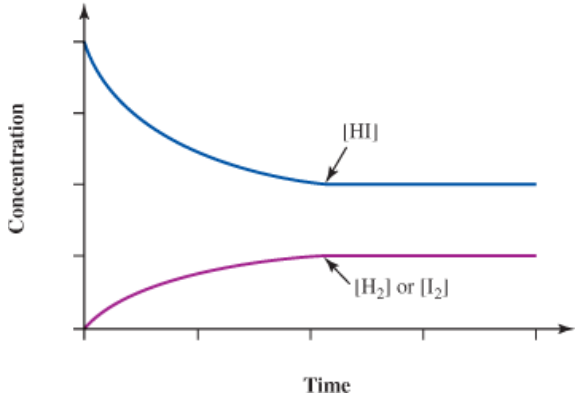


FIGURE 15.5 Concentration–time profile for the decomposition of hydrogen iodide.

Generally, we want to determine the rate of reaction under conditions in which the reverse reaction can be ignored, that is, when the rate of the reaction depends only on the concentration of the reactants.

$$\text{rate of reaction} = \underbrace{k}_{\text{rate constant/coefficient}}[HI]^{\overbrace{n}^{\text{order}}}$$

This can be done if we determine the rate of reaction immediately after placing the reactants into the reaction vessel, when the reaction time has been too short to build up significant amounts of products. This is called the **initial rate** of a reaction.

Such an equation in which the rate of reaction is given as a function of reactant concentrations (in this case [HI]) is called a **rate law**. Note that, because the reaction has been studied under conditions in which the reverse reaction does not contribute to the overall rate, the products do not appear in the rate law. The rate law contains a proportionality constant *k*, which is called the **rate constant** or **rate coefficient** for the reaction, and an exponent *n*, called the **order** with respect to the reactant. The terms 'rate constant' and 'rate coefficient' are often used interchangeably. In this book we will use the term 'rate constant'. The value of the rate constant depends on the particular reaction being studied, as well as on the conditions, such as temperature and pressure, under which the reaction occurs. It is not dependent on the concentrations of reactants. The order can be positive, negative or zero, an integer or a fraction, but *cannot* be deduced from the balanced equation except in very special circumstances. This is a very important point, which we will examine soon.

As we saw earlier, the rate of a reaction does not depend on whether we monitor the consumption of reactants or the formation of products. In fact, which reactant or product concentration we choose to monitor often depends on which data are the easiest to obtain. For example, to study the decomposition of hydrogen iodide into H_2 and I_2, it is easiest to monitor the I_2 concentration, because it is the only coloured substance in the reaction. As the reaction proceeds, purple iodine vapour forms, which can be measured with instruments that relate the intensity of the colour to the iodine concentration.

Thus, if we define the rate of reaction in terms of formation of I_2, we get:

$$\text{rate of reaction} = \frac{d[I_2]}{dt} = k[HI]^n$$

As we have discussed before, in this equation, 'd' stands for an extremely small change. We could also define the reaction rate in terms of consumption of HI:

$$\text{rate of reaction} = -\frac{1}{2}\frac{d[HI]}{dt} = k[HI]^n$$

The rate of consumption of HI is twice the rate of formation of I_2. Once we know the rate of formation of iodine, we also know the rate of formation of hydrogen, because the stoichiometric coefficients of I_2 and H_2 are the same.

WORKED EXAMPLE 15.2

Relationships of rates Within a Reaction

Butane, C_4H_{10}, burns in oxygen to give CO_2 and H_2O according to the equation:

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$$

If the butane concentration is decreasing at a rate of 0.20 mol L^{-1} s^{-1}, what is the rate at which the oxygen concentration is decreasing, and what are the rates at which the product concentrations are increasing?

Analysis

We need to relate the rate of consumption of oxygen and the rates of formation of the products to the given rate of consumption of butane. The chemical equation links amounts of these substances to the amount of butane. The magnitudes of the rates relative to each other are in the same relationship as the coefficients in the balanced equation.

Solution

From our definition of rate of reaction, we can write:

$$\text{rate of reaction} = -\frac{1}{2}\frac{d[C_4H_{10}]}{dt} = -\frac{1}{13}\frac{d[O_2]}{dt} = \frac{1}{8}\frac{d[CO_2]}{dt} = \frac{1}{10}\frac{d[H_2O]}{dt}$$

We are told that:

$$-\frac{d[C_4H_{10}]}{dt} = 0.20 \text{ mol L}^{-1} \text{ s}^{-1}$$

and we can therefore use this, together with our expression for the rate of reaction, to determine $-\frac{d[O_2]}{dt}$:

$$-\frac{1}{2}\frac{d[C_4H_{10}]}{dt} = -\frac{1}{13}\frac{d[O_2]}{dt}$$

Thus:

$$\begin{aligned}\frac{d[O_2]}{dt} &= \frac{13}{2}\frac{d[C_4H_{10}]}{dt} \\ &= \frac{13}{2} \times 0.20 \text{ mol L}^{-1} \text{ s}^{-1} \\ &= 1.30 \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$

We can carry out similar calculations for both H_2O and CO_2. For CO_2:

$$-\frac{1}{2}\frac{d[C_4H_{10}]}{dt} = \frac{1}{8}\frac{d[CO_2]}{dt}$$

Therefore:

$$\begin{aligned}\frac{d[CO_2]}{dt} &= -\frac{8}{2}\frac{d[C_4H_{10}]}{dt} = -4\frac{d[C_4H_{10}]}{dt} \\ &= 4 \times 0.20 \text{ mol L}^{-1} \text{ s}^{-1} \\ &\quad \text{(Note that the negative sign in the calculation disappears due to the way in which the rate is defined; rates are positive.)} \\ &= 0.80 \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$

For H_2O:

$$-\frac{1}{2}\frac{d[C_4H_{10}]}{dt} = \frac{1}{10}\frac{d[H_2O]}{dt}$$

Therefore:

$$\begin{aligned}\frac{d[H_2O]}{dt} &= -\frac{10}{2}\frac{d[C_4H_{10}]}{dt} = -5\frac{d[C_4H_{10}]}{dt} \\ &= 5 \times 0.20 \text{ mol L}^{-1} \text{ s}^{-1} \\ &\quad \text{(Again, we take the positive value as the rate of formation.)} \\ &= 1.00 \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$

Is our answer reasonable?

If what we have calculated is correct, then the ratio of the numerical values of the rates of formation of CO_2 and H_2O, namely 0.80 to 1.00, should be the same as the ratio of the corresponding coefficients in the chemical equation, namely 8 to 10 (the same as 0.80 to 1.00). The ratios match, so we can be confident in our answers.

PRACTICE EXERCISE 15.1

Hydrogen sulfide burns in oxygen to form sulfur dioxide and water:

$$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(g)$$

If sulfur dioxide is being formed at a rate of 0.30 mol L^{-1} s^{-1}, what are the rates of consumption of hydrogen sulfide and oxygen?

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15.4 Types of Rate Laws: Differential and Integrated

In our discussion, we defined the rate law for the decomposition of HI as:

$$\text{rate of reaction} = -\frac{1}{2}\frac{d[HI]}{dt} = k[HI]^n$$

This expresses the *rate of reaction as a function of concentration* and is known as a **differential rate law** (often abbreviated to rate law). Once the order, *n*, is known, we can determine exactly how the rate of reaction depends on the concentration of HI. A second important type of rate law expresses the *concentration as a function of time*. This is called an **integrated rate law**.

We can determine the differential rate law by measuring rate changes when the concentrations are changed. We can determine the integrated rate law by measuring changes in concentrations over time. The two types of rate law are related and, if we know one rate law for a reaction, we can, in most cases, determine the other.

Rate laws help us to identify the steps by which a chemical reaction occurs and thus understand the reaction. Most reactions involve a series of sequential steps. The sum of the individual reaction steps is called the **reaction mechanism**. The formation of ammonia from nitrogen and hydrogen, which we encountered at the beginning of the chapter, is extremely slow at room temperature under atmospheric pressure. This is because the strong H—H single bond and the N≡N triple bond must be broken. To speed this reaction up and make it synthetically useful by using catalysts, the steps that are involved in the reaction must be known.

The Differential Rate Law

To understand the mechanism of a chemical reaction, we must first determine the form of the rate law. Let us look at another hypothetical reaction:

$$C \rightarrow 2D$$

Table 15.2 and figure 15.6 present the data for this reaction. In this reaction we assume that the reverse reaction $2D \rightarrow C$ is much slower than the forward reaction, so we are not concerned about the effect of the reverse reaction on the rate of reaction at any time.

TABLE 15.2 Concentration and time data for the reaction $C \rightarrow 2D$

Time (s)	[*C*] (mol L^{-1})
0	0.70
0.25	0.58
0.50	0.48
0.75	0.40
1.00	0.33
1.25	0.27
1.50	0.23
1.75	0.19
2.00	0.16

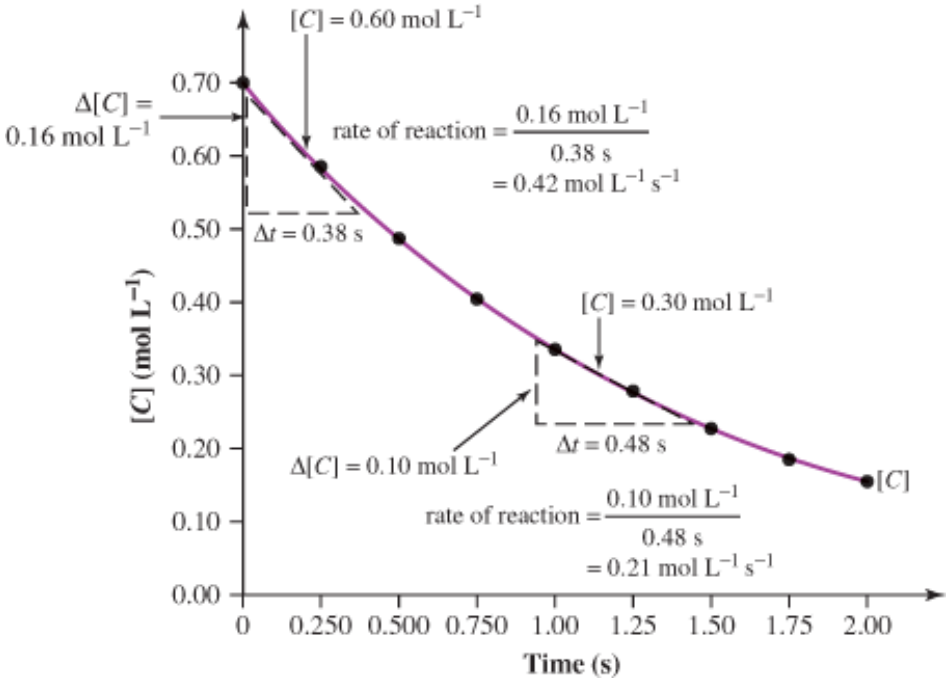


FIGURE 15.6 Determination of the order of the reaction $C \rightarrow 2D$.

From figure 15.6, we can see that the slopes of the tangents to the curve at [*C*] = 0.60 M and 0.30 M give the rates of reaction, 0.42 mol L^{-1} s^{-1} and 0.21 mol L^{-1} s^{-1}, respectively.

When the concentration of *C* is halved, the rate of reaction is also halved. The differential rate law for this reaction is therefore:

$$\text{rate of reaction} = -\frac{d[C]}{dt} = k[C]^1 = k[C]$$

That is, the rate of reaction depends on the concentration of *C* to the first power and we say that the reaction is 'first order in *C*'. (Remember that the order cannot be determined from the stoichiometric coefficient of *C* — in this example it is just coincidence that they are the same. The order can be determined only from experiments.)

WORKED EXAMPLE 15.3

Calculating a Rate Constant from the Rate Data

Use the data in figure 15.6 to calculate the rate constant for the reaction $C \rightarrow 2D$.

Analysis

We know that the rate law for the reaction $C \rightarrow 2D$ is:

$$\text{rate of reaction} = -k[C]$$

Therefore:

$$k = \frac{\text{rate of reaction}}{[C]}$$

We substitute data from figure 15.6 into this equation and solve for *k*.

Solution

For [C] = 0.60 mol L^{-1}, we have found that rate of reaction = 0.42 mol L^{-1} s^{-1}. Inserting this into the equation gives:

$$k = \frac{0.42 \text{ mol L}^{-1} \text{ s}^{-1}}{0.60 \text{ mol L}^{-1}} = 0.70 \text{ s}^{-1}$$

Is our answer reasonable?

We can check whether our calculation is correct by also calculating the rate constant for the other value of the reaction rate shown in figure 15.6. It should be the same as that calculated above, as the rate constant for a reaction is constant at constant temperature.

For [C] = 0.30 mol L^{-1}, rate of reaction = 0.21 mol^{-1} L^{-1} s^{-1}; therefore:

$$k = \frac{0.21 \text{ mol L}^{-1} \text{ s}^{-1}}{0.30 \text{ mol L}^{-1}} = 0.70 \text{ s}^{-1}$$

As the rate constant is the same under both concentration conditions, we can be confident that our answer is correct.

Let's go a step further. Consider the following hypothetical reaction:

$$A + B \rightarrow C$$

Suppose that the data in table 15.3 on the next page have been obtained in a series of five experiments at the same temperature. The form of the rate law for the reaction is:

$$\text{rate of reaction} = k[A]^n[B]^m$$

The values of n and m are found mathematically, and can sometimes be solved by looking for patterns in the rate data. One of the easiest ways to reveal patterns in data is to form ratios of results using different sets of conditions. This procedure is also called the 'method of initial rates'. Because this technique is quite generally useful, let's look in some detail at how it is applied to the problem of finding the rate law exponents.

TABLE 15.3 Concentration and rate data for the hypothetical reaction $A + B \rightarrow C$ determined at the same temperature

	Initial concentrations		
Experiment	A (mol L^{-1})	B (mol L^{-1})	Initial rate of formation of C (mol L^{-1} s^{-1})
1	0.10	0.10	0.20
2	0.20	0.10	0.40
3	0.30	0.10	0.60
4	0.30	0.20	2.40
5	0.30	0.30	5.40

For experiments 1, 2 and 3 in table 15.3, the concentration of B was held constant at 0.10 M. Any change in the rate of reaction for these first three experiments must be due to the change in [A]. The rate law tells us that, when [B] is held constant, the rate of reaction must be proportional to $[A]^n$ so, if we take the ratio of rate laws for experiments 1 and 2, (since $[B]^m$ cancels out) we obtain:

$$\frac{\text{rate of reaction}_{\text{experiment 2}}}{\text{rate of reaction}_{\text{experiment 1}}} = \left(\frac{[A]_{\text{experiment 2}}}{[A]_{\text{experiment 1}}} \right)^n$$

Let's look at the left-hand side of this equation first.

$$\frac{\text{rate of reaction}_{\text{experiment 2}}}{\text{rate of reaction}_{\text{experiment 1}}} = \frac{0.40\ \text{mol L}^{-1}\ \text{s}^{-1}}{0.20\ \text{mol L}^{-1}\ \text{S}^{-1}} = 2.0$$

And for the right-hand side of the equation we have:

$$\left(\frac{[A]_{\text{experiment 2}}}{[A]_{\text{experiment 1}}}\right)^n = \left(\frac{0.20\ \text{mol L}^{-1}}{0.10\ \text{mol L}^{-1}}\right)^n = 2.0^n$$

So doubling [*A*] from experiment 1 to experiment 2 doubles the rate of reaction. If we now combine the left- and right-hand sides of the equation, we can write:

$$2.0 = 2.0^n$$

for experiments 1 and 2.

For the other possible combinations of experiments, we have:

$$3.0 = 3.0^n \text{(for experiments 1 and 3)}$$
$$1.5 = 1.5^n \text{(for experiments 2 and 3)}$$

The only value of *n* that makes all of these equations true is *n* = 1. The reaction must be first order with respect to *A*.

In the final three experiments, the concentration of *B* changes while the concentration of *A* is held constant. This time it is [*B*] that affects the rate. Taking the ratio of rate laws for experiments 3 and 4, we have:

$$\frac{\text{rate of reaction}_{\text{experiment 4}}}{\text{rate of reaction}_{\text{experiment 3}}} = \left(\frac{[B]_{\text{experiment 4}}}{[B]_{\text{experiment 3}}}\right)^m$$

For each unique combination of experiments 3, 4 and 5, we have:

$$4.0 = 2.0^m \text{(for experiments 3 and 4)}$$
$$9.0 = 3.0^m \text{(for experiments 3 and 5)}$$
$$2.25 = 1.5^m \text{(for experiments 4 and 5)}$$

The only value of *m* that makes all of these equations true is *m* = 2. The reaction must be second order with respect to *B*.

Having determined the exponents for the concentration terms, we now know that the rate law for the reaction is:

$$\text{rate of reaction} = k[A]^1[B]^2$$

The reaction is first order with respect to *A* and second order with respect to *B*. *The overall order of a reaction is defined as the sum of the orders for each reactant in the rate law*. Thus, our hypothetical reaction *A* + *B* → *C* has an overall order of 3.

WORKED EXAMPLE 15.4

Determining the Exponents of a Rate Law

Sulfuryl chloride, SO_2Cl_2, is a dense liquid with a pungent odour and is corrosive to the skin and lungs. It is used to manufacture the antiseptic chlorophenol. The following data were collected on the decomposition of SO_2Cl_2 at a certain temperature.

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Initial concentration of SO_2Cl_2 (mol L^{-1})	Initial rate of formation of SO_2 (mol L^{-1} s^{-1})
0.100	2.2×10^{-6}
0.200	4.4×10^{-6}
0.300	6.6×10^{-6}

Determine the rate law and the value of the rate constant for this reaction.

Analysis

The first step is to write the general form of the expected rate law so we can see which exponents have to be determined. Then we study the data to see how the rate of reaction changes when the concentration is changed by a certain factor.

Solution

We expect the rate law to have the form:

$$\text{rate of reaction} = k[SO_2Cl_2]^n$$

Let's examine the data from the first two experiments. Notice that, when the concentration doubles from 0.100 mol L^{-1} to 0.200 mol L^{-1}, the initial rate of reaction also doubles (from 2.2×10^{-6} mol L^{-1} s^{-1} to 4.4×10^{-6} mol L^{-1} s^{-1}). If we look at the first and third experiments, we see that, when the concentration triples (from 0.100 M to 0.300 M), the rate of reaction also triples (from 2.2×10^{-6} mol L^{-1} s^{-1} to 6.6×10^{-6} mol L^{-1} s^{-1}). This behaviour tells us that the reaction must be first order in the SO_2Cl_2 concentration. The rate law is therefore:

$$\text{rate of reaction} = k[SO_2Cl_2]^1 = k[SO_2Cl_2]$$

To evaluate k, we can use any of the three sets of data. Choosing the first set:

$$\begin{aligned} k &= \frac{\text{rate of reaction}}{[SO_2Cl_2]} \\ &= \frac{2.2 \times 10^{-6}\ \text{mol L}^{-1}\ \text{s}^{-1}}{0.100\ \text{mol L}^{-1}} \\ &= 2.2 \times 10^{-5}\ \text{s}^{-1} \end{aligned}$$

Is our answer reasonable?

We should obtain the same value of k by picking any other pair of values. With the last pair of data, at an initial $[SO_2Cl_2]$ of 0.300 mol L^{-1} and an initial rate of reaction of 6.6×10^{-6} mol L^{-1} s^{-1}, we calculate k again to be 2.2×10^{-5} s^{-1}. Keep in mind that the unit of a first-order rate constant is $(\text{time})^{-1}$ (in this example, s^{-1}).

Note that we could also use experiments 2 and 3 to determine the order of the reaction. From the second to the third experiment, the rate of reaction increases by the same factor (1.5) as the concentration, so, using these data too, the reaction must be first order.

To calculate the value of k for the $A + B \rightarrow$ products reaction, we need only substitute rate and concentration data into the rate law.

$$k = \frac{\text{rate}}{[A]^1[B]^2}$$

Using the data from experiment 1 in table 15.3:

$$k = \frac{0.20\ \text{mol L}^{-1}\ \text{s}^{-1}}{\left(0.10\ \text{mol L}^{-1}\right)\left(0.10\ \text{mol L}^{-1}\right)^2}$$

$$= \frac{0.20\ \text{mol L}^{-1}\ \text{s}^{-1}}{0.0010\ \text{mol}^3\ \text{L}^{-3}}$$

After cancelling units, the value of k with the net units is:

$$k = 2.0 \times 10^2\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}$$

Note that the unit of a third-order rate constant is (concentration)$^{-2}$ (time)$^{-1}$.

The rate of a reaction always has the unit (concentration) (time)$^{-1}$. However, it is important to understand that the units of the rate constant depend on the order of the reaction.

For example, for a first-order reaction, the unit is (time)$^{-1}$, and for a second-order reaction the unit is (concentration)$^{-1}$ (time)$^{-1}$. This can also be rationalised from

$$\text{rate of reaction} = k[A]^n$$

- If $n = 1$, the unit for $[A]^n$ is concentration, so the unit for k is (time)$^{-1}$.
- If $n = 2$, the unit for $[A]^n$ is (concentration)^2, so the unit for k is (concentration)$^{-1}$ (time)$^{-1}$.

PRACTICE EXERCISE 15.2

Use the data from the other four experiments (table 15.3) to calculate k for this reaction. What do you notice about the values of k?

Table 15.4 summarises the reasoning used to determine the order for each reactant from experimental data.

TABLE 15.4 Relationship between the order of a reaction and changes in concentration and rate

Factor by which the concentration is changed	Factor by which the rate of reaction changes	Exponent of the concentration term in the rate law
2, 3, 4	rate of reaction is unchanged	0, 0, 0
2	$2 = 2^1$	1
3	$3 = 3^1$	1
4	$4 = 4^1$	1
2	$4 = 2^2$	2
3	$9 = 3^2$	2
4	$16 = 4^2$	2

2	$8 = 2^3$	3
3	$27 = 3^3$	3
4	$64 = 4^3$	3

PRACTICE EXERCISE 15.3

The following data were measured at the same temperature for the reduction of nitric oxide with hydrogen.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

Initial concentration		
[NO] (mol L^{-1})	**[H_2] (mol L^{-1})**	**Initial rate of formation of H_2O (mol L^{-1} s^{-1})**
0.10	0.10	1.23×10^{-3}
0.10	0.20	2.46×10^{-3}
0.20	0.10	4.92×10^{-3}

What is the rate law for the reaction?

WORKED EXAMPLE 15.5

Calculating Reaction Rates from the Rate Law

In the stratosphere, molecular oxygen, O_2, can be broken down into two oxygen atoms by ultraviolet radiation from the sun. When one of these oxygen atoms strikes an ozone molecule, O_3, in the stratosphere, the ozone molecule is destroyed and two oxygen molecules are formed.

$$O(g) + O_3(g) \rightarrow 2O_2(g)$$

This reaction is part of the natural cycle of ozone destruction and formation in the stratosphere. The experimentally determined rate law for the reaction is:

$$\text{rate of reaction} = k[O_3][O]$$

with a rate constant of $k = 4.15 \times 10^5$ mol^{-1} L s^{-1} at the temperature of the experiment. The reactant concentrations at an altitude of 25 km are: $[O_3] = 1.2 \times 10^{-8}$ mol L^{-1} and $[O] = 1.7 \times 10^{-14}$ mol L^{-1}. What is the rate of ozone destruction for this reaction at an altitude of 25 km?.

Analysis

Because we already know the rate law and that the reaction is first order for both [O] and [O_3], the answer to this question is obtained by substituting the given molar concentrations into the

rate law.

Solution

Substituting the given values into the rate law gives:

$$\begin{aligned}\text{rate of reaction} &= \left(4.15 \times 10^{5}\,\text{mol}^{-1}\,\text{L}\,\text{s}^{-1}\right)\left(1.2 \times 10^{-8}\,\text{mol}\,\text{L}^{-1}\right)\left(1.7 \times 10^{-14}\,\text{mol}\,\text{L}^{-1}\right) \\ &= 8.5 \times 10^{-17}\,\text{mol}1^{-1}\,\text{s}^{-1}\end{aligned}$$

Note that the units of rate of reaction are mol L^{-1} s^{-1}, which is (concentration) $(\text{time})^{-1}$, consistent with what we learned earlier (see p. 632).

Is our answer reasonable?

There is obviously no simple check. Multiplying the powers of 10 for the rate constant and the concentrations together reassures us that the rate of reaction is of the correct order of magnitude, and we can see that the answer has the correct units. It is important to realise that the units of the rate constant *k* are *always* such that the calculated rate of reaction has the units (concentration) $(\text{time})^{-1}$, mol L^{-1} s^{-1} in this example. This means that the unit of a rate constant is different for a reaction of overall zero, first, second or third order etc. We show this in other examples later in this chapter.

PRACTICE EXERCISE 15.4

The following reaction:

$$BrO_3 + 3SO_3^{2-} \rightarrow Br + 3SO_4^{2-}$$

has the rate law:

$$\text{rate of reaction} = k[BrO_3]\left[SO_3^{2-}\right].$$

What is the order of the reaction with respect to each reactant? What is the overall order of the reaction?

The Integrated Rate Law

So far, we have looked at differential rate laws, that is, rate laws that express the rate of reaction as a function of concentration. Integrated rate laws are also useful. Recall that integrated rate laws express concentration as a function of time. Consider the hypothetical reaction:

$$A \rightarrow \text{products}$$

The differential rate law has the form:

$$\text{rate of reaction} = -\frac{d[A]}{dt} = k[A]^n$$

The integrated rate laws for first order ($n = 1$), second order ($n = 2$) and zero order ($n = 0$) reactions are developed individually.

First-order Rate Laws

Let's assume that our hypothetical reaction $A \rightarrow$ products is first order in A. The differential rate law is then:

$$\text{rate of reaction} = -\frac{d[A]}{dt} = k[A]$$

Rearrangement gives:

$$-\frac{d[A]}{[A]} = k dt$$

We now want to look at the development of the concentration from the beginning of the reaction (at $t = 0$) until a certain reaction time t. This means we have to integrate this rate equation.

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = k\int_{t=0}^{t} dt$$

Since $\int \frac{d[A]}{[A]} = \ln[A]$ (ignoring the constant of integration), we obtain:

$$\begin{aligned} -(\ln[A]_t - \ln[A]_0) &= kt - kt_0 \\ -\ln[A]_t - \ln[A]_0 &= kt \\ \ln[A]_t &= -kt + \ln[A]_0 \end{aligned}$$

in which $[A]_t$ is the concentration at time t and $[A]_0$ is the initial concentration. The *integrated firstorder rate law* is $\ln[A]_t = - kt + \ln[A]_0$, which shows how the concentration of A changes with time. Thus, if the initial concentration and the rate constant are known, $[A]$ at any time can be calculated. The integrated first-order rate law can also be expressed in terms of the ratio of $[A]_t$ and $[A]_0$:

$$\begin{aligned} \ln\frac{[A]_0}{[A]_t} &= kt \\ [A]_t &= [A]_0 e^{-kt} \end{aligned}$$

The last equation shows that, for first-order reactions, the concentration of A decays exponentially with time.

WORKED EXAMPLE 15.6

Concentration–time Calculations for First-order Reactions

Dinitrogen pentoxide, N_2O_5, is not very stable. In the gas phase or dissolved in a nonpolar solvent, such as tetrachloromethane, it decomposes by a first-order reaction into N_2O_4 and O_2.

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

The experimentally determined rate law is:

$$\text{rate of reaction} = k[N_2O_5]$$

At 45 °C, the rate constant for the reaction in tetrachloromethane is 6.22×10^{-4} s^{-1}. If the initial concentration of N_2O_5 in the solution is 0.100 M, how long will it take for the concentration to drop to 0.0100 M?

Analysis

To solve the problem, we substitute quantities into:

$$\ln\frac{[N_2O_5]_0}{[N_2O_5]_t} = kt$$

and solve for *t*.

Solution

First, we assemble the data.

$$[N_2O_5]_0 = 0.100\ \text{M} \quad [N_2O_5]_t = 0.0100\ \text{M}$$
$$k = 6.22 \times 10^{-4}\ \text{s}^{-1} \quad t = \ ?$$

Substituting this into the equation:

$$\ln\frac{0.100\ \text{M}}{0.0100\ \text{M}} = (6.22 \times 10^{-4}\ \text{s}^{-1})t$$

Since the unit for concentration (M) cancels out, we have:

$$\begin{aligned} \ln 10.0 &= (6.22 \times 10^{-4}\ \text{s}^{-1})t \\ 2.303 &= (6.22 \times 10^{-4}\ \text{s}^{-1})t \end{aligned}$$

As we have seen in earlier chapters, when taking a logarithm of a quantity, the number of digits written *after the decimal point* equals the number of significant figures in the quantity. Here, 10.0 has three significant figures, so the natural logarithm of 10.0, which is 2.303, has three digits after the decimal.

Solving for *t*:

$$\begin{aligned} t &= \frac{2.303}{6.22 \times 10^{-4}\ \text{s}^{-1}} \\ &= 3.70 \times 10^{3}\ \text{s} \end{aligned}$$

This is the time in seconds.

Is our answer reasonable?

We can substitute the time we obtained, along with the given initial concentration, into our equation and see whether we get back the given concentration at time *t*.

$$\begin{aligned} [A]_t = [A]_0 e^{-kt} &= 0.100\ \text{M} \times e^{(-6.22\times10^{-14}\ \text{s}^{-1} \times 3.70\times10^{3}\ \text{s})} \\ &= 0.01\ \text{M} \end{aligned}$$

which is exactly what we started with.

PRACTICE EXERCISE 15.5

If the initial concentration of N_2O_5 in a tetrachloromethane solution at 45 °C is 0.500 M (see worked example 15.6), what will its concentration be after exactly 1 hour?

The equation $\ln[A]_t = -kt + \ln[A]_0$ is of the form $y = mx + c$, where a plot of *y* versus *x* gives a straight line with the slope 'm' and the intercept 'c'.

$$\ln[A]_t = -kt + \ln[A]_0$$
$$y = mx + c$$

For first-order reactions a plot of the natural logarithm of concentration versus reaction time always gives a straight line. This fact is often used to determine the order of a reaction. For the reaction $A \rightarrow$ products, the plot of $\ln[A]_t$ versus t is a straight line, if the reaction is first order. Conversely, if the plot does not give a straight line, then the reaction is not first order. Worked example 15.7 illustrates the procedure.

WORKED EXAMPLE 15.7

Determining the Order of a Reaction

The following data are for the reaction $N_2O_5(g) \rightarrow N_2O_4(g) + \frac{1}{2}O_2(g)$.

Time (s)	$[N_2O_5]$ (mol L^{-1})
0	2.000×10^{-1}
50	1.414×10^{-1}
100	1.000×10^{-1}
200	5.000×10^{-2}
300	2.500×10^{-2}
400	1.250×10^{-2}

(a) Show that the rate law is first order in $[N_2O_5]$.

(b) Calculate the value of the rate constant.

Analysis

(a) If a plot of $\ln[N_2O_5]$ versus time, according to $\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$, gives a straight line, the reaction must be first order in $[N_2O_5]$.

(b) The slope of the plot in (a), if it is a straight line, is equivalent to the negative of the rate constant.

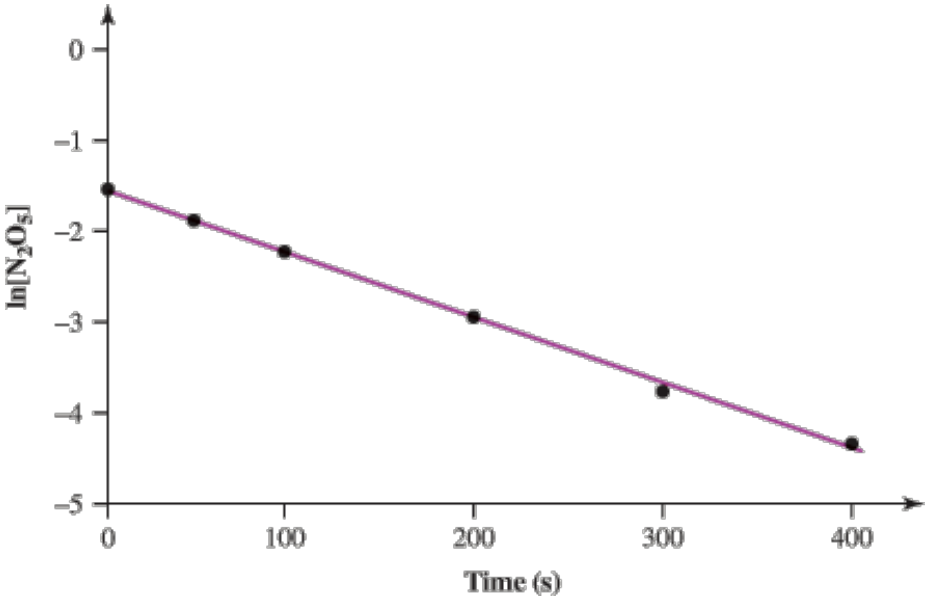
Solution

First we calculate the natural logarithms of the $[N_2O_5]$ values, which gives the following data:

Time (s)	$\ln[N_2O_5]$
0	-1.609
50	-1.956
100	-2.303

200	-2.996
300	-3.689
400	-4.382

We then plot $\ln[N_2O_5]$ versus time.



The plot is a straight line, which confirms that the reaction is first order in $[N_2O_5]$ (we could also use a calculator to do this analysis). In this case, the slope of the line equals $-k$. This gives us:

$$k = -\text{slope} = 6.930 \times 10^{-3}\text{s}^{-1}$$

Is our answer reasonable?

We can substitute this value back into the original equation $\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$ and ensure we obtain the same $[N_2O_5]$ given in the table of data. Doing this shows that our answer is correct.

PRACTICE EXERCISE 15.6

Using the data given in worked example 15.7,
calculate $[N_2O_5]$ at t = 150 s.

Half-life of First-order Reactions

For a first-order reaction, the half-life of the reactant can be obtained from:

$$\ln\frac{[A]_0}{[A]_t} = kt$$

by setting $[A]_t$ equal to half of the initial concentration $[A]_0$.

$$[A]_t = \frac{1}{2}[A]_0$$

Substituting $\frac{1}{2}[A]_0$ for $[A]_t$ and $t_{\frac{1}{2}}$ for t in the original equation gives:

$$\ln \frac{[A]_0}{\frac{1}{2}[A]_0} = kt_{\frac{1}{2}}$$

Note that the left-hand side of the equation simplifies to ln2, and so, to solve the equation for $t_{\frac{1}{2}}$ we have:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Note that *the half-life of a first-order reaction does not depend on the initial concentration of the reactant.* This can be illustrated by one of the most common first-order events in nature, the change that radioactive isotopes undergo during radioactive decay. In fact, you have probably heard the term *half-life* used in reference to the life spans of radioactive substances.

^{131}I, an unstable, radioactive isotope of iodine, is used in nuclear medicine in both diagnosis and therapy of thyroid disorders, such as thyroid cancer and thyrotoxicosis. The thyroid gland is a small organ located just below the 'Adam's apple' and astride the windpipe. It uses iodide ions to make a hormone, so, when a patient is given a dose of $^{131}I^-$ mixed with nonradio active I^-, both ions are taken up by the thyroid gland (see figure 15.7). The temporary change in radioactivity of the gland is a measure of thyroid activity. ^{131}I undergoes a nuclear reaction where it emits beta radiation (see chapter 27) and changes into a stable isotope of xenon. The intensity of the radiation decreases, or decays, with time (see figure 15.8). Notice that the time it takes for the first half of the ^{131}I to disappear is 8 days. Then, during the next 8 days, half of the remaining ^{131}I disappears, and so on. Regardless of the initial amount, it takes 8 days for half of that amount of ^{131}I to disappear, which means that the half-life of ^{131}I is a constant.

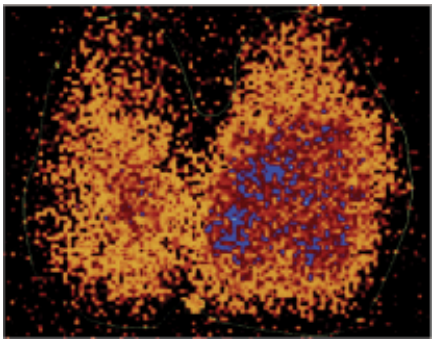


FIGURE 15.7 Scintigram of thyroid glands after the patient was injected with radioactive iodine. This shows the activity of the gland from blue (most active) to yellow (least active). Pasieka Pasieka

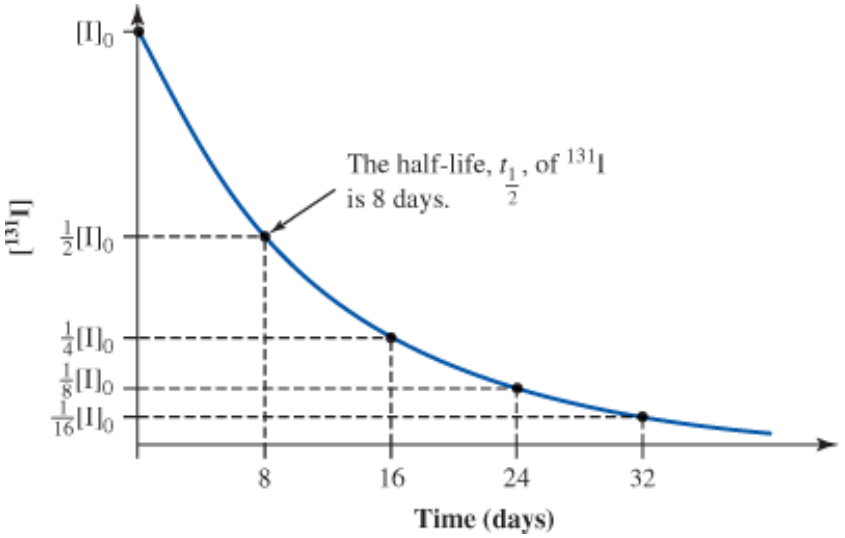


FIGURE 15.8 First-order radioactive decay of ^{131}I. The initial concentration of the isotope is represented by $[I]_0$.

^{131}I is also one of the most dangerous radioisotopes released in nuclear explosions or accidents. If it is present in high levels in the environment, such as after radioactive fallout, it is absorbed by the body after eating contaminated food and concentrates in the thyroid gland. When ^{131}I decays, it can damage the thyroid gland and may lead to thyroid cancer. One possible treatment is an iodine supplement, which increases the total amount of iodine in the body. This, therefore, reduces the relative proportion of ^{131}I and also lowers the uptake and retention of this radioactive isotope in the body. Such supplements were distributed to people living near the Fukushima nuclear power plant in Japan after it exploded in 2011.

WORKED EXAMPLE 15.8

Half-life Calculations

The half-life of radioactive ^{131}I is 8.0 days. What fraction of the initial ^{131}I would be present in a patient after 32.0 days if none of it were eliminated through natural body processes?

Analysis

Having learned that ^{131}I is a radioactive isotope and so decays by a first-order process, we know that the half-life is constant and does not depend on the ^{131}I concentration.

Solution

We can solve the problem using the integrated first-order rate law. We'll need the first-order rate constant k, which we can obtain from the half-life by rearranging:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{8.0\ \text{day}} = 0.0866\ \text{day}^{-1}$$

Then we can use $\ln\frac{[^{131}I]_0}{[^{131}I]_t} = kt$ to calculate the fraction $\frac{[^{131}I]_0}{[^{131}I]_t}$:

$$\ln\frac{[^{131}I]_0}{[^{131}I]_t} = kt = \left(0.0866\ \text{day}^{-1}\right)(32.0\ \text{day}) = 2.77$$

Taking the antilogarithm of both sides, we have:

$$\frac{[^{131}I]_0}{[^{131}I]_t} = e^{2.77} = 16.0$$

Is our answer reasonable?

A period of 32.0 days is exactly four half-lives. If we take the fraction initially present to be 1, we can set up a table.

Half-life	0	1	2	3	4

Fraction	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$

Half of the ^{131}I is lost in the first half-life, half of that disappears in the second half-life, and so on. Therefore, the fraction remaining after four half-lives is $\frac{1}{16}$.

The initial concentration, $[^{131}I]_0$, is 16.0 times as large as the concentration after 32.0 days. The fraction remaining after 32.0 days is $\frac{1}{16}$, which is exactly what we obtained using the mathematical approach.

Second-order Rate Laws

For a general reaction involving one reactant, which is second order in [*A*]

$$A \rightarrow \text{products}$$

the second-order differential rate law is:

$$\text{rate of reaction} = -\frac{d[A]}{dt} = k[A]^2$$

Again, to look at how the concentration of *B* changes over time, we have to rearrange this equation to give $-\frac{d[A]}{[A]^2} = kdt$, and then integrate this between the start of the reaction ($t = 0$) and a certain reaction time (t).

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = k\int_{t=0}^{t} dt$$

As $\int \frac{d[A]}{[A]^2} = -\frac{1}{[A]}$, and ignoring the constant of integration, we obtain:

$$\begin{aligned}
\left(\frac{-1}{[A]_t} - \frac{-1}{[A]_0}\right) &= kt - kt_0 \\
-\left(\frac{-1}{[A]_t} + \frac{1}{[A]_0}\right) &= kt \\
\frac{1}{[A]_t} - \frac{1}{[A]_0} &= kt \\
\frac{1}{[A]_t} &= kt + \frac{1}{[A]_0}
\end{aligned}$$

This equation is the *integrated second-order rate law*. It shows that for second-order reactions the reciprocal of the concentration is related linearly to time.

WORKED EXAMPLE 15.9

Concentration–time Calculations for Second-order Reactions

Nitrosyl chloride, NOCl, decomposes slowly to NO and Cl_2.

$$2NOCl \rightarrow 2NO + Cl_2$$

The rate law shows that the rate of reaction is second order in [NOCl].

$$\text{rate of reaction} = k[NOCl]^2$$

The rate constant k equals 0.020 mol^{-1} L s^{-1} at a certain temperature. If the initial concentration of NOCl in a closed reaction vessel is 0.050 M, what is the concentration after 30 minutes?

Analysis

We are given a rate law and can see that it is for a second-order reaction. We must calculate $[NOCl]_t$, the molar concentration of NOCl, after 30 min (1800 s) using $\frac{1}{[NOCl]_t} = kt + \frac{1}{[NOCl]_0}$.

Solution

We know that:

$$[NOCl]_0 = 0.050\ M \quad k = 0.020\ mol^{-1}\ L\ s^{-1}$$
$$[NOCl]_t = ?\ M \quad t = 1800\ s$$

The general integrated second-order rate law is:

$$\frac{1}{[NOCl]_t} = kt + \frac{1}{[NOCl]_0}$$

Making the substitution gives:

$$\frac{1}{[NOCl]_t} = \left(0.020\ mol^{-1}\ L\ s^{-1} \times 1800\ s\right) + \frac{1}{0.050\ mol\ L^{-1}}$$

Solving for $\frac{1}{[NOCl]_t}$ gives:

$$\frac{1}{[NOCl]_t} = 36\ mol^{-1}\ L + 20\ mol\ L^{-1}$$
$$\frac{1}{[NOCl]_t} = 56\ mol^{-1}\ L$$

Taking the reciprocals of both sides gives us the value of [NOCl]:

$$[NOCl]_t = \frac{1}{56\ mol^{-1}\ L}$$
$$= 0.018\ mol\ L^{-1}$$
$$= 0.018\ M$$

The molar concentration of NOCl has decreased from 0.050 M to 0.018 M after 30 minutes.

Is our answer reasonable?

The concentration of NOCl has decreased, as it must. We can check the calculation by substituting this value into the original equation.

PRACTICE EXERCISE 15.7

For the reaction in worked example 15.9, determine how long it would take for the NOCl concentration to drop from 0.040 M to 0.010 M.

The rate constant for a second-order reaction with a rate law following $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ can be determined graphically by a method similar to that used for a first-order reaction. The equation corresponds to an equation for a straight line:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + c$$

When a reaction is second order, a plot of $\frac{1}{[A]_t}$ versus t should yield a straight line with a slope k. This is illustrated in figure 15.9b for the decomposition of HI, according to $2HI(g) \rightarrow H_2(g) + I_2(g)$, using data from worked example 15.1. Figure 15.9a shows a plot of ln[HI] versus time; the fact that this is a curve confirms the reaction is not first order in [HI].

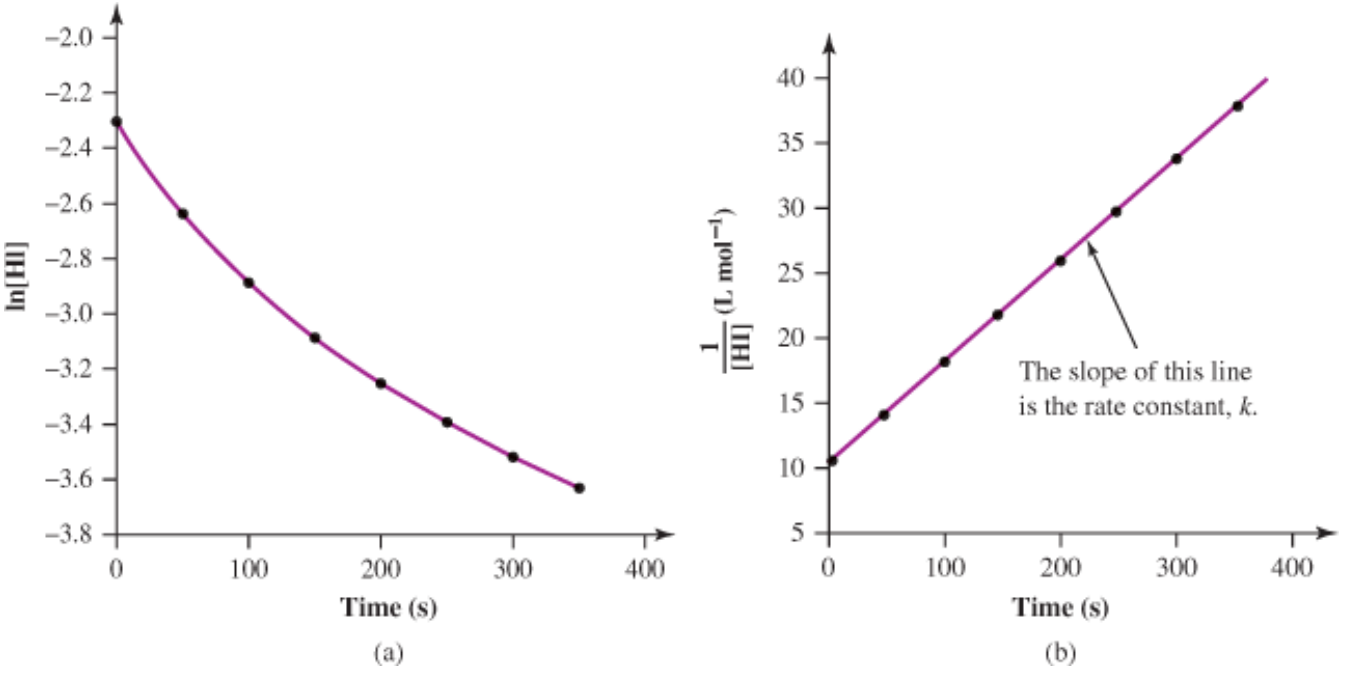


FIGURE 15.9 Second-order kinetics:
(a) a graph of ln[HI] versus time and
(b) a graph of $\frac{1}{[HI]}$ versus time for the data in worked example 15.1.

Half-life of Second-order Reactions

After one half-life of a second-order reaction has elapsed, we have:

$$[A]_t = \frac{[A]_0}{2}$$

Inserting this into $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ gives:

$$\begin{aligned} \frac{1}{\frac{[A]_0}{2}} &= kt_{\frac{1}{2}} + \frac{1}{[A]_0} \\ \frac{1}{[A]_0} &= kt_{\frac{1}{2}} \\ t_{\frac{1}{2}} &= \frac{1}{k[A]_0} \end{aligned}$$

Thus, in contrast to first-order reactions, the half-life of a second-order reaction is inversely proportional to the initial concentration of the reactant.

WORKED EXAMPLE 15.10

Half-life Calculations

The reaction $2HI(g) \rightarrow H_2(g) + I_2(g)$ has the rate law, rate = $k[HI]^2$, with $k = 0.079\ mol^{-1}\ L\ s^{-1}$ at 508 °C. What is the half-life for this reaction at this temperature when the initial HI concentration is 0.050 M?

Analysis

The rate law tells us that the reaction is second order. To calculate the half-life, we need to use $t_{\frac{1}{2}} = \frac{1}{k[HI]_0}$

Solution

The initial concentration is 0.050 mol L^{-1} and $k = 0.079\ mol^{-1}\ L\ s^{-1}$. Substituting these values into $t_{\frac{1}{2}} = \frac{1}{k[HI]_0}$ gives:

$$\begin{aligned} t_{\frac{1}{2}} &= \frac{1}{\left(0.079\ \text{mol}^{-1}\ \text{L}\ \text{s}^{-1}\right)\left(0.050\ \text{mol}\ \text{L}^{-1}\right)} \\ &= 2.5 \times 10^2\ \text{s} \end{aligned}$$

Is our answer reasonable?

Substituting this value back into the equation above shows that this answer is correct.

PRACTICE EXERCISE 15.8

Suppose that the value of $t_{\frac{1}{2}}$ for a certain

reaction was found to be independent of the initial concentration of the reactants. What could you say about the order of the reaction?

Zero-order Rate Laws

While most reactions that involve only one reactant are first- or second-order reactions, there are reactions for which the rate of the reaction is constant; that is, it does not vary with concentration. An example is the thermal decomposition of bromoethane on a zinc surface, which acts as a catalyst.

$$C_2H_5Br(g) \xrightarrow{Zn} CH_2{=}CH_2(g) + HBr(g)$$

The reaction occurs at the surface of the zinc metal, which is saturated with bromoethane. Therefore, the reaction rate is not dependent on the concentration of bromoethane. Such reactions are called *zero-order reactions*. For the general zero-order reaction $A \rightarrow$ products, we can write the rate law as:

$$\text{rate of reaction} = -\frac{d[A]}{dt} = k[A]_0 = k$$

How does the concentration of *A* change over time? As before, we arrange the rate law to give $-d[A] = k\,dt$ and, by integration between the beginning of the reaction ($t = 0$) and a certain reaction time (t), the *integrated rate law for a zero-order reaction* can be obtained.

$$\begin{aligned} -\int_{[A]_0}^{[A]_t} d[A] &= k\int_{t=0}^{t} dt \\ -([A]_t - [A]_0) &= kt - kt_0 \\ [A]_0 - [A]_t &= kt \\ [A]_t &= -kt + [A]_0 \end{aligned}$$

This equation corresponds to an equation for a straight line.

$$\begin{array}{ccccc} [A]_t & = & -kt & + & [A]_0 \\ \updownarrow & & \updownarrow\updownarrow & & \updownarrow \\ y & = & mx & + & c \end{array}$$

A plot of [*A*] versus time gives a straight line of slope $-k$, as shown in figure 15.10.

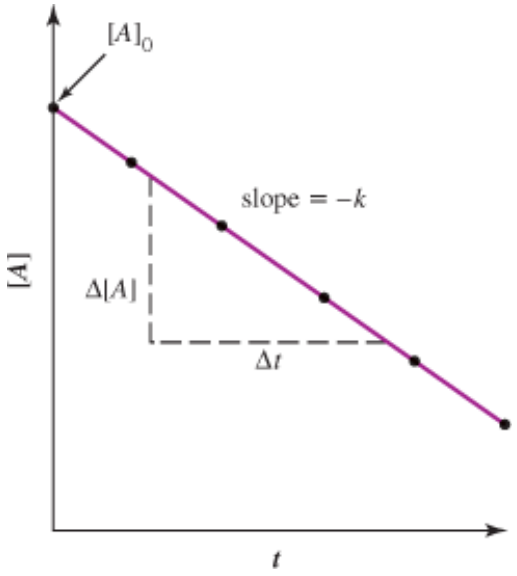


FIGURE 15.10 For a zero-order reaction, [*A*] versus *t* is a straight line with slope $-k$.

The half-life of a zero-order reaction is $[A]_t = \frac{[A]_0}{2}$ when $t = t_{\frac{1}{2}}$. Inserting this into the equation $[A]_t = -kt + [A]_0$ gives:

$$\frac{[A]_0}{2} = -kt_{\frac{1}{2}} + [A]_0$$

$$kt_{\frac{1}{2}} = \frac{[A]_0}{2}$$

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$

For a zero-order reaction, the half-life is proportional to the concentration of the reactant.

Many reactions which require surfaces of metals show zero-order kinetics. The example shown in figure 15.11 is the decomposition of dinitrogen oxide into nitrogen and oxygen on a hot platinum surface:

$$2N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g)$$

When the platinum surface is completely covered with N_2O molecules, an increase in $[N_2O]$ does not change the rate of the reaction.

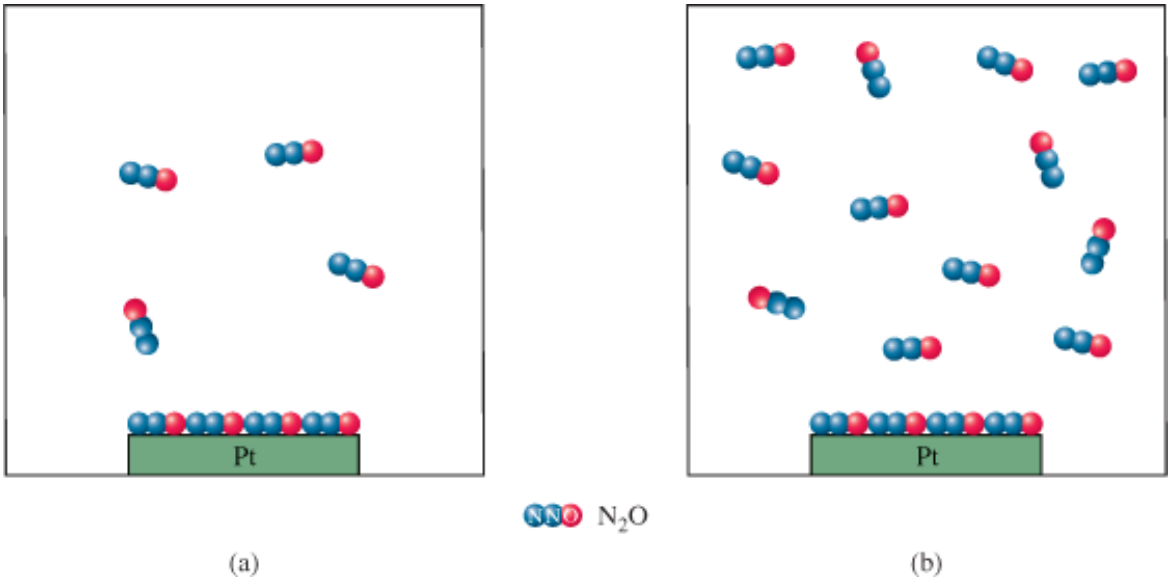


FIGURE 15.11 The decomposition reaction $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$ takes place on a platinum surface. The rate of decomposition of N_2O is the same in **(a)** and **(b)**, regardless of the concentration of N_2O, because the platinum surface can accommodate only a certain number of molecules. As a result, this reaction is zero order in $[N_2O]$.

Also, many thermal decomposition reactions follow zero-order kinetics, where the reaction rate is independent of the concentration of the reactant. Ethanol metabolism in the body is catalysed by the enzyme alcohol dehydrogenase. Because only a limited amount of ethanol can be removed in this way, if there is a high concentration of ethanol in the blood, metabolism can follow zero-order kinetics (see also pp. 672–3).

Before moving on to look at the theory of chemical kinetics, study table 15.5, which summarises the kinetics for reactions of different orders.

TABLE 15.5 Summary of the kinetics for reactions of the type $A \rightarrow$ products that are zero, first or second order in $[A]$

	Zero order	First order	Second order
Rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$

Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Linear graph	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Slope of linear graph	$-k$	$-k$	k
Units of rate constant	mol L^{-1} s^{-1}	s^{-1}	mol^{-1} L s^{-1}
Half-life $\left(t_{\frac{1}{2}}\right)$	$\frac{[A]_0}{2k}$	$\frac{\ln 2}{k}$	$\frac{1}{k[A]_0}$

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15.5 Theory of Chemical Kinetics

In section 15.2 we mentioned that nearly all reactions proceed faster at higher temperatures. Generally, the rate of reaction increases by a factor of about two or three for each 10 °C increase in temperature, although the exact amount of increase differs from one reaction to another. Temperature evidently has a significant effect on reaction rate. To understand why, we need to develop some theoretical models that explain our observations. One of the simplest models is called **collision theory**.

Collision Theory

The basic principle of collision theory is that the rate of a reaction is proportional to the number of effective collisions per second among the reactant molecules. An *effective collision* is one that actually results in the formation of product molecules. Anything that can increase the frequency of effective collisions should, therefore, increase the rate.

One of the several factors that influence the number of effective collisions per second is *concentration*. As reactant concentrations increase, the number of collisions per second of all types, including effective collisions, also increases.

Not every collision between reactant molecules actually results in a chemical change. We know this because the reactant atoms or molecules in a gas or a liquid undergo an enormous number of collisions per second with each other. If every collision were effective, all reactions would be over in an instant. *Only a very small fraction of all the collisions can really lead to a net change.* Why is this so?

Molecular Orientation

In most reactions, when two reactant molecules collide they must be oriented correctly for a reaction to occur. For example, the reaction represented by the following equation:

$$2NO_2Cl \rightarrow 2NO_2 + Cl_2$$

appears to proceed by a two-step mechanism, which we will discuss in section 15.6. At this point, it is sufficient to know that one step involves the collision of an NO_2Cl molecule with a chlorine atom, Cl.

$$NO_2Cl + Cl \rightarrow NO_2 + Cl_2$$

The orientation of the NO_2Cl molecule when hit by the Cl atom is important (see figure 15.12). The orientation shown in figure 15.12a cannot result in the formation of Cl_2 because the two Cl atoms are not being brought close enough together for a new Cl—Cl bond to form as an N—Cl bond breaks. Figure 15.12b shows the necessary orientation of NO_2Cl and Cl that leads to successful product formation.

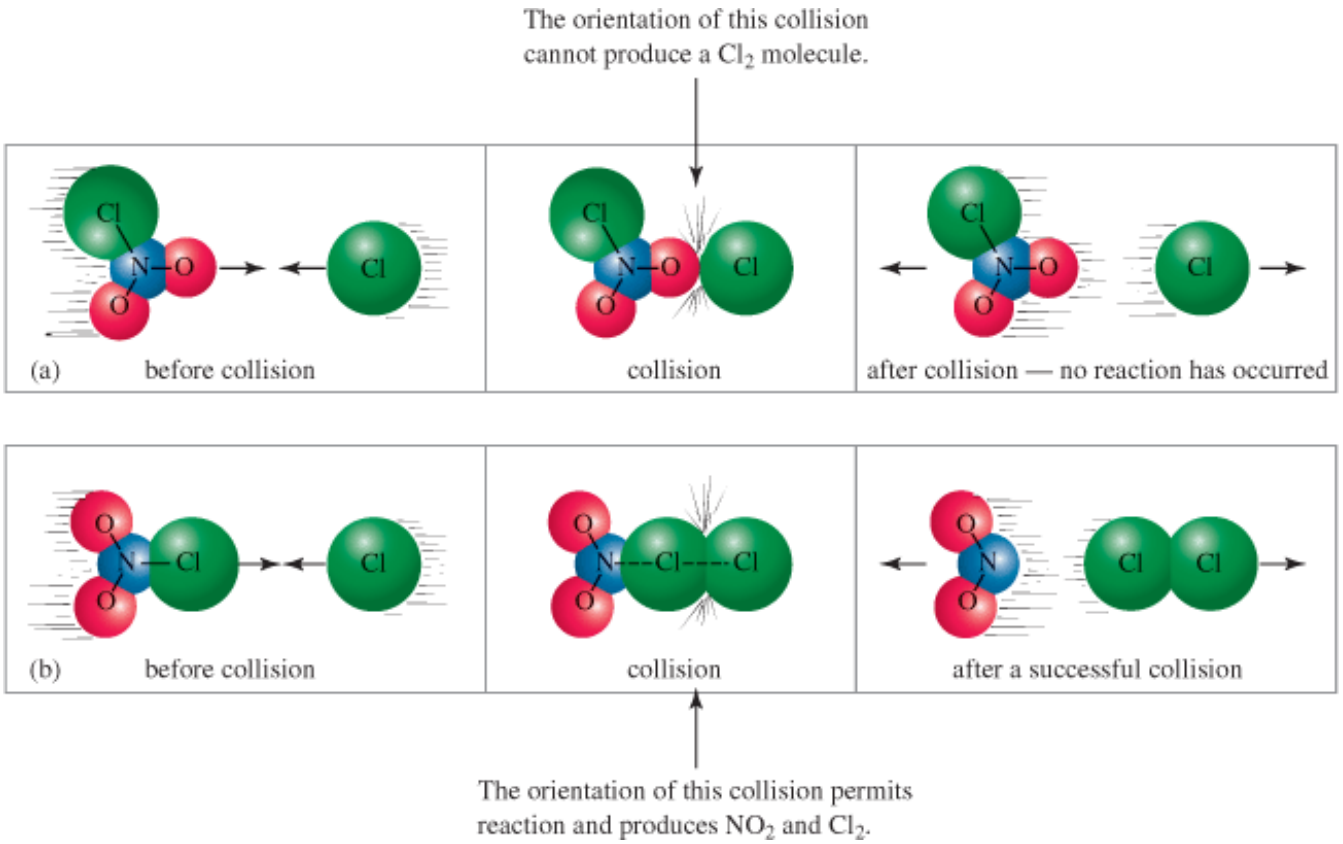


FIGURE 15.12 The importance of molecular orientation during a collision in a reaction. The key step in the decomposition of NO_2Cl to NO_2 and Cl_2 is the collision of Cl with a NO_2Cl molecule.

(a) An ineffectively oriented collision

(b) An effectively oriented collision.

Activation Energy

Not all collisions, even those correctly oriented, are energetic enough to result in the formation of products; this is the major reason why only a small percentage of all collisions actually lead to a chemical change.

Why is this so? This question was first addressed by Svante Arrhenius (Nobel Prize in chemistry, 1903) in the 1880s (figure 15.13). He proposed the existence of a *threshold* energy, the **activation energy (E_a)**, which must be overcome for a reaction to occur. This can be rationalised by considering the previous reaction of NO_2Cl with Cl. In this reaction, an N—Cl bond must break and a Cl—Cl bond must form.

Breaking an N—Cl bond requires a considerable energy of 188 kJ mol^{-1}, which must come from somewhere. The collision theory postulates that the energy required to break the bond comes from the *kinetic energy* (KE) of the molecules before the collision. This kinetic energy is converted into *potential energy* (PE) as the molecules are distorted during a collision; old bonds in the reactant molecules are broken, and new bonds are formed in the product molecules. For most chemical reactions, the activation energy is quite large, and only a small fraction of all well-oriented, colliding molecules have it.



FIGURE 15.13 Svante Arrhenius (1859–1927) is one of the founders of physical chemistry. He was awarded the Nobel Prize in chemistry in 1903 for his work on the theory of ionic dissociation. NYPL/Science Source

The reaction progress can be plotted as shown in figure 15.14, which is called a *potential energy diagram*.

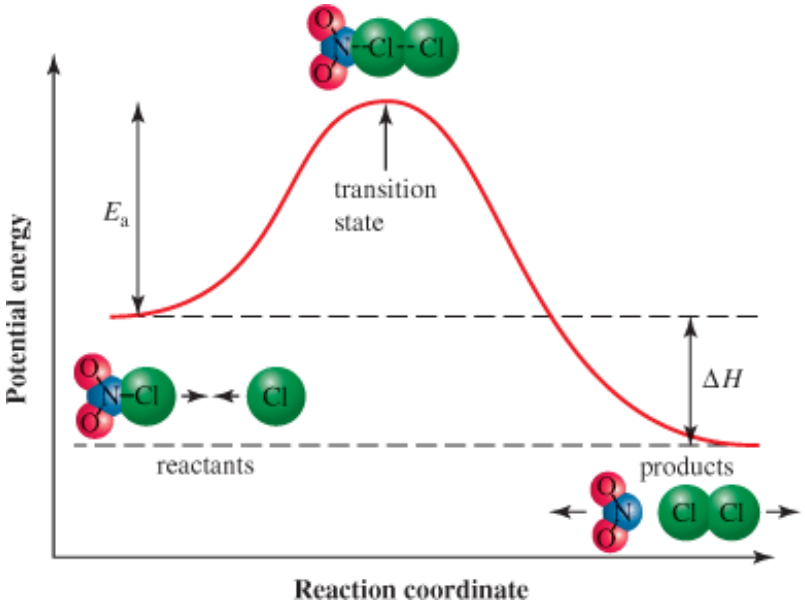


FIGURE 15.14 Potential energy diagram for the reaction $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$. The activation energy, E_a, is the combined kinetic energy that the colliding particles must have for the reaction to occur. ΔH is the enthalpy difference between products and reactants. In an exothermic reaction, which is shown here, ΔH is negative ($\Delta H < 0$).

The vertical axis represents potential energy, which changes during a reaction as the kinetic energy of the colliding particles is converted into potential energy. The horizontal axis is called the **reaction coordinate**, and it represents the extent to which the reactants have changed to the products. The arrangement found on the top of the potential energy 'hill' (or barrier) is called the **transition state**. At the transition state, sufficient energy is concentrated to allow the bonds in the reactants to break. As they break, energy is redistributed and new bonds form, giving products. Once the transition state is reached, the reaction can either proceed to give products or, in the reverse direction, to give reactants. A transition state has a definite geometry, a definite arrangement of bonding and nonbonding electrons, and a definite distribution of electron density and charge; the old bonds are not completely broken and the new bonds have not yet been formed. Because a transition state is at an energy maximum on an energy diagram, we cannot isolate it and cannot determine its structure experimentally. Its lifetime is of the order of a picosecond (the duration of a single bond vibration). However, even though we cannot observe a transition state directly by experimental

means, we can often infer a great deal about its probable structure from other experimental observations.

The difference in energy between the reactants and the transition state is called the activation energy, E_a. The activation energy is the minimum energy required for a reaction to occur; it can be considered an energy barrier for the reaction. If the activation energy is large, very few molecular collisions occur with sufficient energy to reach the transition state, and the reaction is slow. If the activation energy is small, many collisions generate sufficient energy to reach the transition state, and the reaction is fast.

In a reaction that occurs in two or more steps, each step has its own transition state and activation energy. Figure 15.15 shows an energy diagram for a hypothetical reaction $A + B \rightarrow C + D$, which proceeds in two steps. A **reaction intermediate** corresponds to an energy minimum between two transition states, in this case transition states 1 and 2. Note that, because the energies of the reaction intermediates are higher than the energies of either the reactants or the products, these intermediates are highly reactive and can only rarely be isolated. However, because intermediates have a certain lifetime (in contrast to transition states), searching for the presence of a reaction intermediate with optical or other fast recording methods may provide experimental support for a reaction mechanism. It is advisable that you become familiar with the definition of reaction intermediates and transition states in order to avoid mixing them up.

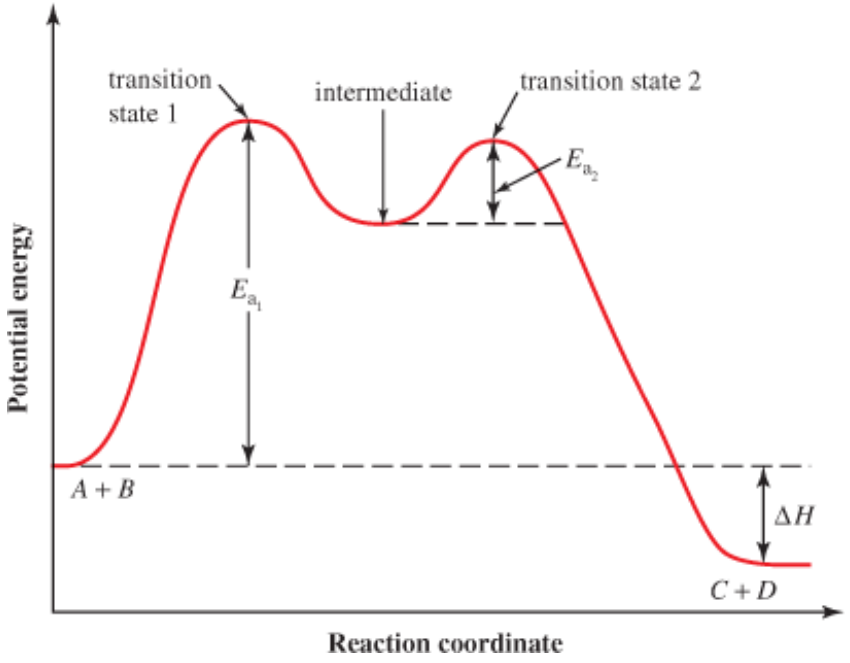


FIGURE 15.15 Energy diagram for a two-step reaction involving the formation of an intermediate. The enthalpy of the reactants is higher than that of the products, and ΔH for the conversion of $A + B$ to $C + D$ is therefore negative.

Both the reaction of NO_2Cl with Cl to give NO_2 and Cl_2 shown in figure 15.14 and our hypothetical reaction $A + B \rightarrow C + D$ in figure 15.15 are *exothermic*, as indicated by the fact that the products have a lower potential energy than the reactants (energy difference, or enthalpy of reaction $\Delta H < 0$). A potential energy diagram for an *endothermic* reaction, where the potential energy of the products is higher than that of the reactants ($\Delta H > 0$), is shown in figure 15.16.

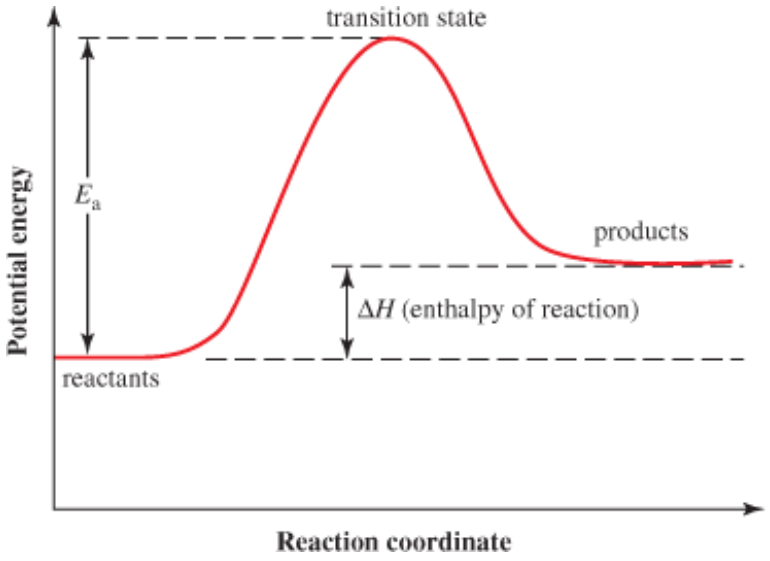


FIGURE 15.16 A potential energy diagram for an endothermic reaction.

It is important to understand that ΔH has no influence on the rate of the reaction. *The rate of a reaction is solely determined by the height of the activation barrier, E_a.*

Let's come back to our reaction of NO_2Cl with Cl atoms in figure 15.14. A certain minimum energy, E_a, is required for an NO_2Cl and a Cl atom species to get over the hill and form products. This is energy provided by the collision between these species. A collision between an NO_2Cl molecule and a Cl atom with small kinetic energies does not provide enough energy to get over the barrier, and no reaction occurs — even if their orientation is ideal. At a given temperature, only a certain fraction of the collisions possess enough energy to be effective and form products.

The concept that a reaction involving two molecules can occur only after successful a collision between these species seems quite logical. However, many reactions involve only one molecule: for example, the decomposition of N_2O_5 to N_2O_4 and O_2 shown in worked example 15.7. How do molecules in such reactions acquire the energy required to surmount the energy barrier associated with breaking the bonds? This question was addressed for reactions in the gas phase by the English scientists Sir Cyril Hinshelwood (Nobel Prize in chemistry in 1956) and Fredrick Alexander Lindemann (figure 15.17) who suggested that the required activation energy is accumulated through collisions between these molecules, which produce energised (‘activated’) molecules. Qualitatively, the rate of the unimolecular reaction is therefore proportional to the concentration of activated molecules, which in turn is proportional to the concentration of unenergised molecules.





FIGURE 15.17 (a) Sir Cyril Hinshelwood (Nobel Prize in chemistry in 1956) and (b) Frederick Lindemann, Chief Scientific Advisor to Winston Churchill during World War II.
Ray Nelson

Temperature Effects: The Arrhenius Equation

With the concept of activation energy, we can explain why the rate of a reaction increases so much with increasing temperature. The two plots in figure 15.18 correspond to different temperatures for the same mixture of reactants. Each curve is a plot of the different fractions of all collisions (vertical axis) that have particular values of kinetic energy of collision (horizontal axis). The total area under a curve then represents the total number of collisions, because all of the fractions must add up to this total. Notice what happens to the plots when the temperature is increased; the maximum point shifts to the right and the curve flattens somewhat.

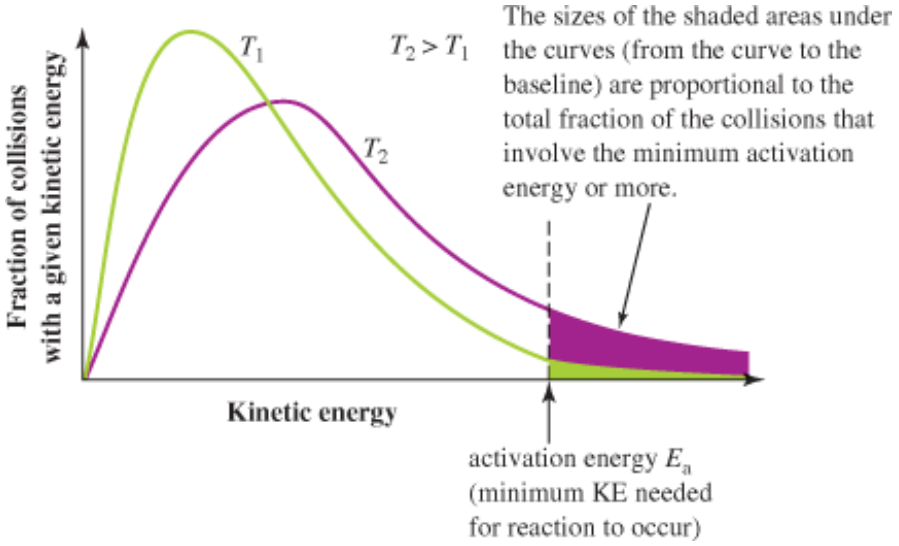


FIGURE 15.18 Kinetic energy distributions for a reaction mixture at two different temperatures T_1 and T_2.

The shaded areas under the curves in figure 15.18 represent the sum of all the fractions of the total collisions that equal or exceed the activation energy. This sum — we could call it the *reacting fraction* — is much greater at the higher temperature than at the lower temperature because a significant fraction of the curve shifts beyond the activation energy with even a modest increase in temperature. In other words, at the higher temperature, a much greater fraction of the collisions result in a chemical change, so the reactants react faster at the higher temperature.

In fact, the fractions of effective collisions increase *exponentially* with temperature. Arrhenius postulated

that the number of collisions having an equal or greater energy than the activation energy is given by the expression:

$$\frac{N}{N_0} = e^{-E_a/RT}$$

$$\begin{aligned} \text{where } N &= \text{number of collisions with at least } E_a \\ N_0 &= \text{total number of collisions} \\ E_a &= \text{activation energy } \left(\text{J mol}^{-1}\right) \\ R &= \text{gas constant } \left(8.314 \text{ J mol}^{-1} \text{ K}^{-1}\right) \\ T &= \text{temperature K.} \end{aligned}$$

The term $e^{-E_a/RT}$ is the probability that any given collision will result in a reaction.

The shapes of the curves in figure 15.18 are given by the so-called Maxwell–Boltzmann distributions. All molecules of a particular chemical species have the same mass so their kinetic energies depend only on the velocities of the particles $\left(\text{kinetic energy} = \frac{1}{2}mv^2\right)$. In any mixture of moving particles, some particles have a low speed (low energy), some have a high speed (high energy), but most have a speed very close to the average. The Maxwell–Boltzmann distribution shows how the speeds (energies) of moving particles in a mixture change with temperature. As you can see in figure 15.18, there are no molecules at zero energy and few molecules at high energy. Most importantly, there is no maximum energy value (the curve does not touch the *x*-axis).

Thus, summarising our discussion so far, two requirements must be satisfied for a successful reaction:

1. The collision energy must equal or exceed the activation energy.
2. The relative orientation of the reactants must allow formation of any new bonds that are necessary to produce the products of the reaction.

With these two requirements, the rate constant *k* can now be expressed as:

$$k = zpe^{-E_a/RT}$$

In this equation, *z* represents the collision frequency (the total number of collisions per second). The factor *p* is called the **steric factor**, and represents the fraction of collisions with correct orientations so that the actual chemical reaction can occur. The factor $e^{-E_a/RT}$ reflects the fraction of collisions with sufficient energy to surmount the activation barrier. This equation is most commonly written as:

$$k = Ae^{-E_a/RT}$$

This is called the **Arrhenius equation**. The factors *zp* are replaced by *A*, which is called the **pre-exponential** or **frequency factor** for this reaction. *A* has the same units as the rate constant and this depends on the order of the reaction. In principle, *A* is dependent on the temperature, since the frequency of collisions increases with increasing temperature. However, this temperature dependence is much smaller than the exponential term. As an approximation, *A* is therefore usually considered as a constant.

How can the activation energy be determined experimentally? Taking the natural logarithm of each side of the Arrhenius equation gives:

$$\ln k = \frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

This is a linear equation of the type $y = mx + c$,

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$y = m\ x + c$$

Thus, by measuring the rate constant at different temperatures for a reaction, a plot of ln k versus $\frac{1}{T}$ gives a straight line (if the reaction obeys the Arrhenius equation). From the slope and the intercept, E_a and the pre-exponential factor A can be determined. Indeed, most reactions obey the Arrhenius equation to a good approximation, which indicates that the collision theory is a physically reasonable model.

WORKED EXAMPLE 15.11

Determination of E_a and the pre-exponential factor A

Consider the second-order decomposition of NO_2 into NO and O_2. The equation is:

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

The following data were collected for the reaction.

k(mol^{-1} L s^{-1})	Temperature (°C)
7.8	400
10	410
14	420
18	430
24	440

Determine the activation energy in kilojoules per mole and the pre-exponential factor A for this reaction.

Analysis

The Arrhenius equation, $\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$, applies, but the use of rate data to determine the activation energy graphically requires that we plot ln k, not k, versus the reciprocal of the temperature in kelvin, so we have to convert the given data into ln$k$ and $\frac{1}{T}$ before we can plot the graph. From the slope of the straight line, E_a can be obtained. The factor A can be determined either graphically, from the intercept, or algebraically, by substitution of the data into the Arrhenius equation. Note that A must have the same units as the rate constant k.

Solution

To illustrate, using the first set of data, the conversions are:

$$\ln k = \ln(7.8) = 2.05$$

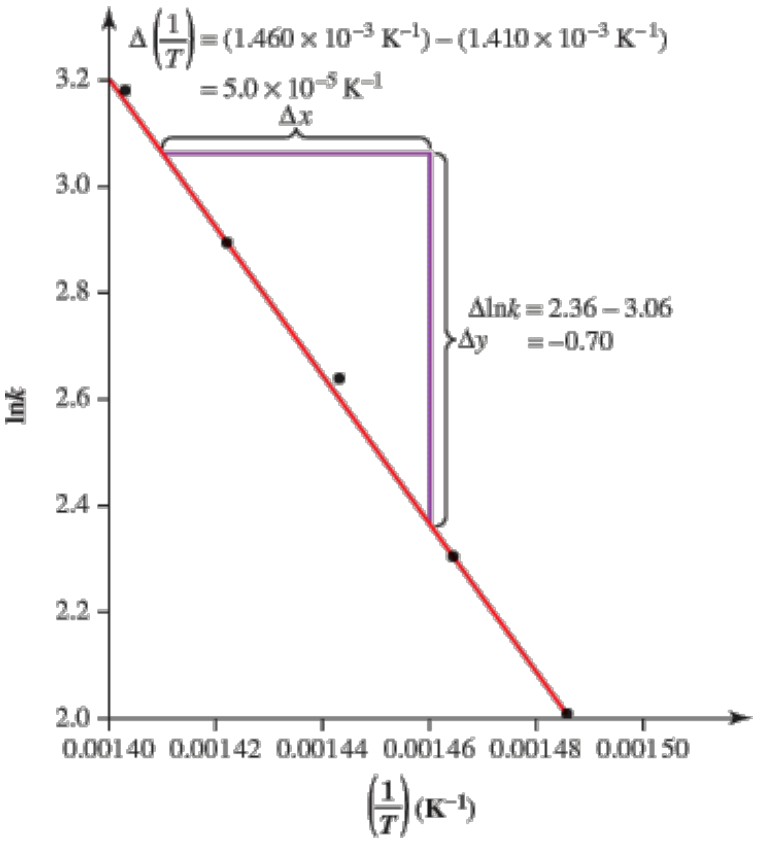
$$\frac{1}{T} = \frac{1}{(400 + 273)\ \text{K}} = \frac{1}{673\ \text{K}} = 1.486 \times 10^{-3}\ \text{K}^{-1}$$

We are carrying extra ‘significant figures’ for the purpose of graphing the data. The remaining

conversions give the following table.

$\ln k$	$\frac{1}{T}\left(K^{-1}\right)$
2.05	1.486×10^{-3}
2.30	1.464×10^{-3}
2.64	1.443×10^{-3}
2.89	1.422×10^{-3}
3.18	1.403×10^{-3}

Then we plot ln$k$ versus $\frac{1}{T}$ as shown in the figure below.



Alternatively, you can use a computer or scientific calculator to calculate the slope of the straight line that best fits the data (linear regression). This will indicate the quality of the linear fit.

(a) To determine E_a, calculate the slope of the straight line as follows:

$$\text{slope} = \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} = \frac{-0.70}{5.0 \times 10^{-5}\text{K}^{-1}}$$

$$= -1.4 \times 10^{4}\ \text{K} = -\frac{E_a}{R}$$

After changing signs and solving for E_a we have:

$$E_a = \left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(1.4 \times 10^{4}\ \text{K}\right)$$

$$= 1.2 \times 10^{5}\ \text{J mol}^{-1}$$

$$= 1.2 \times 10^{2}\ \text{kJ mol}^{-1}$$

(b) To determine A, we must find the y-intercept of the graph. (If you used a computer or

calculator to determine the slope, the linear regression also gives you the intercept.) We do this by using the equation $y = mx + c$, the slope calculated in part (a), and the $\ln k$ versus $\frac{1}{T}$ data given on p. 656. Putting the data into the equation gives five different values for c (22.82, 22.80, 22.85, 22.84 and 22.80), the average of which is 22.82. This corresponds to $\ln A$ n, so taking the exponential of this gives $A = 8.1 \times 10^9$ mol^{-1} L s^{-1}. The units of A are those for a second-order reaction.

Is our answer reasonable?

The activation energy and pre-exponential factor are positive. You can check these values by substituting them back into the original equation.

The activation energy can also be obtained from two rate constants measured at different temperatures. At temperature T_1, the rate constant k_1 is expressed as:

$$\ln k_1 = \frac{E_a}{RT_1} + \ln A$$

At temperature T_2, we then have:

$$\ln k_2 = \frac{E_a}{RT_2} + \ln A$$

Since the pre-exponential factor A is approximately independent of the temperature, subtraction of the first equation from the second gives:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Worked example 15.12 illustrates the use of this equation.

WORKED EXAMPLE 15.12

Calculating the Activation Energy from Two Rate Constants

The decomposition of hydrogen iodide, HI, has rate constants $k = 0.079$ mol^{-1} L s^{-1} at 508 °C and $k = 0.24$ mol^{-1} L s^{-1} at 540 °C. What is the activation energy of this reaction in kJ mol^{-1}?

Analysis

When there are only two data sets, the simplest way to estimate E_a is to solve the equation:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Solution

Let's begin by organising the data; a small table is helpful. Choose one of the rate constants as k_1 (it doesn't matter which one) and then fill in the table.

k (mol^{-1} L s^{-1})	T(K)
0.079	508 + 273 = 781

0.24	540 + 273 = 813

We also have $R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$. Substituting into the initial equation yields:

$$\ln\frac{0.24\ \text{mol}^{-1}\ \text{L s}^{-1}}{0.079\ \text{mol}^{-1}\ \text{L s}^{-1}} = \frac{E_a}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{813\ \text{K}} - \frac{1}{781\ \text{K}}\right)$$

$$\ln 3.0 = -\frac{E_a}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}(0.00123\ \text{K}^{-1} - 0.00128\ \text{K}^{-1})$$

$$1.10 = \frac{E_a}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}(0.000\ 050)$$

Multiplying both sides by $8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$ gives:

$$9.15\ \text{J mol}^{-1}\ \text{K}^{-1} = E_a\left(0.000\ 050\ \text{K}^{-1}\right)$$

Solving for E_a, we have:

$$E_a = 1.8 \times 10^5\ \text{J mol}^{-1}$$

$$= 1.8 \times 10^2\ \text{kJ mol}^{-1}$$

Note that this is of the same order of magnitude as the energy of a single bond.

PRACTICE EXERCISE 15.9

The reaction $2NO_2 \rightarrow 2NO + O_2$ has an activation energy of 111 kJ mol^{-1}. At 400 °C, $k = 7.8\ \text{mol}^{-1}\ \text{L s}^{-1}$. What is the value of k at 430 °C?

Recall from the start of the chapter that the conversion of diamond into graphite is very slow, even though graphite is thermodynamically stable under standard conditions at room temp erature. The reason for this is that the activation energy for the process, which involves breaking strong carbon–carbon bonds, is high (it requires temperatures higher than 1500 °C under exclusion of oxygen). Just because a product is thermo dynamically stable does not mean that its formation will be rapid. A thermodynamically unstable product can exist under standard conditions if a large activation energy is required for its reaction. Because of this, diamond is called *metastable* at atmospheric pressure and room temperature.

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15.6 Reaction Mechanisms

At the beginning of this chapter we mentioned that most reactions do not occur in a single step. Instead, the net overall reaction is the result of a series of simple reactions, each of which is called an elementary reaction. An **elementary reaction** is a reaction in which one or more of the chemical species reacts directly to form products in a single reaction step and with a single transition state. In these cases, the rate law can be written from its chemical equation, using its coefficients as exponents for the concentration terms without requiring experiments to determine the exponents. The entire series of elementary reactions is called the reaction mechanism. For most reactions, the individual elementary reactions cannot actually be observed; instead, we see only the net reaction. Therefore, the mechanism a chemist writes is really a *theory* about what occurs step-by-step as the reactants are changed to the products.

What makes an elementary reaction 'elementary'? Remember that the exponents of the concentration terms for the rate law of an *overall* reaction (the order) bear no necessary relationship to the coefficients in the overall balanced equation. As we keep emphasising, the exponents in the overall rate law must be determined experimentally. So what makes an elementary reaction 'elementary' is that a simple relationship between coefficients and exponents *does exist.*

Because the individual steps in a mechanism sometimes cannot be observed directly, devising a mechanism for a reaction requires some ingenuity. However, we can immediately tell whether a proposed mechanism is feasible. The *overall rate law derived from the mechanism must agree with the observed rate law for the overall reaction*.

Let's see how the exponents of the concentration terms in a rate law for an elementary reaction can be devised. Consider the following example of an elementary reaction that involves collisions between two identical molecules leading directly to the products.

$$2NO_2 \rightarrow NO_3 + NO$$

$$\text{rate of reaction} = k[NO_2]^n$$

How can we predict the value of the exponent *n*? If the NO_2 concentration was doubled, there would be *twice* as many individual NO_2 molecules and *each* would have *twice* as many neighbours with which to collide. The number of NO_2-to-NO_2 collisions per second therefore would increase by a factor of 4, resulting in an increase in the rate by a factor of 4, which is 2^2. Earlier we saw that, when doubling a concentration leads to a fourfold increase in the rate, the concentration of that reactant is raised to the second power in the rate law. Thus, if $2NO_2 \rightarrow NO_3 + NO$ represents an elementary reaction, its rate law should be:

$$\text{rate of reaction} = k[NO_2]^2$$

By definition, the exponent in the rate law for an elementary reaction is the same as the coefficient in the chemical equation. If we found, experimentally, that the exponent in this rate law was not equal to 2, the reaction is not really an elementary reaction. Another way to define an elementary reaction is by its molecularity. **Molecularity** is the number of species that must collide to produce the reaction in an elementary reaction. The order of an elementary reaction is the same as the molecularity of that reaction:

- An elementary reaction involving one molecule is *unimolecular* and has a first-order rate law.
- An elementary reaction involving two species is *bimolecular* and has a second-order rate law.
- An elementary reaction involving three species is *termolecular* and has a third-order rate law. (There is low probability that three molecules will collide with the correct orientation and sufficient energy to surmount the activation barrier, so termolecular reactions are extremely rare.)

Remember that this rule applies only to *elementary reactions*. If all we know is the balanced equation for the overall reaction, the only way we can find the exponents of the rate equation is by doing experiments.

The Rate-determining Step

The rate law of an elementary reaction helps chemists to determine possible reaction mechanisms. How does this work? Let us consider the gaseous reaction:

$$2NO_2Cl \rightarrow 2NO_2 + Cl_2$$

Experimentally, the rate is first order in NO_2Cl, so the rate law is:

$$\text{rate of reaction} = k[NO_2Cl]$$

The first question we might ask is: Could the overall reaction ($2NO_2Cl \rightarrow 2NO_2 + Cl_2$) occur in a single step by the collision of two NO_2Cl molecules? The answer is no, because then it would be an elementary reaction and the predicted rate law would include a squared term, $[NO_2Cl]^2$. But the experimental rate law is first order in NO_2Cl. So the predicted and experimental rate laws don't agree, and we must look further to find the mechanism of the reaction.

On the basis of chemical intuition and other information, chemists believe the actual mechanism of the reaction is the following two-step sequence of elementary reactions.

$$NO_2Cl \xrightarrow{k_1} NO_2 + Cl \quad \text{(slow)}$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2 \quad \text{(fast)}$$

The Cl atom formed here in the first step is an intermediate. In this reaction, we never actually observe the Cl atom because, once it is formed, it quickly reacts in the second step. Recall from section 15.5 that an intermediate is higher in energy and has a more limited lifetime than the reactants and products.

Notice that when the two reactions are added, the intermediate, Cl, drops out and we obtain the net overall reaction $2NO_2Cl \rightarrow 2NO_2 + Cl_2$. *Being able to add the elementary reactions and obtain the overall reaction is another major test of a mechanism.*

In any multistep mechanism, one step is usually much slower than the others. In this mechanism, for example, it is believed that the first step is slow, and that, once a Cl atom forms, it reacts very rapidly with another NO_2Cl molecule to give the final products.

The final products of a multistep reaction cannot appear more rapidly than do the products of the slow step, so the slow step in a mechanism is called the **rate-determining step** or ratelimiting step. In the two-step mechanism for this particular reaction, then, the first reaction is the rate-determining step because the final products cannot be formed faster than the rate at which Cl atoms form.

The rate-determining step is similar to a slow worker on an assembly line. The production rate depends on how quickly the slow worker works, regardless of how fast the other workers are. The factors that control the speed of the rate-determining step therefore also control the overall rate of the reaction. This means that *the rate law for the rate-determining step is directly related to the rate law for the overall reaction.* Note that the rate-determining step can be any of the steps in a sequence of elementary reactions (and not necessarily only the first step, as in our example).

Because the rate-determining step is an elementary reaction, we can predict its rate law from the coefficients of its reactants. The coefficient of NO_2Cl in its relatively slow breakdown to NO_2 and Cl is 1. Therefore, the rate law predicted for the first step is:

$$\text{rate} = k_1[NO_2Cl]$$

Notice that the predicted rate law derived for the two-step mechanism agrees with the experimentally measured rate law. Although scientists may never actually *prove* the correctness of a proposed mechanism, at least considerable support for it can be provided. From the standpoint of kinetics, therefore, the

mechanism is reasonable.

WORKED EXAMPLE 15.13

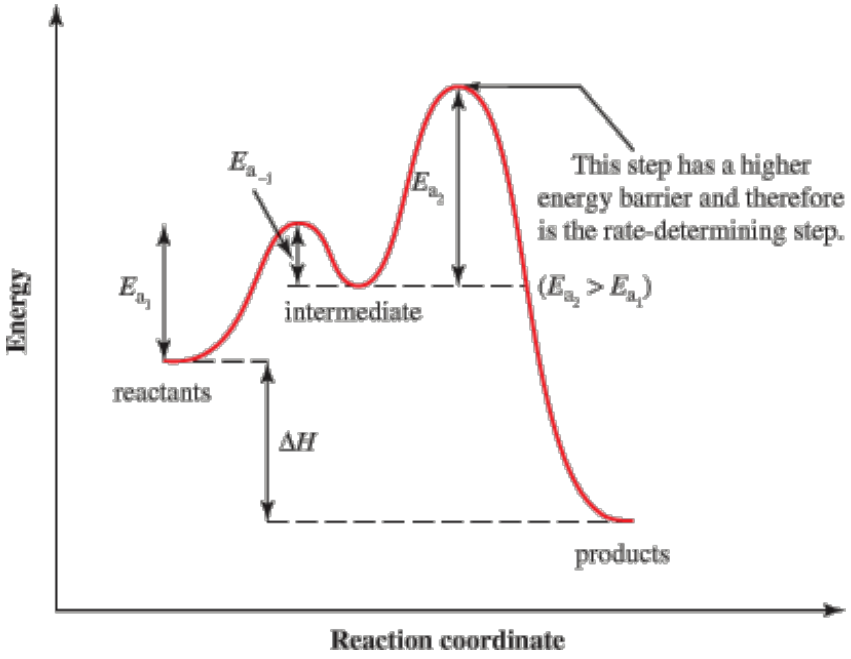
Drawing an Energy Diagram

Draw an energy diagram for a two-step exothermic reaction in which the second step is rate determining.

Analysis

A two-step reaction involves the formation of an intermediate. If the reaction is exothermic, the products must be lower in energy than the reactants. In order for the second step to be rate determining, it must have a higher energy barrier.

Solution



In the diagram, the intermediate is of relatively high energy and is formed in a reversible equilibrium (the activation energy required to re-form the reactants is $E_{a\text{-}1}$). The effective energy required for the reaction is the difference between the energies of the second transition state and the reactants. The intermediate could also be of relatively low energy, but the activation energy for the second transition state will be correspondingly higher.

PRACTICE EXERCISE 15.10

In what way would the energy diagram drawn in worked example 15.13 change if the reaction were endothermic?

Mechanisms with Fast, Reversible Steps

We will now study the following gas phase reaction:

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

The experimentally determined rate law is:

$$\text{rate of reaction} = k[NO]^2[H_2] \quad \text{(experimental)}$$

We can quickly tell from this rate law that $2NO + 2H_2 \rightarrow N_2 + 2H_2O$ is not itself an elementary reaction. If it were, the exponent for $[H_2]$ would be 2. Obviously, a mechanism involving two or more steps must be involved.

A chemically reasonable mechanism that yields the correct form for the rate law consists of the following two steps.

$$2NO + H_2 \rightarrow N_2O + H_2O \quad \text{(slow)}$$
$$N_2O + H_2 \rightarrow N_2 + H_2O \quad \text{(fast)}$$

One test of the mechanism, as we said, is that the two equations must add to give the correct overall equation, and they do. Further, the chemistry of the second step has actually been observed in separate experiments. N_2O is known as 'laughing gas' and is used as an anaesthetic in medicine and dentistry. It does react with H_2 to give N_2 and H_2O. Another test of the mechanism involves the coefficients of NO and H_2 in the predicted rate law for the first step, the supposed rate- determining step.

$$\text{rate of reaction} = k[NO]^2[H_2] \quad \text{(predicted)}$$

Chemistry Research

Reactions of CO_2 in Water: a Simple Kinetic System?

Associate Professor Marcel Maeder, University of Newcastle

In the Chemistry Research feature in chapter 9, we summarised our studies of the equilibrium processes involved in the dissolution of CO_2 in water. Here, we now present the results of our investigations into the kinetics of the reactions of CO_2 in water.

It has been known for many years that there are two important reactions involved in CO_2 dissolving in water. The first is the reversible reaction with water to form carbonic acid:

$$CO_2(aq) + H_2O(l) \underset{k_{-H_2O}}{\overset{k_{H_2O}}{\rightleftharpoons}} H_2CO_3(aq)$$

Dissolved CO_2 can also react with hydroxide ions to give bicarbonate ions:

$$CO_2(aq) + OH^-(aq) \underset{k_{-OH}}{\overset{k_{OH}}{\rightleftharpoons}} HCO_3^-(aq)$$

While the reaction of CO_2 with the hydroxide ion is much faster than that with water, at neutral or acidic pH the reaction with water dominates as the concentration of OH^- is small. At around pH 8.5, the hydroxide ion concentration is high enough for the hydroxide path to catch up, and at higher pH the hydroxide path predominates.

Measuring the forward and reverse rate constants for the above reactions is not necessarily a

straightforward process. One approach has been to rapidly mix a saturated solution of CO_2, to which an appropriate indicator has been added, with a solution of NaOH of similar concentration, and measure the resulting absorbance changes as a function of time. This is done using a stopped-flow spectrometer, an apparatus that mixes two solutions extremely rapidly (in milliseconds) and monitors the absorbance of the resulting solution over a range of wavelengths. A sample series of our results is shown in figure 15.19.

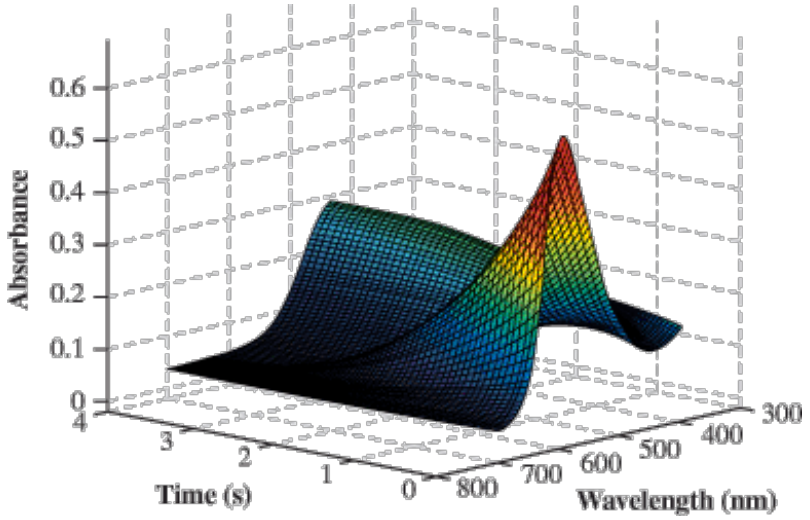


FIGURE 15.19 Absorbance changes over 4 seconds following mixing CO_2 and NaOH.

Figure 15.19 displays the absorbance changes at 25.0 °C of a solution that is 0.030 M in CO_2 and 0.020 M in NaOH, in the presence of 10^{-4} M thymol blue indicator over 4 seconds. The indicator essentially tells us the $[H_3O^+]$ concentration as a function of time and this knowledge, along with equilibrium data, allows the determination of the rate constants through sophisticated computer analysis of the data.

Such analysis gives the concentrations of the major species over time, as shown in figure 15.20a. There is a very fast initial reaction of CO_2 with OH^- that results in a fast decrease in $[CO_2]$ (black trace) and increase in $[CO_3^{2-}]$ (red trace). The reaction then slows down as the slower reaction of CO_2 with water begins to dominate. In a parallel process, carbonate ions are protonated to bicarbonate ions, creating a buffered solution.

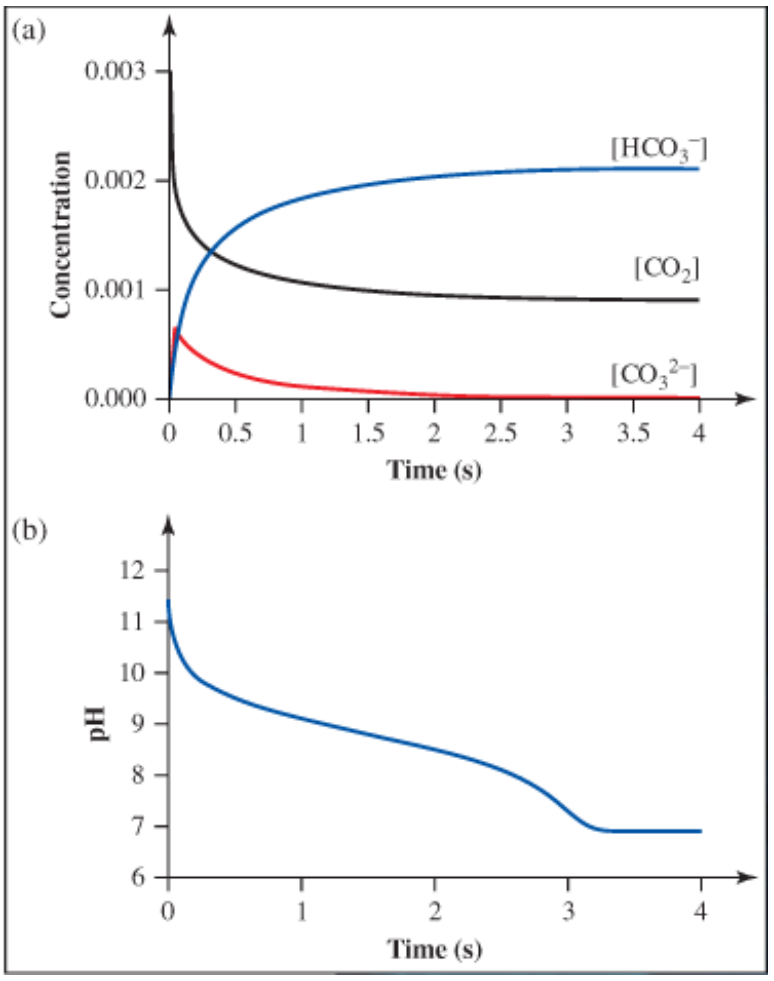


FIGURE 15.20 Changes in
(a) species concentrations and
(b) pH over 4 seconds following mixing CO_2 with NaOH.

The graph of pH as a function of time (figure 15.20b) shows a sharp decrease in pH due to the reaction of OH^-; subsequently the pH drops much more slowly, which is mainly due to the buffer action. After about 2.5 seconds the carbonate is exhausted, there is no buffer action and the pH drops faster again to the reach the equilibrium pH of just below 7.

Although this is an apparently relatively simple system, extensive data are required to obtain a complete kinetic description of the system, and it is necessary to collect kinetic data under a wide variety of initial $[CO_2]$ and $[OH^-]$ conditions. Results from this fundamental research can then be used to help understand any process that involves CO_2 in the second to minute time scale, e.g. respiration, even if these processes are enzymatically catalysed and thus much faster again.

This rate equation does match the experimental rate law, but there is still a serious flaw in the proposed mechanism. If the postulated slow step actually describes an elementary reaction, it would involve the simultaneous collision between three molecules, two NO molecules and one H_2 molecule. As mentioned previously, termolecular processes are very rare. Thus, chemists believe the reaction proceeds by the following three-step sequence of bimolecular elementary reactions.

$$2NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \quad \text{(fast)}$$

$$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O \quad \text{(slow)}$$

$$N_2O_2 + H_2 \xrightarrow{k_3} N_2 + H_2O \quad \text{(fast)}$$

In this mechanism the first step is proposed to be a rapidly established equilibrium in which the unstable intermediate N_2O_2 forms by dimerisation of NO in the forward reaction and then quickly decomposes into NO by the reverse reaction. The rate-determining step is the reaction of N_2O_2 with H_2 to give N_2O and a water molecule. The third step is the reaction shown last. Once again, notice that the three steps add to give the correct net overall change.

Since the second step is rate determining, the rate law for the reaction should match the rate law for this step. We predict this to be:

$$\text{rate of reaction} = k[N_2O_2]\,[H_2]$$

However, the experimental rate law does not contain the species N_2O_2. Therefore, we must find a way to express the concentration of N_2O_2 in terms of the reactants in the overall reaction. To do this, let's look closely at the first step of the mechanism, which we view as a reversible reaction.

The rate of reaction in the forward direction, in which NO is the reactant, is:

$$\text{rate of reaction (forward)} = k_1[NO]^2$$

The rate of the reverse reaction, in which N_2O_2 is the reactant, is:

$$\text{rate of reaction (reverse)} = k_{-1}[N_2O_2]$$

If we view this as a dynamic equilibrium, then the rates of the forward and reverse reactions are equal, which means that:

$$k_1[NO_2]^2 = k_{-1}[N_2O_2]$$

Since we would like to eliminate $[N_2O_2]$ from the rate law (rate = $k[N_2O_2][H_2]$), let's rearrange the above equation.

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

Substituting into the rate law:

$$\text{rate of reaction} = k[N_2O_2]\,[H_2]$$

yields:

$$\text{rate of reaction} = k\left(\frac{k_1}{k_{-1}}\right)[NO]^2[H_2]$$

Combining all the constants into one (k') gives:

$$\text{rate of reaction} = k'[NO]^2[H_2]$$

Now the rate law derived from the mechanism matches the rate law obtained experimentally. The three-step mechanism does appear to be reasonable on the basis of kinetics.

The procedure we have worked through here applies to many reactions that proceed by mechanisms involving sequential steps. Steps that precede the rate-determining step are considered to be rapidly established equilibria involving unstable intermediates.

PRACTICE EXERCISE 15.11

Ozone, O_3, reacts with nitric oxide, NO, to form nitrogen dioxide and oxygen.

$$NO + O_3 \rightarrow NO_2 + O_2$$

This is one of the reactions involved in the formation of photochemical smog. If this reaction occurs in a single step, what is the expected rate law for the reaction?

The Steady-state Approximation

Often, in simple cases of reaction mechanisms, one step is the rate-determining step. However, it is not unusual that, in complex reaction mechanisms, the rate-determining step may vary when the reaction conditions are changed. In such cases, where the rate-determining step cannot easily be chosen, the **steady-state approximation** can be used to analyse the reaction. The basic idea of this method is the assumption that the concentration of any intermediate remains constant as the reaction proceeds. (Remember that an intermediate is neither a reactant nor a product, but it is produced and consumed during the reaction.) This will generally be the case only when the concentration of the intermediate remains low over the duration of the reaction.

Let's consider the following hypothetical reaction.

$$2AB + C_2 \rightarrow A_2B + C_2B$$

This reaction may proceed via the following mechanism.

$$2AB \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2B_2$$

$$A_2B_2 + C_2 \overset{k_2}{\rightarrow} A_2B + C_2B$$

The intermediate in this mechanism is A_2B_2. If the concentration of A_2B_2 remains constant throughout the reaction, or is assumed to remain constant, i.e.:

$$\frac{d[A_2B_2]}{dt} = 0$$

the steady-state approximation can be applied.

Next, all steps that are producing and consuming intermediate A_2B_2 need to be identified, and the rate law for each has to be written. Then the steady-state approximation is applied by setting the total rate of formation of A_2B_2 equal to its total rate of consumption.

$$\text{rate of } A_2B_2 \text{ formation} = \text{rate of } A_2B_2 \text{ consumption, therefore} \frac{d[\mathbf{A_2B_2}]}{dt} = 0$$

The general procedure is demonstrated in the following:

1. Rate of formation of A_2B_2
   In this mechanism, A_2B_2 is produced only in the forward reaction of the first elementary step. The rate law for this step is:
   $$\frac{d[\mathbf{A_2B_2}]}{dt} = k_1[AB]^2$$
2. Rate of consumption of A_2B_2
   A_2B_2 is consumed in the reverse reaction of the first step and in the second step. The rate laws for these steps are:

$$-\frac{d[A_2B_2]}{dt} = k_{-1}[A_2B_2]$$

and

$$-\frac{d[A_2B_2]}{dt} = k_2[A_2B_2][C_2]$$

3. Application of the steady-state condition
   Under steady-state conditions for the intermediate A_2B_2:

$$\begin{aligned} \textit{rate of formation} &= \textit{rate of consumption} \\ k_1[AB]^2 &= k_{-1}[A_2B_2] + k_2[A_2B_2][C_2] = [A_2B_2](k_{-1} + k_2[C_2]) \end{aligned}$$

   If we solve for the concentration of our intermediate $[A_2B_2]$, we get:

$$[A_2B_2] = \frac{k_1[AB]^2}{k_{-1} + k_2[C_2]}$$

4. The rate law for the overall reaction
   Now, the rate law for the overall reaction $2AB + C_2 \rightarrow A_2B + C_2B$ is written. This can be done in various ways, depending on whether we chose a reactant or a product to represent the rate of reaction. In this example we use the decomposition of C_2 to define the rate of reaction.

$$\text{rate of reaction} = -\frac{d[C_2]}{dt}$$

   C_2 is consumed only in the second step of the mechanism, therefore:

$$-\frac{d[C_2]}{dt} = k_2[A_2B_2][C_2]$$

The equation $[A_2B_2] = \frac{k_1[AB]^2}{k_{-1} + k_2[C_2]}$ provides us with an expression for the concentration of our intermediate A_2B_2. Substitution of this expression into the rate law gives:

$$\begin{aligned} \text{rate of reaction} = -\frac{d[C_2]}{dt} &= k_2[C_2]\left(\frac{k_1[AB]^2}{k_{-1} + k_2[C_2]}\right) \\ &= \frac{k_1k_2[C_2][AB]^2}{k_{-1} + k_2[C_2]} \end{aligned}$$

This is the overall rate law for the proposed mechanism based on the steady-state approximation. This rate law is quite complicated (this is common for rate laws determined using the steady-state analysis). The usual way to test the validity of the rate law involves choosing concentration conditions that result in a simplification of the rate law.

For example, if the reaction between AB and C_2 is studied under conditions where the concentration of C_2 is large, the reverse reaction of step 1 can be neglected, since all A_2B_2 formed in the first reaction rapidly reacts with C_2 to produce $A_2B + C_2B$. Then we have:

$$k_2[C_2] >> k_{-1}$$

This reduces the full rate law to:

$$\text{rate of reaction} = \frac{k_1k_2[C_2][AB]^2}{k_2[C_2]} = k_1[AB]^2$$

Thus, if the suggested mechanism is valid, at sufficiently high concentrations of C_2, the reaction should show a second-order dependence on the concentration of AB.

On the other hand, if the reaction is performed under conditions of low C_2 concentrations, the intermediate

A_2B_2 will preferentially decompose into AB through the reverse reaction of step 1 rather than reacting with C_2. Then, we have:

$$k_{-1} >> k_2[C_2]$$

This leads to a rate law of:

$$\text{rate of reaction} = \frac{k_1 k_2}{k_{-1}}[C_2][AB]^2 = k'[C_2][AB]^2$$

Studies under these conditions should show first-order dependence on $[C_2]$ and second-order dependence on $[AB]$, if the assumed mechanism is correct.

WORKED EXAMPLE 15.14

Using the Steady-state Approximation for Constructing a Rate Law

The experimentally determined rate law for the decomposition of ozone ($2O_3 \rightarrow 3O_2$) is:

$$-\frac{d[O_3]}{dt} = k\frac{[O_3]^2}{[O_2]}$$

The following mechanism has been proposed to account for the rate law.

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O \quad \text{(step 1)}$$

$$O + O_3 \xrightarrow{k_2} 2O_2 \quad \text{(step 2)}$$

Derive the rate law for the decomposition of ozone by applying the steady-state approximation to the concentration of atomic oxygen.

Analysis

The procedure to solve such a problem consists of several steps.

(a) Construct the rate law in terms of consumption of ozone.

(b) Construct the steady-state expression for the intermediate O by applying the criterion $\frac{d[O]}{dt} = 0$, which means that rate of formation of O = rate of consumption of O. We have to identify each step that produces or consumes O and write the appropriate rate law for each. The sum of the rate laws that produce O are then set equal to the sum of the rate laws that consume O.

(c) The resulting steady-state approximation is then solved for [O].

(d) The expression from step (b) for [O] is used to substitute for the concentration of the intermediate found in the rate law of step (a). By doing this we obtain an overall rate law that contains only reactant and/or product concentrations.

Solution

(a) The overall reaction is the sum of the two reaction steps. Ozone is consumed in the forward reaction of step 1 and step 2, and is produced in the reverse reaction of step 1. The rate law for the consumption of ozone can then be written as:

$$-\frac{d[O_3]}{dt} = k_1[O_3] - (k_{-1}[O_2][O] + k_2[O_3][O]) \quad \text{(equation 1)}$$

(b) O is produced only in the forward reaction of step 1. Thus, rate of formation of O = $k_1[O_3]$. O is consumed in the reverse reaction of step 1 and in step 2. Therefore, the rate of consumption of O = $k_{-1}[O_2][O] + k_2[O_3][O]$.
Applying the steady-state condition gives:

$$k_1[O_3] = k_{-1}[O_2][O] + k_2[O_3][O]$$

(c) Solving for the concentration of O:

$$\begin{aligned} k_1[O_3] &= [O](k_{-1}[O_2] + k_2[O_3]) \\ [O] &= \frac{k_1[O_3]}{k_{-1}[O_3] + k_2[O_3]} \end{aligned}$$

(d) Substitute for [O] in equation 1:

$$\begin{aligned} -\frac{d[O_3]}{dt} &= k_1[O_3] - \frac{(k_{-1}[O_2] + k_2[O_3])k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} \\ &= k_1[O_3] - \frac{k_1k_{-1}[O_2][O_3] + k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]} \end{aligned}$$

Multiply the first term on the right-hand side by:

$$\frac{k_{-1}[O_2] + k_2[O_3]}{k_{-1}[O_2] + k_2[O_3]}$$

to obtain:

$$\begin{aligned} -\frac{d[O_3]}{dt} &= \frac{k_1[O_3](k_{-1}[O_2] + k_2[O_3]) - k_1k_{-1}[O_2][O_3] + k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]} \\ &= \frac{k_1k_{-1}[O_3][O_2] + k_1k_2[O_3]^2 - k_1k_{-1}[O_3][O_2] + k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]} \end{aligned}$$

$k_1k_{-1}[O_2][O_3]$ cancels out giving:

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]} \qquad \text{(equation 2)}$$

Now when $[O_2]$ is large ($k_{-1}[O_2] >> k_2[O_3]$) the denominator reduces to $k_{-1}[O_2]$, which means that equation 2 reduces to:

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2]}$$

which is effectively:

$$-\frac{d[O_3]}{dt} = \frac{k_{obs}[O_3]^2}{[O_2]}$$

the same as the experimentally determined rate law.

Is our answer reasonable?

The rate law obtained using the steady-state approximation is the same as the observed rate law. This is what we wanted.

PRACTICE EXERCISE 15.12

A possible mechanism for the decomposition

of NO_2Cl is:

$$NO_2Cl \rightarrow NO_2 + Cl$$
$$NO_2Cl + Cl \rightarrow NO_2 + Cl_2$$

What would the predicted rate law be if the second step in the mechanism were the rate-determining step?

Chemical Connections

The Antarctic Ozone Hole

The ozone layer in the stratosphere (>12 km high) shields the Earth from damaging UV radiation from the Sun. Over the past 30 years, evidence has been building that human activities have caused a dangerous reduction in the stratospheric ozone layer. When the ozone hole was detected over Antarctica, its creation was soon linked to an increase in halogen-containing compounds produced from chlorofluorocarbons (CFCs), chlorinated solvents, halons (bromine-containing compounds) and bromomethane released into the atmosphere. These chemicals were once widely used as refrigerants, aerosols, cleaning solvents, fire-fighting chemicals and fumigants. Figure 15.21 shows the development of the ozone hole in the Antarctic spring from 1979 to 2010. The amount of ozone is measured in Dobson units (DU), where 1 DU is defined as the amount of ozone that would constitute a layer 0.01 mm thick at 0 °C and 1.013×10^5 Pa.

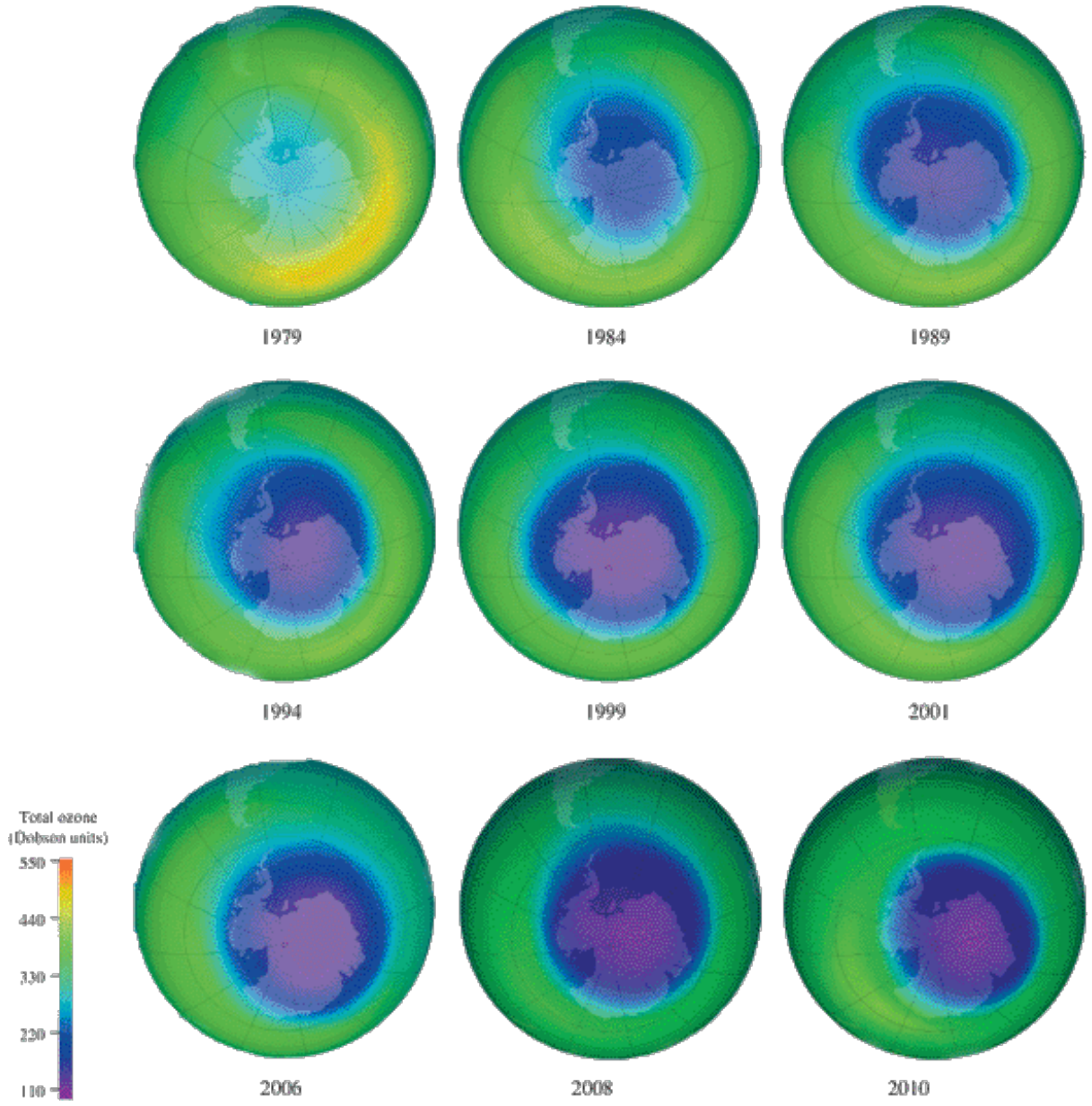


FIGURE 15.21 Average ozone level (Dobson units) for October over the Southern Hemisphere in 1979, 1984, 1989, 1994, 1999, 2001, 2006, 2008 and 2010. NASA Ozone Hole Watch, http://ozonewatch.gsfc.nasa.gov

How does the ozone loss occur? The most commonly found breakdown products (often called *reservoirs*) of CFCs are hydrochloric acid, HCl, and chlorine nitrate, $ClONO_2$. In addition, dinitrogen pentoxide, N_2O_5, is a reservoir of nitrogen oxides and plays an important role in the chemistry of ozone depletion. HCl and $ClONO_2$ (and their bromine counterparts) are converted into more active forms of chlorine (or bromine) on the surface of *polar stratospheric clouds* (PSCs). These PSCs are formed during winter polar nights, when sunlight does not reach the South Pole. A strong circumpolar wind (polar vortex) develops in the middle of the stratosphere; this isolates the air over the polar region from the remaining atmosphere. Because of the lack of sunlight, air within the vortex can get very cold; PSCs form when the temperature falls below –80 °C. These clouds consist of nitric acid trihydrate, $HNO_3 \cdot 3H_2O$, but, as the temperature decreases even further, larger droplets of water ice can form with nitric acid dissolved in them. These PSCs are the key to ozone loss over Antarctica.

The most important reactions leading eventually to the destruction of ozone on PSCs are those that form HNO_3, H_2O and Cl_2 from $ClONO_2$, HCl and N_2O_5 through the intermediate HOCl.

$$\begin{aligned}
HCl + ClONO_2 &\rightarrow HNO_3 + Cl_2 \\
ClONO_2 + H_2O &\rightarrow HNO_3 + HOCl \\
HCl + HOCl &\rightarrow H_2O + Cl_2 \\
N_2O_5 + HCl &\rightarrow HNO_3 + ClONO_2 \\
N_2O_5 + H_2O &\rightarrow 2HNO_3
\end{aligned}$$

Once sunlight returns to the polar region in the Southern Hemisphere spring, the Cl_2 formed in the reactions above is photolysed into chlorine atoms.

$$Cl_2 + h\nu \rightarrow 2Cl$$

Chlorine atoms have an unpaired electron. Such species are called free radicals. Radicals are highly reactive because of the tendency of electrons to become paired by forming ions or covalent bonds.

Although there are high concentrations of active forms of chlorine above the South Pole, there are many more ozone molecules than chlorine species. So, how can the active chlorine destroy nearly all of the ozone? The answer lies in what is known as a *catalytic cycle*. Here, one molecule significantly changes or enables a reaction cycle without itself being altered by the cycle. The following catalytic cycle is believed to be responsible for 70% of the ozone loss over Antarctica.

$$\begin{aligned}
2Cl + 2O_3 &\rightarrow 2ClO + 2O_2 \\
ClO + ClO + M &\rightarrow Cl_2O_2 + M \\
Cl_2O_2 + h\nu &\rightarrow Cl + ClO_2 \\
ClO_2 + M &\rightarrow Cl + O_2 + M \\
\hline
\text{Net:} \quad 2O_3 &\rightarrow 3O_2
\end{aligned}$$

In these equations, *M* stands for a *collision partner*, which assists in providing the energy required to surmount the activation barrier for the reaction, but which is not involved in the reaction itself. In this cycle, two chlorine atoms catalyse the destruction of two ozone molecules to give three oxygen molecules.

As a consequence of the ozone hole, Australians and New Zealanders suffer the highest rates of skin cancer in the world (around 1400 Australians and more than 300 New Zealanders die from skin cancer each year). An international agreement called the Montreal Protocol, originally signed in 1987, limits the production and use of ozone-depleting substances. Since that time, a reduction in the rate of ozone loss has been measured, and the concentration of CFCs in the atmosphere is levelling off. In fact, in the last few years, it appears that the ozone holes have been less severe. It is estimated that, if all countries achieve the targets set by the Montreal Protocol, the ozone in the stratosphere should eventually recover. However, because of a long lag time in chemicals reaching the stratosphere, that recovery is likely to take 50 years.

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15.7 Catalysts

A **catalyst** is a substance that changes the rate of a chemical reaction without being used up. In other words, all of the catalyst added at the start of a reaction is present chemically unchanged after the reaction has gone to completion. The action caused by a catalyst is called **catalysis**. Broadly speaking, there are two kinds of catalysts; *positive catalysts* speed up reactions, and *negative catalysts*, usually called *inhibitors*, slow reactions down. In future, when we use the term 'catalyst' we mean positive catalyst.

Although the catalyst is not part of the overall reaction, it does participate by changing the mechanism of the reaction. The catalyst provides a path to the products that has a rate-determining step with a lower activation energy than that of the uncatalysed reaction (see figure 15.22). Because the activation energy along this new route is lower, a greater fraction of the collisions of the reactant molecules have the minimum energy needed to react, so the reaction proceeds faster. Note that a catalyst cannot change ΔH for a reaction. An endothermic reaction can not become exothermic by using a catalyst.

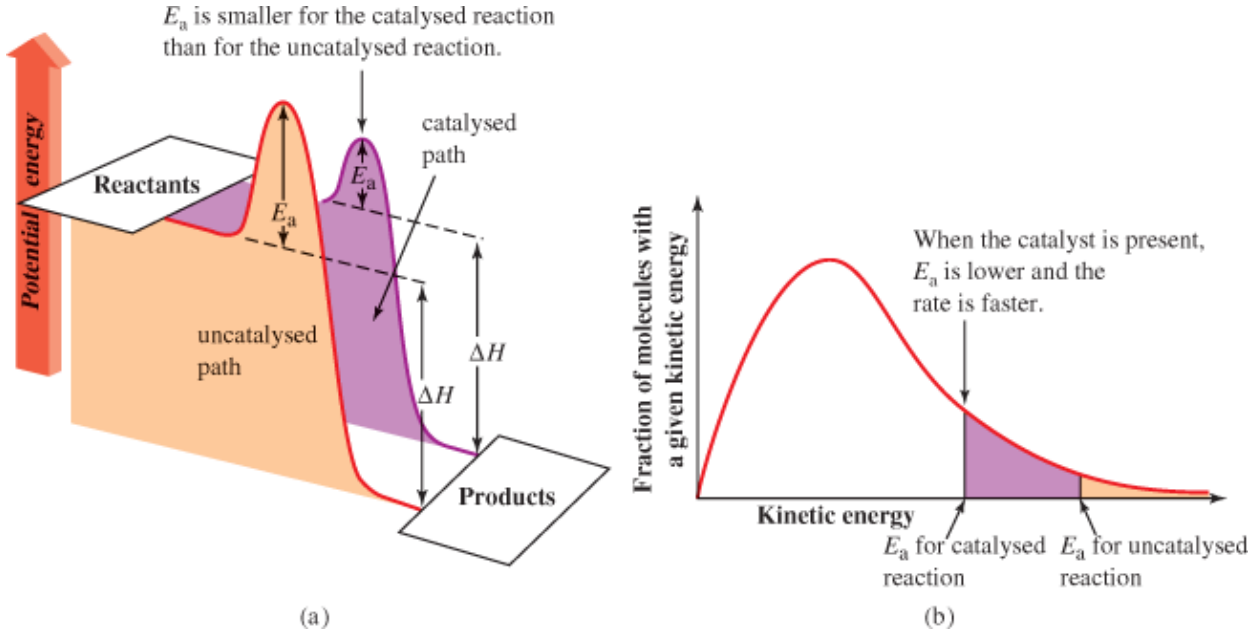


FIGURE 15.22 Effect of a catalyst on a reaction:

(a) The catalyst provides an alternative, lower energy path from the reactants to the products, which proceeds through a different pathway involving different intermediates.

(b) A larger fraction of molecules have sufficient energy to react when the catalysed path is available. Although not shown, the purple shading continues to the end of the graph.

Catalysts can be divided into two groups — **homogeneous catalysts**, which exist in the same phase as the reactants, and **heterogeneous catalysts**, which exist in a separate phase.

Homogeneous Catalysts

Homogeneous catalysts are in the same phase as the reactants. An example of homogeneous catalysis is found in the *lead chamber process* for manufacturing sulfuric acid. Sulfuric acid is one of the most important chemicals in industry. It is also the acid used in lead car batteries (see section 12.6). To make sulfuric acid by this process, sulfur is burned to give SO_2, which is then oxidised to SO_3. The SO_3 is dissolved in water to give H_2SO_4.

$$S + O_2 \rightarrow SO_2$$

$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Unassisted, the second reaction, oxidation of SO_2 to SO_3, occurs slowly. In the lead chamber process, the SO_2 is combined with a mixture of NO, NO_2, air and steam in large lead-lined reaction chambers. The NO_2 readily oxidises

the SO_2 to give NO and SO_3. The NO is then reoxidised to NO_2 by oxygen.

$$NO_2 + SO_2 \rightarrow NO + SO_3$$
$$NO + \frac{1}{2}O_2 \rightarrow NO_2$$

The NO_2 serves as a catalyst by being an oxygen carrier and by providing a lower energy path for the oxidation of SO_2 to SO_3. Notice, as must be true for any catalyst, the NO_2 is regenerated; it has not been permanently changed.

Heterogeneous Catalysts

Heterogeneous catalysts are in a separate phase from the reactants. A heterogeneous catalyst is commonly a solid and usually functions by promoting a reaction on its surface. One or more of the reactant molecules are adsorbed onto the surface of the catalyst, where an interaction with the surface increases their reactivity. An example is the industrial synthesis of ammonia from hydrogen and nitrogen by the Haber–Bosch process.

$$3H_2 + N_2 \rightarrow 2NH_2$$

The Haber–Bosch process (figure 15.23) is one of the most important processes in industry, as it harnesses the abundance of nitrogen in the atmosphere to generate ammonia (nitrogen fixation). Ammonia is the precursor to nitrate fertilisers and other products.

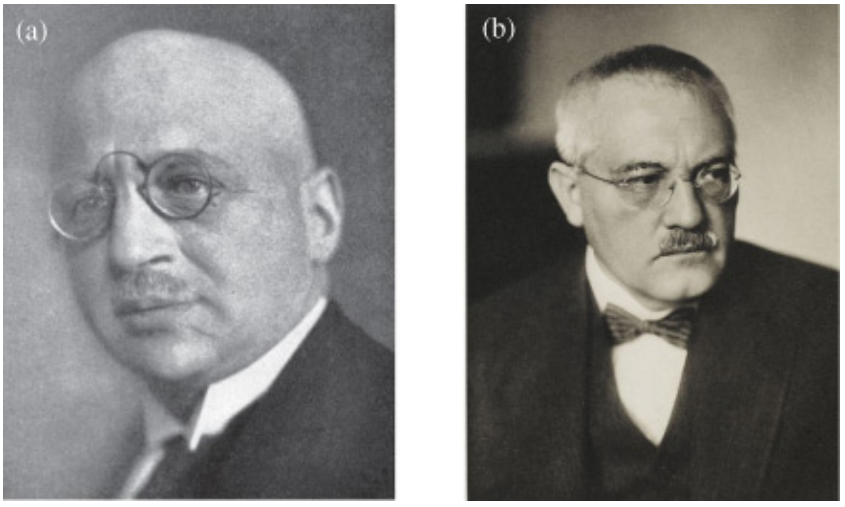


FIGURE 15.23 (a) Fritz Haber (Nobel Prize in chemistry, 1918) and (b) Carl Bosch (Nobel Prize in chemistry, 1931), who developed the Haber–Bosch process of ammonia synthesis.
SPL

As we have mentioned earlier, without a catalyst, this reaction is extremely slow. In the Haber– Bosch process, the reaction takes place on the surface of an iron catalyst that contains traces of aluminium and potassium oxides. It is thought that hydrogen and nitrogen molecules dissociate into atoms while being held on the catalytic surface. The hydrogen atoms then combine with the nitrogen atoms to form ammonia. Finally, the completed ammonia molecule breaks away, freeing the surface of the catalyst for further reaction. This sequence of steps is illustrated in figure 15.24.

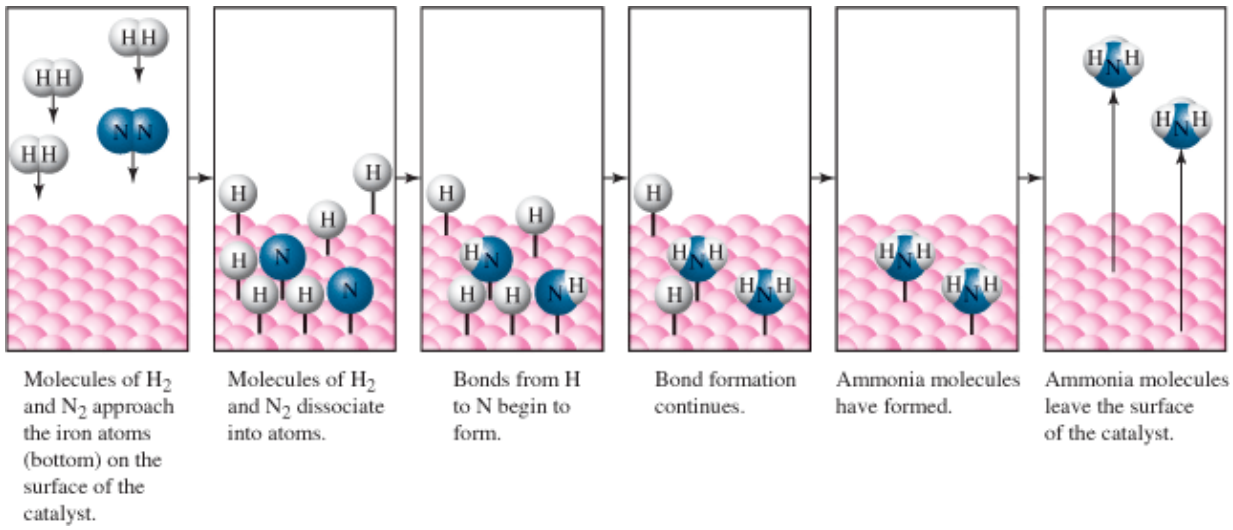


FIGURE 15.24 The Haber–Bosch process. Catalytic formation of ammonia molecules from hydrogen and nitrogen on the surface of a catalyst. Mary Evans Picture Library

Heterogeneous catalysts are used in many important commercial processes. The petroleum industry uses heterogeneous catalysts to crack hydrocarbons into smaller fragments and then re-form them into the useful components of petrol. The availability of such catalysts allows refineries to produce petrol, jet fuel and heating oil from crude oil in any ratio necessary to meet the demands of the marketplace.

A vehicle that uses unleaded petrol is equipped with a catalytic converter (figure 15.25) designed to lower the concentrations of exhaust pollutants, such as carbon monoxide, unburned hydrocarbons and nitrogen oxides. Air is introduced into the exhaust stream that then passes over a catalyst that adsorbs CO, NO and O_2. The NO dissociates into N and O atoms, and the O_2 also dissociates into atoms. Pairing of nitrogen atoms then produces N_2, and oxidation of CO by oxygen atoms produces CO_2. Unburned hydrocarbons are also oxidised to CO_2 and H_2O. The catalysts in catalytic converters are deactivated or 'poisoned' by lead-based octane boosters such as tetraethyl lead, $Pb(C_2H_5)_4$, and 'leaded' petrol cannot be legally used in vehicles anymore.



FIGURE 15.25 A modern three-way catalytic converter of the type used in most new cars. Charles D Winters

Enzyme Kinetics

Some of the most powerful homogeneous catalysts are enzymes. Enzymes (often called *biocatalysts*) consist of proteins and contain a specially shaped area called an 'active site' that lowers the energy of the transition state of the reaction being catalysed. They are very specific and usually have a dramatic effect on the reaction they control. For example, the activation energy for the acidic hydrolysis of sucrose into glucose and fructose is 107 kJ mol^{-1}. The enzyme saccharase (enzyme names have the suffix *-ase*) reduces the activation barrier of this reaction to 36 kJ mol^{-1}, which accelerates the rate by a factor of 10^{12} at blood temperature (310 K). Enzyme catalysis can be represented by a series of elementary reactions (see p. 658). Qualitatively, the starting materials, or *substrates*, *S*, are reversibly bound in the *active sites* of the enzyme, where they form an *enzyme–substrate complex*, *E·S*. The enzyme enables the

conversion of the substrate into the product, *P*, which is then released from the enzyme complex. Like all catalysts, the enzyme remains unchanged after the reaction.

Chemistry Research

Ab initio Kinetic Modelling

Professor Michelle Coote, Australian National University

Kinetic models are equations for predicting the overall outcome of a chemical process based on a total picture of the reaction conditions. To achieve a working kinetic model of a reaction, the rate expressions and rate constants for every *kinetically distinct* reaction in the process, including any possible side reactions, need to be determined. The resulting equations are solved simultaneously to give time-dependent values for the yields of the various products, as a function of the starting concentrations of the reagents. Of course, obtaining accurate values of the rate constants can be a major challenge, as they are generally not directly measurable. Instead, parameters are normally 'measured' by fitting the assumed kinetic model to the data that *are* actually measured: the time-dependent reactant and product concentrations. However, this presumes that the kinetic model is correct. If an invalid model is used, the kinetic parameters may contain hidden systematic errors that could make them less relevant. Such data may be useful to regenerate results relevant to the system to which they were fitted but, beyond that, their predictive value may be quite limited. The use of model fitting can also make it difficult to gain a precise understanding of the fundamental process involved. This is because different models can be made to fit the same data regardless of their physical validity by treating the various kinetic parameter values as 'fudge factors'. These problems become particularly significant for complicated real-world chemical reactions such as the multi-step processes involved in radical polymerisation (see section 26.3). For radical polymerisation there may be hundreds or even thousands of kinetically different reactions taking place. In such cases, a 'complete' kinetic model has too many unknown kinetic parameters to be fitted to the available data, and major simplifications are required to reduce the number of parameters to a manageable size (typically fewer than five).

To address these problems, researchers at the Australian National University have developed a new approach to kinetic modelling based on quantum chemistry. Instead of 'measuring' rate constants via model fitting, Professor Michelle Coote, who leads the group, makes predictions using well-established laws of quantum mechanics and statistical thermodynamics. In this way, the *ab initio* (from the Latin term meaning 'from the beginning') kinetic parameters are totally independent of any assumed kinetic model or measured experimental data. This means that, when they are used as inputs to a kinetic model, the kinetic model predictions are also totally independent of the measured experimental data, and their validity can be properly tested (see figure 15.26). This is in stark contrast to the conventional approach, where the model 'predictions' are tested against the same or similar data to which the model was originally fitted. Clearly it is much harder for an incorrect model to make accurate predictions when there are no fudge factors to help!

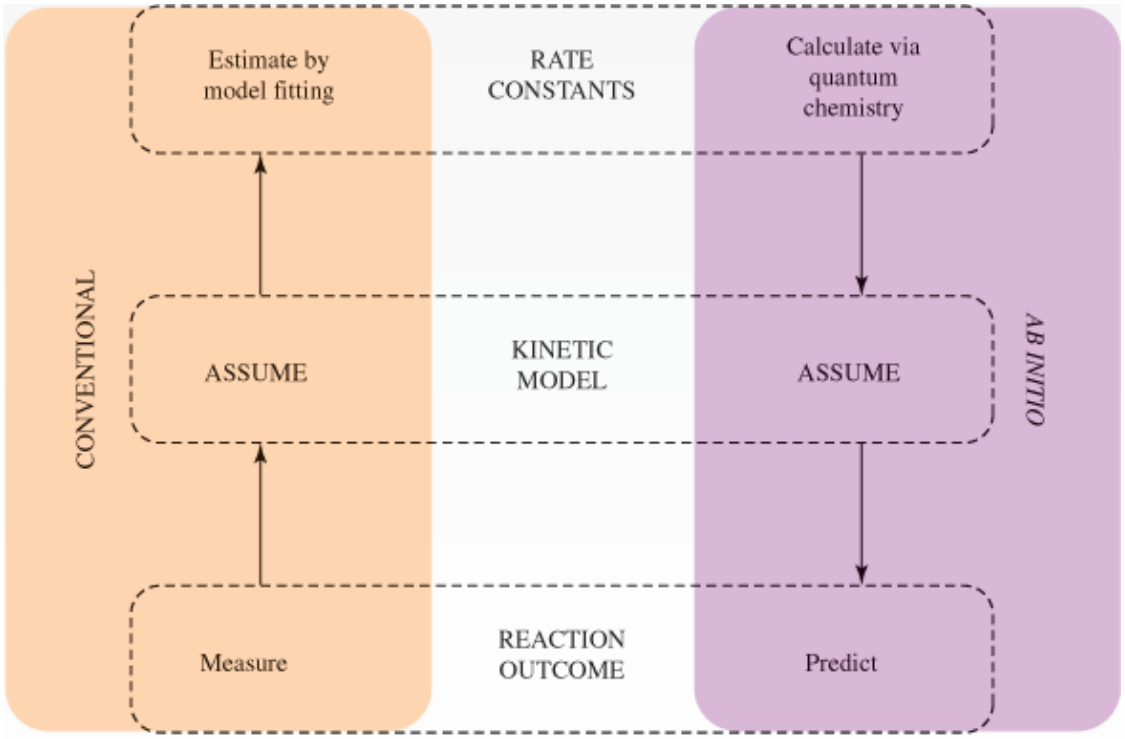


FIGURE 15.26 The relationship between conventional and *ab initio* kinetic methods.

The *ab initio* approach also makes it easier to design better models in the first place. Quantum chemical calculations can be used to identify reaction mechanisms and test whether model assumptions are correct. For example, we can use theory to determine if a given side reaction occurs, or if a rate constant is dependent on chain length. Moreover, because each kinetic parameter is calculated independently, there are fewer practical restrictions on the maximum number of parameters a model can contain, and the need for simplifying assumptions is thus greatly reduced.

So why are all reactions not analysed this way? Until recently, the *ab initio* prediction of accurate kinetic parameters for most types of chemical reactions has not been possible. The problem is that there are no simple analytical solutions to a many-electron Schrödinger equation, and the numerical solutions are therefore incredibly complex. Although very accurate methods exist, they tend to require large amounts of computer power, with the computational cost increasing exponentially with the size of the chemical system. As a result, it is usually necessary to introduce major numerical approximations and/or to simplify the chemical system (for example, by replacing remote substituents with hydrogen atoms); both strategies are a potential source of error. However, rapid advances in computer power, coupled with the development of new, more efficient algorithms, are helping Professor Coote's group to overcome these problems, and the predictions of theory are now starting to rival or even better those of experiment. Even for complex polymeric reactions, researchers at the Australian National University have developed chemically accurate techniques for predicting rate constants and have used them to successfully predict the outcomes of multi-component polymerisation processes (see figure 15.27). Chemistry is now entering a new era of computer-led research whereby quantum chemistry can be used to understand chemical reactions at the molecular level *and* to predict the macroscopic outcome of an overall chemical process. This will allow chemists to design, test and optimise new reagents and catalysts *in silico*, prior to experimental testing.

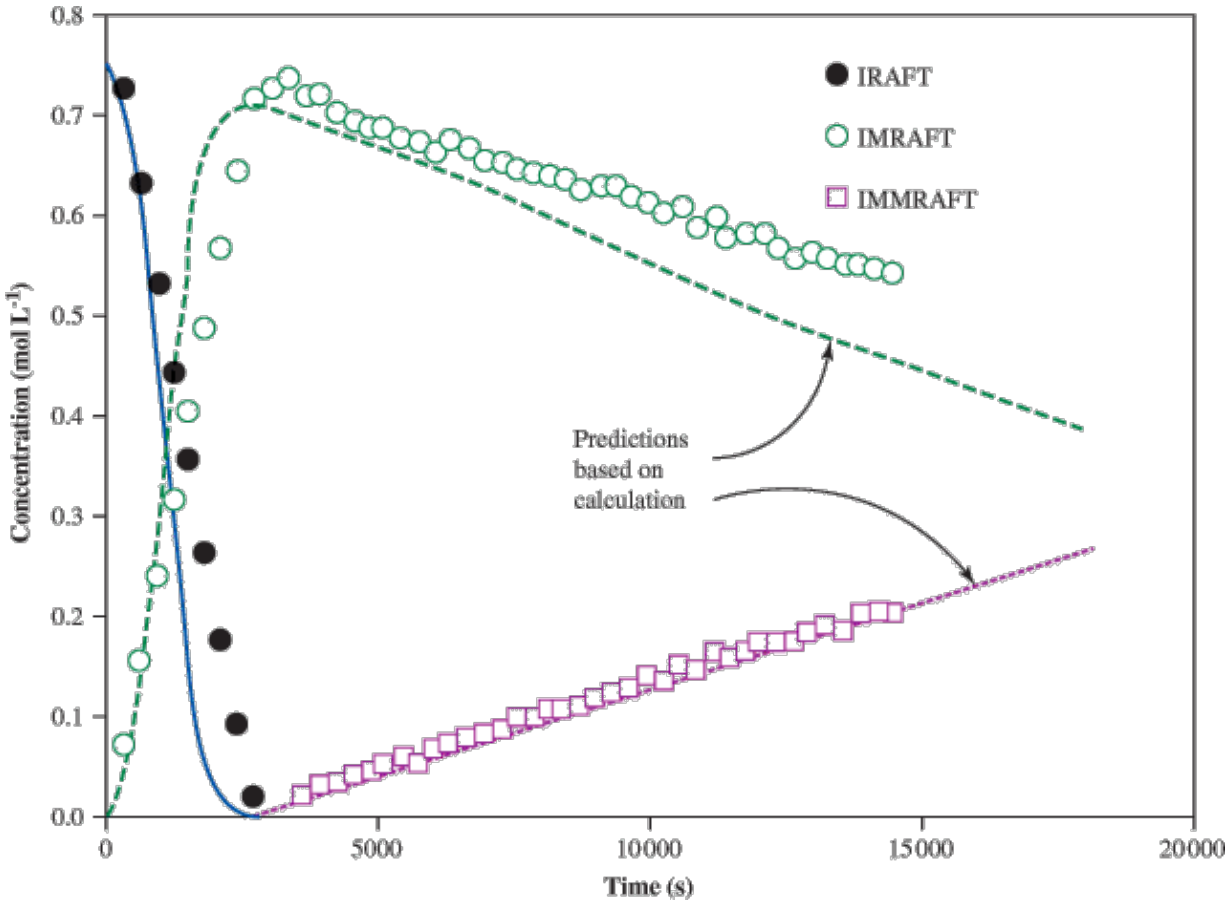


FIGURE 15.27 Measured levels of starting material (IRAFT), first reaction product (IMRAFT) and second reaction product (IMMRAFT) for the cyanoisopropyl dithiobenzoate mediated polymerisation of styrene.

There are two different hypotheses for how the substrate is bound into the enzyme, which we very briefly discuss here. The *lock-and-key* hypothesis assumes that the substrate simply 'fits' into the active site to form the enzyme–substrate complex. This is schematically shown in figure 15.28.

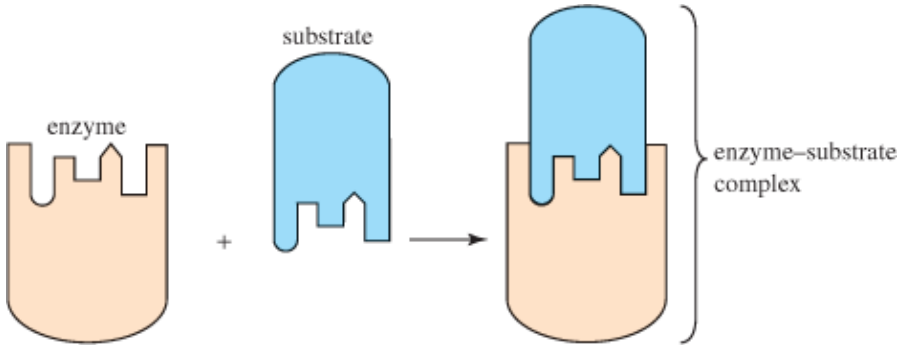


FIGURE 15.28 Schematic presentation of the lock-and-key model in substrate binding by an enzyme.

The *induced fit* hypothesis assumes that the enzyme molecule changes shape as the substrate molecule comes close — the incoming substrate *induces* the structural change. This more sophisticated model is based on the fact that the free rotation along single bonds makes molecules flexible.

Unprotected exposure to intense sunlight can lead to the formation of genotoxic products in DNA. The importance of efficient mechanisms for the repair of such UV lesions is demonstrated by hereditary diseases such as xeroderma pigmentosum; patients suffering this disease lack enzymes that repair UV-induced DNA damage, which leads to carcinomas and other skin malignancies at a young age. Figure 15.29 shows the structure of an enzyme–substrate complex of DNA photolyase and a DNA duplex containing a damaged site, which was caused by UV irradiation. In prokaryotes, plants and many animals (such as marsupials), DNA photolyases are mainly responsible for repairing UV-light-induced lesions in DNA. In the enzyme–substrate complex, the lesion is 'flipped' out of the duplex DNA into the active site of the enzyme and 'flipped' back into the DNA helix after the repair process is complete.

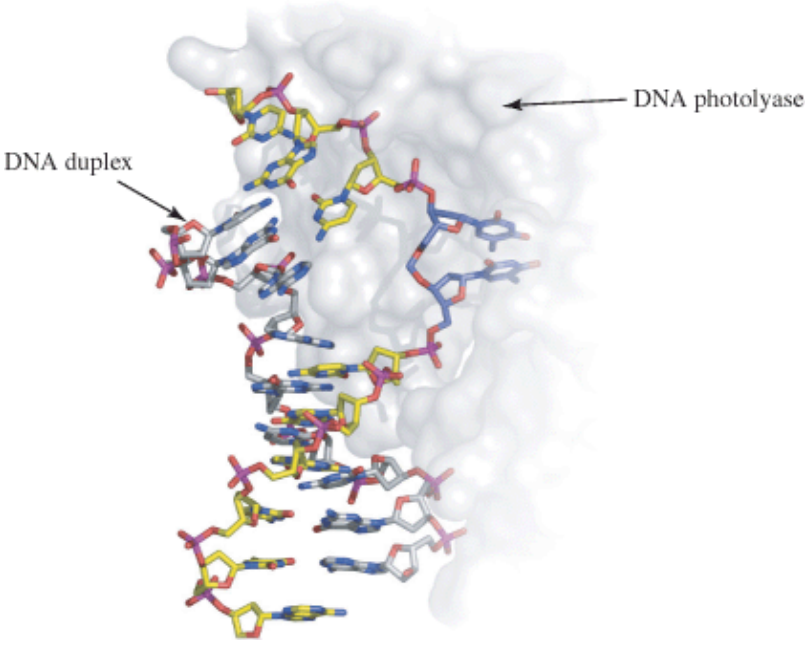


FIGURE 15.29 Illustration of an enzyme– substrate complex of DNA photolyase and a DNA duplex containing a site damaged by exposure to UV radiation. The surface of the enzyme is represented by van der Waals radii, whereas the structure of the DNA duplex is shown as a tube model.

The action of an enzyme can be described by the **Michaelis–Menten mechanism**. The rate of an enzyme-catalysed reaction in which the substrate *S* is converted into the product *P* is found to be dependent on the concentration of the enzyme *E*, even though the enzyme does not undergo a net change. Thus, the mechanism of the reaction can be written as:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E \cdot S$$

$$E \cdot S \overset{k_2}{\rightarrow} P + E$$

Since the product *P* is formed only in the second reaction and not in the first reaction, the rate law for formation of *P* is:

$$\frac{\mathrm{d}[P]}{\mathrm{d}t} = k_2[E \cdot S]$$

E·S is the reactive intermediate, and its concentration can be described using the steady-state approximation, where rate of formation equals rate of consumption, i.e. $\frac{\mathrm{d}[E \cdot S]}{\mathrm{d}t} = 0$.

Therefore, we have:

$$\frac{\mathrm{d}[E \cdot S]}{\mathrm{d}t} = \underbrace{k_1[E][S]}_{\text{formation of } E\cdot S} - \underbrace{(k_{-1}[E \cdot S] + k_2[E \cdot S])}_{\text{consumption of } E\cdot S} = 0$$

This gives:

$$k_1[E][S] = k_{-1}[E \cdot S] + k_2[E \cdot S]$$

$$[E \cdot S] = \frac{k_1[E \cdot S]}{k_2 + k_{-1}}$$

[*E*] and [*S*] are the concentrations of the free enzyme and free substrate, respectively. If we consider $[E]_0$ as the total concentration of the enzyme, we have:

$$[E]_0 = [E \cdot S] + [E] = \text{constant}$$

(because *E* is a catalyst, which does not undergo net change) or after rearrangement:

$$[E] = [E]_0 - [E \cdot S]$$

Since the concentration of *S* is much larger than that of the enzyme, the free substrate concentration is almost the same as the total substrate concentration $[S]_{\text{total}}$. As an approximation, we can therefore assume that $[S] = [S]_{\text{total}}$. We now have:

$$
\begin{aligned}
[E \cdot S] &= \frac{k_1([E]_0 - [E \cdot S])[S]}{k_2 + k_{-1}} \\
[E \cdot S] &= \frac{k_1[E]_0[S] - k_1[E \cdot S][S]}{k_2 + k_{-1}} \\
[E \cdot S](k_2 + k_{-1}) &= k_1[E]_0[S] - k_1[E \cdot S][S] \\
[E \cdot S](k_2 + k_{-1}) + k_1[E \cdot S][S] &= k_1[E]_0[S] \\
[E \cdot S](k_2 + k_{-1} + k_1[S]) &= k_1[E]_0[S] \\
[E \cdot S] &= \frac{k_1[E]_0[S]}{k_2 + k_{-1} + k_1[S]}
\end{aligned}
$$

With this expression for [*E*·*S*], we can now rewrite the rate law for the formation of *P* as shown below.

$$\frac{d[P]}{dt} = k_2[E \cdot S] = \frac{k_2 k_1[E]_0[S]}{k_2 + k_{-1} + k_1[S]} = \frac{k_2[E]_0[S]}{K_M + [S]} \qquad \text{(equation 1)}$$

is called the **Michaelis–Menten equation** with the **Michaelis constant**:

$$K_M = \frac{k_2 + k_{-1}}{k_1}$$

According to equation equation 1, the rate of enzyme catalysis (enzymolysis) depends *linearly* on the enzyme concentration $[E]_0$, but in a more complicated way on the substrate concentration [*S*]. When [*S*] >> K_M, the rate law in equation equation 1 reduces to:

$$\frac{d[P]}{dt} = k_2[E]_0 = \text{rate}_{max}$$

showing that the rate is zero order in *S*. Under these conditions the enzyme is saturated, the rate of the enzyme reaction is constant and at its maximum, rate_{max} (see p. 650). Under these conditions, the Michaelis–Menten equation can then be written as:

$$\text{rate of reaction} = \frac{d[P]}{dt} = \frac{\text{rate}_{max}[S]}{K_M + [S]} \qquad \text{(equation 2)}$$

On the other hand, when the substrate concentration is small and [S] << K_M, the rate law in equation equation 1 reduces to:

$$\frac{d[P]}{dt} = \frac{k_2}{K_M}[E]_0[S]$$

which shows that the rate of product formation depends both on the concentration of enzyme and substrate. This behaviour is shown in figure 15.30.

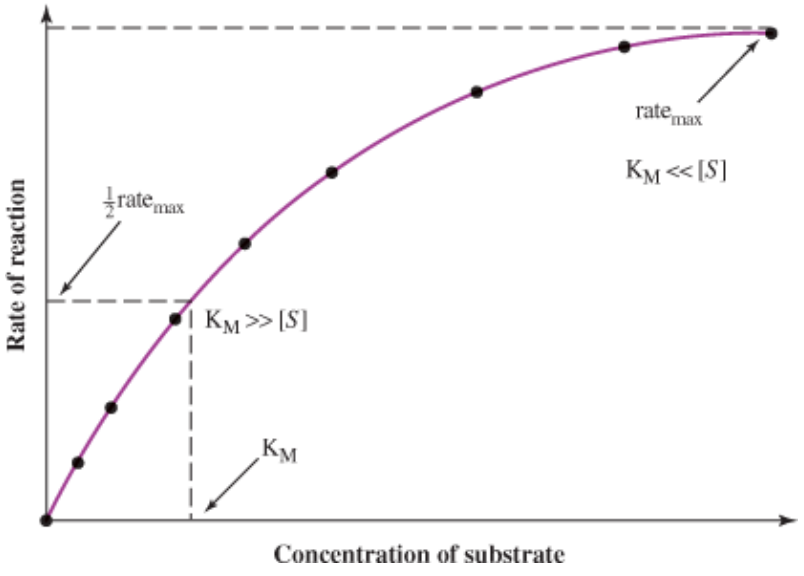


FIGURE 15.30 Saturation curve for an enzyme reaction showing the relationship between the substrate concentration and reaction rate.

The Michaelis–Menten equation is the basic equation of enzyme kinetics, in which K_M has a simple operational definition. At the substrate concentration where [*S*] = K_M, equation equation 2 becomes:

$$\text{rate of reaction} = \frac{\text{rate}_{max}}{2}$$

Here, K_M is the substrate concentration at which the rate of reaction is half of the maximum. Thus, if an enzyme has a small K_M (K_M varies widely with the identity of the enzyme and the nature of the substrate), it achieves maximal catalytic efficiency at low substrate concentrations.

The activity of enzymes can be reduced or even eliminated by enzyme inhibitors, which can bind to the enzyme or the enzyme–substrate complex (reversible inhibitors). Irreversible inhibitors inactivate enzymes by forming covalent bonds which modify the active site of the enzyme.

Enzymes are not used only in biological systems. Their unique properties as highly specific catalysts have inspired scientists to use them in the chemical industry and other applications. Because of the limited number of available enzymes and their lack of stability in organic solvents and at higher temperatures, protein engineering is a highly active research field, where new enzymes with novel properties are designed. Examples of enzymes in our daily life include: contact lens cleaners, which contain enzymes called proteases that remove proteins on contact lenses to prevent infections; biological detergents such as laundry soap, which contain proteases to assist in the removal of protein stains from clothes; machine dishwashing detergents, which contain amylases to remove resistant starch residues, and lipases to help in the removal of fatty and oily stains; and cellulases used in biological fabric conditioners.

In this chapter, we have learned the fundamentals of chemical kinetics. We will apply some of the concepts we have learned here in chapter 18 when we look at the reactions of haloalkanes.

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SUMMARY

Reaction Rates

Chemical kinetics is the study of the rate of a chemical reaction by determining the changes in concentrations of reactants and products. The rate of change in concentration (for reactions in solution) or pressure (for gas-phase reactions) at a particular time is called the instantaneous rate of change of concentration.

The time required for half of a reactant to disappear is the half-life, $t_{\frac{1}{2}}$.

Factors that Affect Reaction Rates

Reaction rates are controlled by five factors: (1) the chemical nature of the reactants, (2) the physical nature of the reactants, (3) the concentrations of the reactants, (4) the temperature and (5) the presence of catalysts. The rates of heterogeneous reactions are determined largely by the area of contact between the phases; the rates of homogeneous reactions are determined by the concentrations of the reactants. The rate of a reaction is measured by monitoring the change in reactant or product concentrations with time and, for the general reaction $aA + bB \rightarrow cC + dD$, is defined as:

$$\text{rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Overview of Rate Laws

The rate law for a reaction relates the rate of the reaction to the molar concentrations of the reactants. The rate of a reaction is proportional to the product of the molar concentrations of the reactants, each raised to an appropriate power (order of the reactant). These exponents must be determined by experiments in which the concentrations are varied and the effects on the rate of the reaction are measured. The proportionality constant, k, is called the rate constant. Its value depends on temperature but not on the concentrations of the reactants. The sum of the exponents in the rate law is defined as the order (or overall order) of the reaction.

$$\text{rate of reaction} = k[\text{reactants}]^n$$

Types of Rate Laws: Differential and Integrated

The differential rate law shows how the rate of a reaction in solution or in the gas phase depends on concentrations. The integrated rate law shows how the concentrations depend on time.

Equations exist that relate the concentration of a reactant at a given time t to the initial concentration and the rate constant. For a first-order reaction, the half-life is a constant that depends only on the rate constant for the reaction; it is independent of the initial concentration. The half-life of a second-order reaction is inversely proportional to both the initial concentration of the re actant and to the rate constant. The half-life of a zero-order reaction is proportional to the initial concentration of the reactant but is inversely proportional to the rate constant.

Theory of Chemical Kinetics

According to the collision theory, the rate of a reaction depends on the number of effective collisions per second between the re actant particles, which is an extremely small fraction of the total number of collisions per second. This fraction is small partly because collisions usually do not result in products unless the reactant molecules are suitably oriented. The major reason, however, is that the colliding molecules must jointly possess a minimum molecular kinetic energy, called the activation energy, E_a. As the temperature increases, a larger fraction of the collisions has this necessary energy, making more

collisions effective each second and the reaction faster.

The enthalpy of a reaction is the net potential energy difference between the reactants and the products. In reversible reactions, the values of E_a for both the forward and reverse reactions can be identified on a potential energy diagram. The species at the maximum on an energy diagram is called the transition state. In a multi-step reaction, a reaction intermediate is characterised as an energy minimum between two transition states. Intermediates have higher energies than reactants and products.

The Arrhenius equation shows how changes in temperature affect a rate constant. The Arrhenius equation also enables us to determine E_a, either graphically or by a calculation using the appropriate form of the Arrhenius equation. The calculation requires two rate constants determined at two different temperatures. The activation energy and the rate constant at one temperature can be used to calculate the rate constant at another temperature.

Reaction Mechanisms

The detailed sequence of elementary reactions that lead to the net chemical change is the mechanism of the reaction. Support for a mechanism comes from matching the predicted rate law for the mechanism with the rate law obtained from experimental data. For the rate-determining step, or for any elementary reaction, the corresponding rate law has exponents equal to the coefficients in the balanced equation. In more complicated reaction mechanisms, where the rate-determining step cannot be easily identified, the steady-state approximation can be used to derive the rate law.

Catalysts

Catalysts are substances that change a reaction rate but are not consumed by the reaction. Negative catalysts inhibit reactions. Positive catalysts provide alternative paths for reactions for which at least one step has a smaller activation energy than the uncatalysed reaction. Homogeneous catalysts are in the same phase as the reactants. Heterogeneous catalysts provide a path of lower activation energy by having a surface on which the reactants are adsorbed and react. Catalysts in living systems are called enzymes. Enzyme kinetics can be described by the Michaelis–Menten equation, which contains the Michaelis constant K_M; this represents the ratio of the rate constants for formation of the enzyme–substrate complex and the enzyme reaction to form products.

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Rate law of a reaction *(section 15.4)*

This shows the dependence of the rate of reaction on the concentration of one or more reactants (and occasionally products), each of which is raised to a particular exponent. The overall order of a reaction is given by the sum of these exponents. The rate constant for a reaction can be calculated from this, given the appropriate rate data.

$$\ln[A]_t = -kt + \ln[A]_0$$

Integrated first-order rate law *(section 15.4)*

For a first-order reaction with known k, this equation is used to calculate the concentration of a reactant at some specified time after the start of the reaction, or to calculate the time required for the concentration to drop to a specified value.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

Integrated second-order rate law *(section 15.4)*

For a second-order reaction with known k, this equation is used to calculate the concentration of a reactant at a specified time after the start of the reaction, or to calculate the time required for the concentration to drop to a specified value.

$$[A]_t = -kt + [A]_0$$

Integrated zero-order rate law *(section 15.4)*

For a zero-order reaction with known k, this equation is used to calculate the concentration of a reactant at some specified time after the start of the reaction, or to calculate the time required for the concentration to drop to a specified value.

Half-life *(section 15.4)*

Zero order: $t_{\frac{1}{2}} = \frac{[A]_0}{2k}$

First order: $t_{\frac{1}{2}} = \frac{\ln 2}{k}$

Second order: $t_{\frac{1}{2}} = \frac{1}{k[A]_0}$

Arrhenius equation *(section 15.5)*

These equations are used to calculate a half-life from experimental data and reaction order, or to calculate the rate of disappearance of a reactant.

$$k = Ae^{-E_a/RT}$$

Michaelis–Menten equation *(section 15.7)*

This equation allows graphical determination of an activation energy and relates rate constants, activation energy and temperature.

$$\text{rate} = \frac{\text{rate}_{max}[S]}{K_M + [S]}$$

This is the basic equation of enzyme kinetics.

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REVIEW QUESTIONS

Reaction Rates

15.1 What does ‘rate of reaction’ mean in qualitative terms?

15.2 Give an example from everyday experience of: (a) a very fast reaction, (b) a moderately fast reaction and (c) a slow reaction.

15.3 In terms of rates of reaction, what is an explosion?

15.4 What is meant by the term ‘half-life’?

Factors that Affect Reaction Rates

15.5 From an economic point of view, why would industrial corporations want to know about the factors that affect the rate of a reaction?

15.6 Suppose we compared two reactions, one requiring the simultaneous collision of three molecules and the other requiring a collision between two molecules. From the standpoint of statistics, and all other factors being equal, which reaction should be faster? Explain your answer.

15.7 List the five factors that affect the rates of chemical reactions.

15.8 How does an instantaneous rate of reaction differ from an average rate of reaction?

15.9 Explain how the initial instantaneous rate of reaction can be determined from experimental concentration versus time data.

15.10 What is a ‘homogeneous reaction’? Give an example.

15.11 What is a ‘heterogeneous reaction’? Give an example.

15.12 Why are chemical reactions usually carried out in solution?

15.13 What is the major factor that affects the rate of a heterogeneous reaction?

15.14 How does particle size affect the rate of a heterogeneous reaction? Why?

15.15 The rate of hardening of epoxy glue depends on the amount of hardener that is mixed into the glue. What factor affecting rates of reaction does this illustrate?

15.16 What is a ‘catalyst’?

15.17 In cool weather, the number of chirps per minute from crickets diminishes. How can this be explained?

15.18 On the basis of what you learned in chapters 6 and 7, why do foods cook faster in a pressure cooker than in an open pot of boiling water?

15.19 People who have been submerged in very cold water and who are believed to have drowned can sometimes be revived. On the other hand, people who have been submerged in warmer water for the same length of time have died. Explain this in terms of factors that affect the rates of chemical reactions.

Overview of Rate Laws

15.20 What are the units of rate of reaction?

15.21 What is a ‘rate law’? What is the proportionality constant called?

15.22 What is meant by the ‘order’ of a reaction?

15.23 What are the units of the rate constant for: (a) a first-order reaction, (b) a second-order reaction and (c) a zero-order reaction?

15.24 How must the exponents in a rate law be determined?

Types of Rate Laws: Differential and Integrated

15.25 How does the dependence of rate of reaction on concentration differ between a zero-order and a

first-order reaction?

15.26 Is there any way to use the coefficients in the balanced overall equation for a reaction to predict with certainty what the exponents are in the rate law?

15.27 If the concentration of a reactant is doubled and the rate of reaction is unchanged, what is the order of the reaction with respect to that reactant?

15.28 If the concentration of a reactant is doubled and the rate of reaction doubles, what is the order of the reaction with respect to that reactant?

15.29 If the concentration of a reactant is doubled, by what factor will the rate of reaction increase if the reaction is second order with respect to that reactant?

15.30 In an experiment, the concentration of a reactant was tripled. The rate of reaction increased by a factor of 27. What is the order of the reaction with respect to that reactant?

15.31 Biological reactions usually involve the interaction of an enzyme with a substrate, the substance that actually undergoes the chemical change. In many cases, the rate of reaction depends on the concentration of the enzyme, but is independent of the substrate concentration. What is the order of the reaction with respect to the substrate in such instances?

15.32 A reaction has the following rate law:

$$\text{rate} = k[A]^2[B][C]$$

What are the units of the rate constant, *k*?

15.33 Give the equations that relate concentration to time for: (a) a first-order reaction and (b) a second-order reaction.

15.34 How is the half-life of a first-order reaction affected by the initial concentration of the reactant?

15.35 How is the half-life of a second-order reaction affected by the initial reactant concentration?

15.36 Derive the equations for $t_{\frac{1}{2}}$ for first- and second-order reactions.

15.37 The integrated rate law for a zero-order reaction is:

$$[A]_t - [A]_0 = kt$$

Derive an equation for the half-life of a zero-order reaction.

15.38 The rate law for a certain enzymatic reaction is zero order with respect to the substrate. The rate constant for the reaction is 6.4×10^2 mol L^{-1} s^{-1}. If the initial concentration of the substrate is 0.275 mol L^{-1}, what is the initial rate of the reaction?

Theory of Chemical Kinetics

15.39 What is the basic postulate of the collision theory?

15.40 What two factors influence the effectiveness of molecular collisions in producing chemical change?

15.41 In terms of the kinetic theory, why does an increase in temperature increase the rate of reaction?

15.42 Draw the potential energy diagram for an endothermic reaction. Indicate on the diagram the activation energy for both the forward and reverse reactions. Also indicate the enthalpy of reaction.

15.43 Explain, in terms of the law of conservation of energy, why an endothermic reaction leads to a cooling of the reaction mixture (provided heat cannot enter from outside the system).

15.44 Define the term ‘transition state’.

15.45 Draw a potential energy diagram for an exothermic reaction and indicate on the diagram the location of the transition state.

15.46 Suppose a certain slow reaction is found to have a very small activation energy. What does this

suggest about the importance of molecular orientation in the formation of the transition state?

15.47 The decomposition of carbon dioxide:

$$CO_2 \rightarrow CO + O$$

has a very large activation energy of approximately 460 kJ mol^{-1}. Explain why this is consistent with a mechanism that involves breaking a C═O bond.

15.48 State the Arrhenius equation (which relates the rate constant to temperature and activation energy), and define the symbols.

Reaction Mechanisms

15.49 What is the definition of an 'elementary reaction'? How are elementary reactions related to the mechanism of a reaction?

15.50 What is a 'rate-determining step'?

15.51 In what way is the rate law for a reaction related to the rate-determining step?

15.52 The following mechanism has been proposed for a particular reaction:

$$\begin{aligned} 2NO &\rightarrow N_2O_2 \\ N_2O_2 + H_2 &\rightarrow N_2O + H_2O \\ N_2O + H_2 &\rightarrow N_2 + H_2O \end{aligned}$$

What is the net overall change that occurs in this reaction?

15.53 If the experimental rate law for the mechanism in question 15.52 is second order in [NO] and first order in [H_2], which of the reaction steps is the rate-determining step?

15.54 If the reaction $NO_2 + CO \rightarrow NO + CO_2$ occurs by a one-step collision process, what would be the expected rate law for the reaction? The actual rate law is rate = $k[NO_2]^2$. Could the reaction actually occur by a one-step collision between NO_2 and CO? Explain.

15.55 Oxidation of NO to NO_2, one of the reactions in the production of smog, appears to involve carbon monoxide. A possible mechanism is:

$$\begin{aligned} CO + OH &\rightarrow CO_2 + H \\ H + O_2 &\rightarrow HOO \\ HOO + NO &\rightarrow OH + NO_2 \end{aligned}$$

Write the net chemical equation for the reaction.

15.56 Show that the following two mechanisms give the same net overall reaction.

Mechanism 1:

$$\begin{aligned} OCl^- + H_2O &\rightarrow HOCl + OH^- \\ HOCl + I^- &\rightarrow HOI + Cl^- \\ HOI + OH^- &\rightarrow H_2O + OI^- \end{aligned}$$

Mechanism 2:

$$\begin{aligned} OCl^- + H_2O &\rightarrow HOCl + OH^- \\ I^- + HOCl &\rightarrow ICl + OH^- \\ ICl + 2OH^- &\rightarrow OI^- + Cl^- + H_2O \end{aligned}$$

15.57 The experimental rate law for the reaction $NO_2 + CO \rightarrow CO_2 + NO$ is:

$$\text{rate of reaction} = k[NO_2]^2$$

If the mechanism is:

$$2NO_2 \rightarrow NO_3 + NO \quad \text{(slow)}$$
$$NO_3 + CO \rightarrow NO_2 + CO_2 \quad \text{(fast)}$$

show that the predicted rate law is the same as the experimental rate law.

15.58 The following mechanism has been proposed for the reduction of NO_3^- by $MoCl_6^{2-}$.

$$MoCl_6^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MoCl_5^- + Cl^-$$
$$NO_3^- + MoCl_5^- \xrightarrow{k_2} MoOCl_5 + NO_2^-$$

What is the intermediate?

Derive an expression for the rate law, where:

$$\text{rate of reaction} = \frac{d[NO_2^-]}{dt}$$

for the overall reaction, using the steady-state approximation.

15.59 Consider the hypothetical reaction:

$$Y \rightarrow A + Z$$

which is assumed to occur by the following mechanism:

$$2Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y^* + Y$$
$$Y^* \xrightarrow{k_2} A + Z$$

(Y^* represents an *activated* molecule, which has enough energy to surmount the activation barrier).

(a) Derive a rate law for the production of A using the steady-state approximation.

(b) Assuming that this reaction is known to be first order, under what conditions does your derived rate law agree with this observation?

(c) Explain how a chemical reaction can be first order when, even in a simple case (for example the present reaction), molecules must collide to build up enough energy to get over the energy barrier? Why aren't all reactions at least second order?

15.60 Enzymes are biological catalysts. One proposed mechanism for enzyme catalysis of the reaction $A \rightarrow B$ is:

$$E + A \rightarrow E \cdot A \quad \text{(step 1)}$$
$$E \cdot A \rightarrow E + B \quad \text{(step 2)}$$

where E is the enzyme. What is the overall rate law for this reaction if step 1 is the slower step? What is the overall rate law if step 2 is the slower step?

Catalysts

15.61 How does a catalyst increase the rate of a chemical reaction?

15.62 What is a 'homogeneous catalyst'? How does it function?

15.63 What is a 'heterogeneous catalyst'? How does it function?

15.64 What is the difference in meaning between 'adsorption' and 'absorption'? Which one applies to heterogeneous catalysts?

15.65 What is the function of the catalytic converter in the exhaust system of a car? Why should leaded petrol not be used in cars equipped with catalytic converters?

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15.66 The following data were collected at a certain temperature for the decomposition of sulfuryl chloride, SO_2Cl_2, a chemical used in a variety of organic syntheses.

$$SO_2Cl_2 \rightarrow SO_2Cl_2$$

Time (min)	$[SO_2Cl_2]$ (mol L^{-1})
0	0.1000
100	0.0876
200	0.0768
300	0.0673
400	0.0590
500	0.0517
600	0.0453
700	0.0397
800	0.0348
900	0.0305
1000	0.0267
1100	0.0234

Draw a graph of concentration versus time and determine the rate of formation of SO_2 at t = 200 min and t = 600 min.

15.67 The following data were collected for the decomposition of acetaldehyde, CH_3CHO (used in the manufacture of a variety of chemicals including perfumes, dyes and plastics), into methane and carbon monoxide. The data were collected at a temperature of 530 °C.

$$CH_3CHO \rightarrow CH_4 + CO$$

Time (s)	$[CH_3CHO]$ (mol L^{-1})
0	0.200
20	0.153
40	0.124
60	0.104
80	0.090
100	0.079
120	0.070
140	0.063
160	0.058
180	0.053
200	0.049

Draw a graph of concentration versus time and determine the rate of reaction after 60 s and after 120 s.

15.68 In the catalysed formation of ammonia according to the reaction $3H_2 + N_2 \rightarrow 2NH_3$, how does the rate of consumption of hydrogen compare with the rate of consumption of nitrogen? How does the rate of formation of NH_3 compare with the rate of consumption of nitrogen?

15.69 For the reaction $2A\ 2 + B \rightarrow 3C$, it was found that the rate of consumption of B was 0.30 mol L^{-1} s^{-1}. What were the rate of consumption of A and the rate of formation of C?

15.70 In the combustion of hexane (a low-boiling component of petrol):

$$2C_6H_{14}(g) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(g)$$

it was found that the rate of consumption of C_6H_{14} was 1.20 mol L^{-1} s^{-1}.

(a) What was the rate of consumption of O_2?

(b) What was the rate of formation of CO_2?

(c) What was the rate of formation of H_2O?

15.71 At a certain moment in the reaction:

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

N_2O_5 was found to be decomposing at a rate of 2.5×10^{-6} mol L^{-1} s^{-1}. What were the rates of formation of NO_2 and O_2?

15.72 Calculate the rate of the reaction:

$$H_2SeO_3 + 6I^- + 4H^+ \rightarrow Se + 2I_3^- + 3H_2O$$

given that the rate law for the reaction (at 0 °C) is:

$$\text{rate of reaction} = \left(5.0 \times 10^5 L^5 mol^{-5} s^{-1}\right)[H_2SeO_3]\,[I^-]^3\left[H^+\right]^2$$

and the reactant concentrations are $[H_2SeO_3] = 2.0 \times 10^{-2}$ M, $[I^-] = 2.0 \times 10^{-3}$ M, and $[H^+] = 1.0 \times 10^{-3}$ M.

15.73 Calculate the rate of the reaction:

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(1)$$

given that the rate law for the reaction is:

$$\text{rate of reaction} = \left(1.3 \times 10^{11} mol^{-1} L\ s^{-1}\right)[OH^-]\left[H_3O^+\right]$$

for neutral water where $[H_3O^+] = 1.0 \times 10^{-7}$ M and $[OH^-] = 1.0 \times 10^{-7}$ M.

15.74 The oxidation of NO (released in small amounts in the exhaust of cars) produces the brownish-red gas NO_2, which is a component of urban air pollution.

$$2NO + O_2 \rightarrow 2NO_2$$

The rate law for the reaction is rate of reaction = $k[NO]^2[O_2]$. At 25 °C, $k = 7.1 \times 10^9$ L^2 mol^{-2} s^{-1}. What would the rate of the reaction be if $[NO] = 0.0010$ mol L^{-1} and $[O_2] = 0.034$ mol L^{-1}?

15.75 The rate law for the decomposition of N_2O_5 is:

$$\text{rate of reaction} = k[N_2O_5]$$

If $k = 1.0 \times 10^{-5}$ s^{-1}, what is the rate of reaction when the N_2O_5 concentration is 0.0010 mol L^{-1}?

15.76 For the reaction:

$$2HCrO_4 + 3HSO_3 + 5H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 5H_2O$$

the rate law is:

$$\text{rate of reaction} = k[HCrO_4^-][HSO_3^-]^2[H^+]$$

(a) What is the order of the reaction with respect to each reactant?

(b) What is the overall order of the reaction?

15.77 A key elementary reaction in the destruction of stratospheric ozone from nitrogen oxides in jet exhaust of high-flying aircraft is the reaction:

$$NO + O_3 \rightarrow NO_2 + O_2$$

The rate law is:

$$\text{rate of reaction} = k[NO][O_3]$$

(a) What is the order with respect to each reactant?

(b) What is the overall order of the reaction?

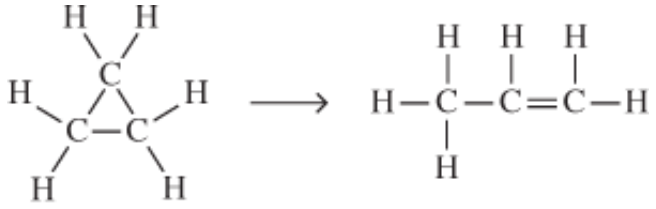
15.78 The following data refer to the hypothetical reaction:

$$M + N \rightarrow P + Q$$

Initial concentration		
[*M*] (mol L^{-1})	**[*N*] (mol L^{-1})**	**Initial of reaction (mol $L^{-1}s^{-1}$)**
0.010	0.010	2.5×10^{-3}
0.020	0.010	5.0×10^{-3}
0.020	0.030	4.5×10^{-2}

What is the rate law for the reaction? What is the value of the rate constant (with correct units)?

15.79 Cyclopropane, C_3H_6, is a gas used as a general anaesthetic. It undergoes a slow rearrangement to propene.



cyclopropane propene

At a certain temperature, the following rate data were obtained.

Initial concentration of C_3H_6 (mol L^{-1})	Rate of formation of propene (mol L^{-1} s^{-1})
0.050	2.95×10^{-5}
0.100	5.90×10^{-5}
0.150	8.85×10^{-5}

What is the rate law for the reaction? What is the value of the rate constant? Include the correct

units.

15.80 The reaction of iodide ions with hypochlorite ions, OCl^- (the active ingredient in 'chlorine bleach'), follows the equation $OCl^- + I^- \rightarrow OI^- + Cl^-$. It is a rapid reaction that gives the following rate data.

Initial concentration		
$[OCl^-]$ (mol L^{-1})	**$[I^-]$ (mol L^{-1})**	**Rate of formation of Cl^- (mol L^{-1} s^{-1})**
1.7×10^{-3}	1.7×10^{-3}	1.75×10^{4}
3.4×10^{-3}	1.7×10^{-3}	3.50×10^{4}
1.7×10^{-3}	3.4×10^{-3}	3.50×10^{4}

What is the rate law for the reaction? Determine the value of the rate constant with its correct units.

15.81 The formation of small amounts of nitric oxide, NO, in car engines is the first step in the formation of smog. Nitric oxide is readily oxidised to nitrogen dioxide by the reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The following data were collected in a study of the rate of this reaction.

Initial concentration		
$[O_2]$ (mol L^{-1})	**[NO] (mol L^{-1})**	**Rate of formation of NO2 (mol L^{-1} s^{-1})**
0.0010	0.0010	7.10
0.0040	0.0010	28.4
0.0040	0.0030	255.6

What is the rate law for the reaction? What is the rate constant with its correct units?

15.82 At a certain temperature the following data were collected for the reaction $2ICl + H_2 \rightarrow I_2 + 2HCl$.

Initial concentration		
[ICl] (mol L^{-1})	**$[H_2]$ (mol L^{-1})**	**Rate of formation of I_2 (mol L^{-1} s^{-1})**
0.10	0.10	0.0015
0.20	0.10	0.0030
0.10	0.0500	0.00075

Determine the rate law and the rate constant (with correct units) for the reaction.

15.83 The following data were obtained for the reaction of $(CH_3)_3CBr$ with hydroxide ions at 55 °C.

$$(CH_3)_3CBr + OH \rightarrow (CH_3)_3COH + Br$$

Initial concentration

$[(CH_3)_3CBr]$ (mol L^{-1})	$[OH^-]$ (mol L^{-1})	Rate of formation of $(CH_3)_3COH$ (mol L^{-1} s^{-1})
0.10	0.10	1.0×10^{-3}
0.20	0.10	2.0×10^{-3}
0.30	0.10	3.0×10^{-3}
0.10	0.20	1.0×10^{-3}
0.10	0.30	1.0×10^{-3}

What is the rate law for the reaction? What is the value of the rate constant (with correct units) at this temperature?

15.84 Data for the decomposition of SO_2Cl_2 according to the equation $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ were given in question 15.66. Show graphically that these data fit a first-order rate law. Graphically determine the rate constant for the reaction.

15.85 For the data in question 15.67, decide graphically whether the reaction is first or second order. Determine the rate constant for the reaction described in that question.

15.86 The decomposition of SO_2Cl_2 described in question 15.66 has a first-order rate constant $k = 2.2 \times 10^{-5}$ s^{-1} at 320 °C. If the initial SO_2Cl_2 concentration in a container is 0.0040 M, what is its concentration: (a) after 1.00 hour and (b) after 1.00 day?

15.87 If it takes 75.0 min for the concentration of a reactant to drop to 20% of its initial value in a first-order reaction, what is the rate constant for the reaction in the units min^{-1}?

15.88 The concentration of a drug in the body is often expressed in units of milligrams per kilogram of body weight. The initial dose of a drug in an animal was 25.0 mg/kg body weight. After 2.00 hours, this concentration had dropped to 15.0 mg/kg body weight. If the drug is eliminated metabolically by a firstorder process, what is the rate constant for the process in units of min^{-1}?

15.89 In question 15.88, what must the initial dose of the drug be in order for the drug concentration 3.00 h afterward to be 5.0 mg/kg body weight?

15.90 The decomposition of hydrogen iodide follows the equation $2HI(g) \rightarrow H_2(g) + I_2(g)$. The reaction is second order and has a rate constant of 1.6×10^{-3} mol^{-1} L s^{-1} at 700 °C. If the initial concentration of HI in a container is 3.4×10^{-2} M, how long will it take for the concentration to be reduced to 8.0×10^{-4} M?

15.91 The second-order rate constant for the decomposition of HI at 700 °C was given in question 15.90. At 2.5×10^3 min after a particular experiment had begun, the HI concentration was equal to 4.5×10^{-4} mol L^{-1}. What was the initial molar concentration of HI in the reaction vessel?

15.92 The half-life of a certain first-order reaction is 15 min. What fraction of the original reactant concentration remains after 2.0 h?

15.93 Strontium-90 has a half-life of 28 years. How long will it take for all of the strontium-90 presently on Earth to be reduced to $\frac{1}{32}$ of its present amount?

15.94 Using the graph from question 15.66, determine the time required for the SO_2Cl_2 concentration to drop from 0.100 mol L^{-1} to 0.050 mol L^{-1}. How long does it take for the concentration to drop from 0.050 mol L^{-1} to 0.025 mol L^{-1}? What is the order of this reaction? (*Hint:* How is the half-life related to concentration?)

15.95 Using the graph from question 15.67, determine how long it takes for the CH_3CHO concentration

to decrease from 0.200 mol L^{-1} to 0.100 mol L^{-1}. How long does it take the concentration to drop from 0.100 mol L^{-1} to 0.050 mol L^{-1}? What is the order of this reaction? (*Hint:* How is the half-life related to concentration?)

15.96 A certain first-order reaction has a rate constant $k = 1.6 \times 10^{-3}$ s^{-1}. What is the half-life for this reaction?

15.97 The decomposition of NOCl, the compound that gives a yellow-orange colour to aqua regia (a mixture of concentrated HCl and HNO_3 that is able to dissolve gold and platinum) follows the reaction $2NOCl \rightarrow 2NO + Cl_2$. It is a second-order reaction with $k = 6.7 \times 10^{-4}$ mol^{-1} L s^{-1} at 400 K. What is the half-life of this reaction if the initial concentration of NOCl is 0.20 mol L^{-1}?

15.98 The following data were collected for a reaction.

Rate constant (mol^{-1} L s^{-1})	Temperature (°C)
2.88×10^{-4}	320
4.87×10^{-4}	340
7.96×10^{-4}	360
1.26×10^{-3}	380
1.94×10^{-3}	400

Determine the activation energy for the reaction in kJ mol^{-1} both graphically and by calculation using $\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$. For the calculation of E_a, use the first and last rows of data in the table in this question.

15.99 Rate constants were measured at various temperatures for the reaction:

$$HI(g) + CH_3I(g) \rightarrow CH_4(g) + I_2(g)$$

The following data were obtained.

Rate constant (mol^{-1} L s^{-1})	Temperature (°C)
1.91×10^{-2}	205
2.74×10^{-2}	210
3.90×10^{-2}	215
5.51×10^{-2}	220
7.73×10^{-2}	225
1.08×10^{-1}	230

Determine the activation energy in kJ mol^{-1} both graphically and by calculation using $\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$. For the calculation of E_a, use the first and last rows of data in the table above.

15.100 The reaction $2NOCl \rightarrow 2NO + Cl_2$ has $k = 9.3 \times 10^{-5}$ mol^{-1} L s^{-1} at 100 °C and $k = 1.0 \times 10^{-3}$ mol^{-1} L s^{-1} at 130 °C. What is E_a for this reaction in kJ mol^{-1}? Use the data at 100 °C to calculate the pre-exponential factor *A*. (*Hint: A* has the same unit as the rate constant.)

15.101 The conversion of cyclopropane, an anaesthetic, to propene (see question 15.79) has a rate constant $k = 1.3 \times 10^{-6}$ s^{-1} at 400 °C and $k = 1.1 \times 10^{-5}$ s^{-1} at 430 °C.

(a) What is the activation energy in kJ mol^{-1}?

(b) What is the value of the pre-exponential factor, *A*, for this reaction?

(c) What is the rate constant for the reaction at 350 °C?

15.102 The reaction of CO_2 with water to form carbonic acid, $CO_2(aq) + H_2O(l) \rightarrow H_2CO_3(aq)$, has $k = 3.75 \times 10^{-2}$ s^{-1} at 25 °C and $k = 2.1 \times 10^{-3}$ s^{-1} at 0 °C. What is the activation energy for this reaction in kJ mol^{-1}?

15.103 If a reaction has $k = 3.0 \times 10^{-4}$ s^{-1} at 25 °C and an activation energy of 100.0 kJ mol^{-1}, what is the value of *k* at 50 °C?

15.104 The decomposition of N_2O_5 has an activation energy of 103 kJ mol^{-1} and a pre-exponential factor of 4.3×10^{13} s^{-1}. What is the rate constant for this decomposition at: (a) 20 °C and (b) 100 °C?

15.105 At 35 °C, the rate constant for the reaction:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

is $k = 6.2 \times 10^{-5}$ s^{-1}. The activation energy for the reaction is 108 kJ mol^{-1}. What is the rate constant for the reaction at 45 °C?

15.106 A sucrase enzyme breaks down 0.15 M lactose every 37 minutes. What is the reaction rate in:

(a) M min^{-1}?

(b) mM min^{-1}?

(c) mol min^{-1} in a 500 mL flask?

15.107 The following mechanism has been suggested for the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$:

$$I_2(g) \overset{k_1}{\rightarrow} 2I(g)$$

$$2I(g) \overset{k_2}{\rightarrow} I_2(g)$$

$$H_2(g) + 2I(g) \overset{k_3}{\rightarrow} 2HI(g)$$

Derive the rate law using the steady-state approximation.

15.108 A possible mechanism for the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ is:

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

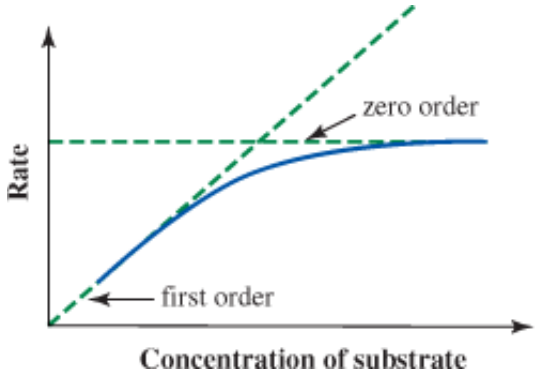
$$NO_2 + NO_3 \overset{k_2}{\rightarrow} NO + NO_2 + O_2$$

$$NO + NO_3 \overset{k_3}{\rightarrow} 2NO_2$$

What is the rate law derived using the steady-state approximation?

15.109 The decomposition of many substances on the surface of a heterogeneous catalyst shows the

following relationship between reaction rate and substrate concentration.



Why does the rate law change from first order to zero order in the concentration of the substrate?

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15.110 For the reaction and data given in question 15.67, make a graph of concentration versus time for the formation of CH_4. What are the rates of formation of CH_4 at t = 40 s and t = 100 s?

15.111 The age of wine can be determined by measuring the trace amount of radioactive tritium, ^3H, present in a sample. Tritium is formed from hydrogen in water vapour in the upper atmosphere by cosmic bombardment, so all naturally occurring water contains a small amount of this isotope. Once the water is in a bottle of wine, however, the formation of additional tritium from the water is negligible, so the tritium initially present gradually diminishes by a first-order radioactive decay with a half-life of 12.5 years. If a bottle of wine is found to have a tritium concentration that is 0.100 that of freshly bottled wine (i.e. $[^3H]_t = 0.100\ [^3H]_0$), what is the age of the wine?

15.112 ^{14}C dating can be used to estimate the age of formerly living materials because the uptake of ^{14}C from carbon dioxide in the atmosphere stops once the organism dies. If tissue samples from a mummy contain about 81.0% of the ^{14}C expected in living tissue, how old is the mummy? The half-life for decay of ^{14}C is 5730 years.

15.113 One of the reactions that occurs in polluted air in urban areas is $2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g)$. It is believed that a species with the formula NO_3 is involved in the mechanism, and the observed rate law for the overall reaction is:

$$\text{rate of reaction} = k[NO_2]\,[O_3]$$

Propose a mechanism for this reaction that includes the species NO_3 and is consistent with the observed rate law.

15.114 Suppose a reaction occurs with the mechanism:

$$2A \rightleftharpoons A_2 \qquad \text{(step 1, fast)}$$
$$A_2 + E \rightarrow B + C \qquad \text{(step 2, slow)}$$

in which step 1 is a very rapid reversible reaction that can be considered to be essentially an equilibrium (forward and reverse reactions occurring at the same rate) and step 2 is slow.

(a) Write the rate law for the forward reaction in step 1.

(b) Write the rate law for the reverse reaction in step 1.

(c) Write the rate law for the rate-determining step.

(d) What is the chemical equation for the net reaction that occurs in this chemical change?

(e) Use the results from parts (a) and (b) to rewrite the rate law of the rate-determining step in terms of the concentrations of the reactants in the overall balanced equation for the reaction.

15.115 A reaction that has the stoichiometry:

$$2A + B \rightarrow \text{products}$$

was found to yield the following data.

Initial concentration (mol L^{-1})		
[A]	**[B]**	**Initial rate of reaction of *A* (mol L^{-1} s^{-1})**
0.020	0.030	0.0150
0.025	0.030	0.0188
0.025	0.040	0.0334

(a) What is the rate law for the reaction?

(b) What is the rate constant for the reaction? Give the correct units.

15.116 The decomposition of urea, $(NH_2)_2CO$, in 0.10 M HCl follows the equation:

$$(NH_2)_2CO(aq) + H_3O^+(aq) \rightarrow 2NH_4^+(aq) + CO_2(g) + H_2O(1)$$

At 60 °C, $k = 5.84 \times 10^{-6}$ min^{-1} and, at 70 °C, $k = 2.25 \times 10^{-5}$ min^{-1}. If this reaction is run at 80 °C starting with a urea concentration of 0.0020 M, how long will it take for the urea concentration to drop to 0.0012 M?

15.117 Show that for a reaction that obeys the general rate law:

$$\text{rate} = k[A]^n$$

a graph of log(rate) versus log[*A*] should yield a straight line with a slope equal to the order of the reaction. For the reaction in question 15.66, measure the rate of the reaction at t = 150, 300, 450 and 600 s. Then graph log(rate) versus log[SO_2Cl_2] and determine the order of the reaction with respect to SO_2Cl_2.

15.118 The bonding in O_2 was discussed in section 5.7 as was the bonding in N_2. Molecular nitrogen is very unreactive, whereas molecular oxygen is very reactive. On the basis of what you have learned in this chapter, what fact about O_2 is responsible, at least in part, for its reactivity? What might account for the low degree of reactivity of molecular nitrogen?

15.119 It was mentioned that the rates of many reactions approximately double for each 10 °C rise in temperature. Assuming a starting temperature of 25 °C, what would the activation energy be, in kJ mol^{-1}, if the rate of a reaction were to be twice as large at 35 °C?

15.120 The rate at which crickets chirp depends on the ambient temperature, because crickets are cold-blooded insects whose body temperature follows the temperature of their environment. It has been found that the temperature in °C can be estimated by counting the number of chirps in 8 seconds and then adding 4. In other words, t_C = (number of chirps in 8 seconds) + 4.

(a) Calculate the number of chirps in 8 seconds for temperatures of 20, 25, 30 and 35 °C.

(b) The number of chirps per unit of time is directly proportional to the rate constant for a biochemical reaction involved in the cricket's chirp. On the basis of this assumption, make a graph of ln(chirps in 8 s) versus $\left(\frac{1}{T}\right)$. Calculate the activation energy for the biochemical reaction involved.

(c) How many chirps would a cricket make in 8 seconds at a temperature of 40 °C?

15.121 The cooking of an egg involves the denaturation of a protein called albumen. The time required to achieve a particular degree of denaturation is inversely proportional to the rate constant for the process. This reaction has a high activation energy, E_a = 418 kJ mol^{-1}. Calculate how long it would take to cook a traditional 3-minute egg on top of a cold mountain on a day when the atmospheric pressure there is 47 kPa.

15.122 Which of the following cannot be a unit for reaction rate. Explain your answers.

(a) mol L^{-1} s^{-1}

(b) g L^{-1} s^{-1}

(c) % s^{-1}

(d) g s^{-1}

(e) $mol\ s^{-1}$

(f) $mol\ L^{-1}$

15.123 The enthalpies of formation of Al_2O_3 and B_2O_3 are -1676 and -1274 kJ mol^{-1}, respectively. Do these data indicate the rate of oxidation of aluminium and boron? Explain your answer.

15.124 Which one of the following reactions is the most rapid at room temperature. Which reaction is the slowest? Explain your answers.

(a) $2H_2 + O_2 \rightarrow 2H_2O$

(b) $H^+ + OH^- \rightarrow H_2O$

(c) $C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O$

(d) $H + OH \rightarrow H_2O$

15.125 Which one of the following burns easily and why?

(a) steel bar

(b) steel wool

(c) steel sheet

(d) steel pipe

15.126 The rate constant for a reaction is $2.90 \times 10^{-9}\ s^{-1}$ at 454 K with an activation energy of 178.5 kJ mol^{-1}. What is the value of the rate constant at 395 K?

15.127 The rate constant for a reaction is $1.72 \times 10^{-4}\ s^{-1}$ at 298 K and $2.75 \times 10^{-1}\ s^{-1}$ at 301 K. What is the activation energy in kJ mol^{-1}?

15.128 The activation energy of a unimolecular reaction is 190.2 kJ mol^{-1} at 295 K. What is the value of the rate constant?

15.129 The following rate data have been measured for the reaction $A + B + C \rightarrow D$.

Initial concentration (mol L^{-1})			
[*A*]	**[*B*]**	**[*C*]**	**Rate (mol L^{-1} s^{-1})**
0.20	0.75	0.25	1.1×10^{1}
0.10	0.25	0.25	6.1×10^{-1}
0.20	0.25	0.25	1.2×10^{0}
0.20	0.75	0.75	3.3×10^{1}

What is the rate law for the reaction? What is the overall order of the reaction? Determine the value of the rate constant (with the correct units).

15.130 The following rate data have been measured for the reaction $E + F + G \rightarrow H$.

Initial concentration (mol L^{-1})			
[*E*]	**[*F*]**	**[*G*]**	**Rate (mol L^{-1} s^{-1})**
0.10	0.050	0.050	1.1×10^{-6}
0.050	0.050	0.050	2.6×10^{-7}

0.10	0.15	0.10	1.9×10^{-5}
0.10	0.15	0.050	9.5×10^{-6}

What is the rate law for the reaction? What is the overall order of the reaction? Determine the value of the rate constant (with the correct units).

15.131 (a) What is the half-life of a first-order reaction where $k = 2.0 \times 10^{-1}\ s^{-1}$.

(b) After what time does only 1% of reactant remain?

(c) Why is it not possible to calculate the half-life of a second-order reaction if the rate constant is the only kinetic information you have?

15.132 Calculate the activation energy for the reaction $ClO_3^- + H_2O \rightarrow ClO_4^- + H_2$ from the following data.

k (s^{-1})	Temperature (°C)
2.0×10^{-3}	25
4.0×10^{-3}	35
8.0×10^{-3}	45
1.6×10^{-3}	55

15.133 Calculate the activation energy for a second-order reaction using the following kinetic data: k = 4 L mol^{-1} s^{-1} at 37 °C and k = 8.0 L mol^{-1} s^{-1} at 87 °C.

15.134 (a) Calculate the average rate of a chemical reaction if the concentration of reactant *A* is 0.45 M after 3.0 min and 0.20 M after 8.0 min.

(b) Why do we refer to the average rate when we are calculating a reaction time interval?

15.135 Why is the following reaction not likely to take place in one step.

$$4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g)$$

15.136 The reaction in question 15.135 is believed to take place in the following three steps.

$$HBr(g) + O_2(g) \rightarrow HOOBr(g) \quad \text{(step 1, slow)}$$
$$HOOBr(g) + HBr(g) \rightarrow 2HOBr(g) \quad \text{(step 2, fast)}$$
$$2HOBr(g) + 2HBr(g) \rightarrow 2H_2O(g) + 2Br_2(g) \quad \text{(step 3, fast)}$$

(a) Add the three steps to show that it gives the correct overall reaction:

$$4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g)$$

(b) Identify any reaction intermediates or catalysts.

(c) Which step is the rate-determining step? Explain.

15.137 The hypothetical reaction $A + B \rightarrow 2C + D$ has an activation energy of 130 kJ and ΔH = -40 kJ.

(a) Draw and label a potential energy diagram for this reaction.

(b) Calculate the activation energy for the reverse reaction.

(c) What is ΔH for the reverse reaction?

15.138 (a) Why is there concern over explosions taking place at sawmills or grain storage buildings?

(b) Which of the five factors that affect the rate of a reaction increases the rate by increasing the fraction of collisions that are successful?

15.139 (a) Name two advantages of using a catalyst to speed up a chemical reaction rather than using heat.

(b) Name two things that a catalyst does not change in a chemical reaction.

15.140 Which of the five factors that affect the rate of a reaction is illustrated in each of the following:

(a) Food is sometimes frozen before it is used.

(b) Small sticks of wood are often used to start a fire.

(c) In hospitals, the speed of the healing process is often increased in an oxygen tent.

15.141 Why would you expect the rate of the reaction:

$$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$$

at room temperature to be much faster than the rate of the reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(1)$$

at room temperature?

15.142 Consider the reaction $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$. What would be the effect on the rate of reaction if:

(a) powdered zinc was used instead of a solid piece of zinc metal?

(b) the concentration of HCl(aq) was doubled?

(c) the temperature was increased?

15.143 Sketch a potential energy diagram for the general reaction $A + B \rightarrow C + D$, where $\Delta H_{reverse} = -10$ kJ mol^{-1} and $E_{a\ forward} = +40$ kJ mol^{-1}.

15.144 In the decomposition reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, oxygen gas is produced at an average rate of 9.1×10^{-1} mol L^{-1} s^{-1}. Over the same period, what is the average rate of the following?

(a) production of nitrogen dioxide

(b) loss of dinitrogen pentoxide

15.145 Consider the formation of ammonia according to $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. If the rate of loss of hydrogen gas is 0.03 mol L^{-1} s^{-1}, what is the rate of production of ammonia?

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KEY TERM

activation energy (E_a)
Arrhenius equation
average rate
catalysis
catalyst
chemical kinetics
collision theory
differential rate law
elementary reaction
frequency factor
half-life $\left(t_{\frac{1}{2}}\right)$
heterogeneous catalyst
heterogeneous reaction
homogeneous catalyst
homogeneous reaction
initial rate
instantaneous rate of change of concentration
integrated rate law
Michaelis constant
Michaelis–Menten equation
Michaelis–Menten mechanism
molecularity
order
pre-exponential factor
rate coefficient
rate constant
rate law
rate of reaction
rate-determining step
reaction coordinate
reaction intermediate
reaction mechanism
steady-state approximation
steric factor
transition state

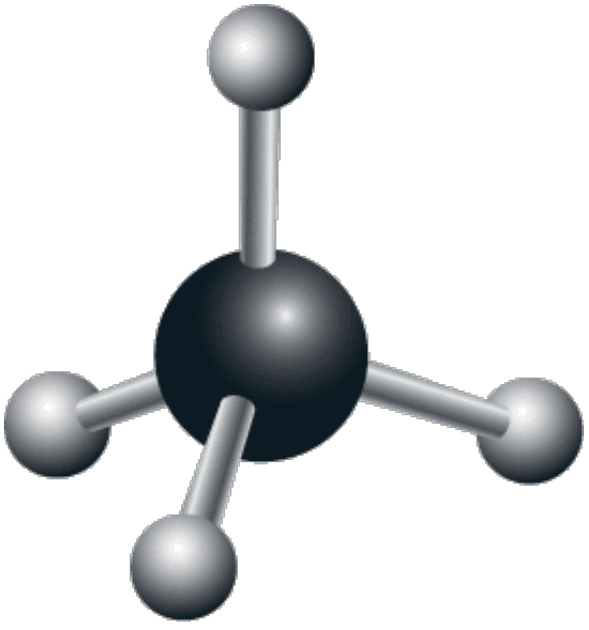
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CHAPTER

16 The Chemistry of Carbon

Scientists have estimated that, deep in the world's oceans and permafrost, more than 500 gigatonnes of carbon lies trapped in the form of methane locked within cages made from molecules of H_2O. These frozen cages are called clathrate hydrates (shown burning in the photograph) and their discovery may have important implications for the environment. Methane is known as natural gas as it is found naturally in many places. Methane has the formula CH_4 (see ball-and-stick model), which makes it one of the simplest forms of molecular carbon, and it represents an important energy source. Our current natural gas reservoirs, such as those in the Timor Sea to the north-west of Australia and those present in the coal seams in central Queensland and New South Wales, vastly outweigh the estimated amount of methane that is trapped within the watery cages in the oceans and icecaps. However, as global warming raises the Earth's temperature, more and more of this simple molecule may be released into the atmosphere and its impact as a greenhouse gas could prove to be very significant. Carbon dioxide, CO_2, is another simple gaseous molecule that contains carbon and is also involved in global warming. These two simple forms of carbon may hold the key to controlling the climate of our entire planet.

Methane and carbon dioxide are examples of molecules that involve only one atom of carbon. Carbon atoms can actually combine covalently with each other and with other elements to form an enormous variety of molecules other than CO_2 and CH_4. At the molecular level of life, nature uses compounds of carbon, and the amazing variety of living systems arises from the properties of this element. There are many millions of compounds that contain carbon including colourful dyes, drugs, perfumes, synthetic and natural fibres, plastics, flavourings, foods and fuels. The list covers almost everything we encounter in our normal lives and also includes the carbohydrates, proteins, vitamins, fats, cell membranes and enzymes that make up our own bodies.





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Organic chemistry is the study of the properties, preparation, identification and modification of compounds involving carbon. The myriad forms of carbon-containing molecules would be overwhelming but for the fact that we can classify them according to the presence of similarly reacting *functional groups*, the natures of which we will introduce over the next several chapters. However, before dealing with these systems, we will first look at hydrocarbons, organic molecules containing only carbon and hydrogen. Hydrocarbons make up the framework supporting the functional groups that are present in most important molecules. In this chapter, we begin our study of organic compounds with alkanes, the simplest type of organic compounds. Then we will progress to the first functional groups, unsaturated systems containing double and triple bonds and, finally, we will look at cyclic unsaturated systems called aromatics.

KEY TOPICS

16.1 Introduction to hydrocarbons
16.2 Alkanes
16.3 Alkenes and alkynes
16.4 Reactions of alkanes
16.5 Reactions of alkenes
16.6 Reactions of alkynes
16.7 Aromatic compounds
16.8 Reactions of aromatic compounds: electrophilic aromatic substitution

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16.1 Introduction to Hydrocarbons

A **hydrocarbon** is a compound composed of only carbon and hydrogen. Figure 16.1 shows the four classes of hydrocarbons, along with the characteristic type of bonding between carbon atoms in each.

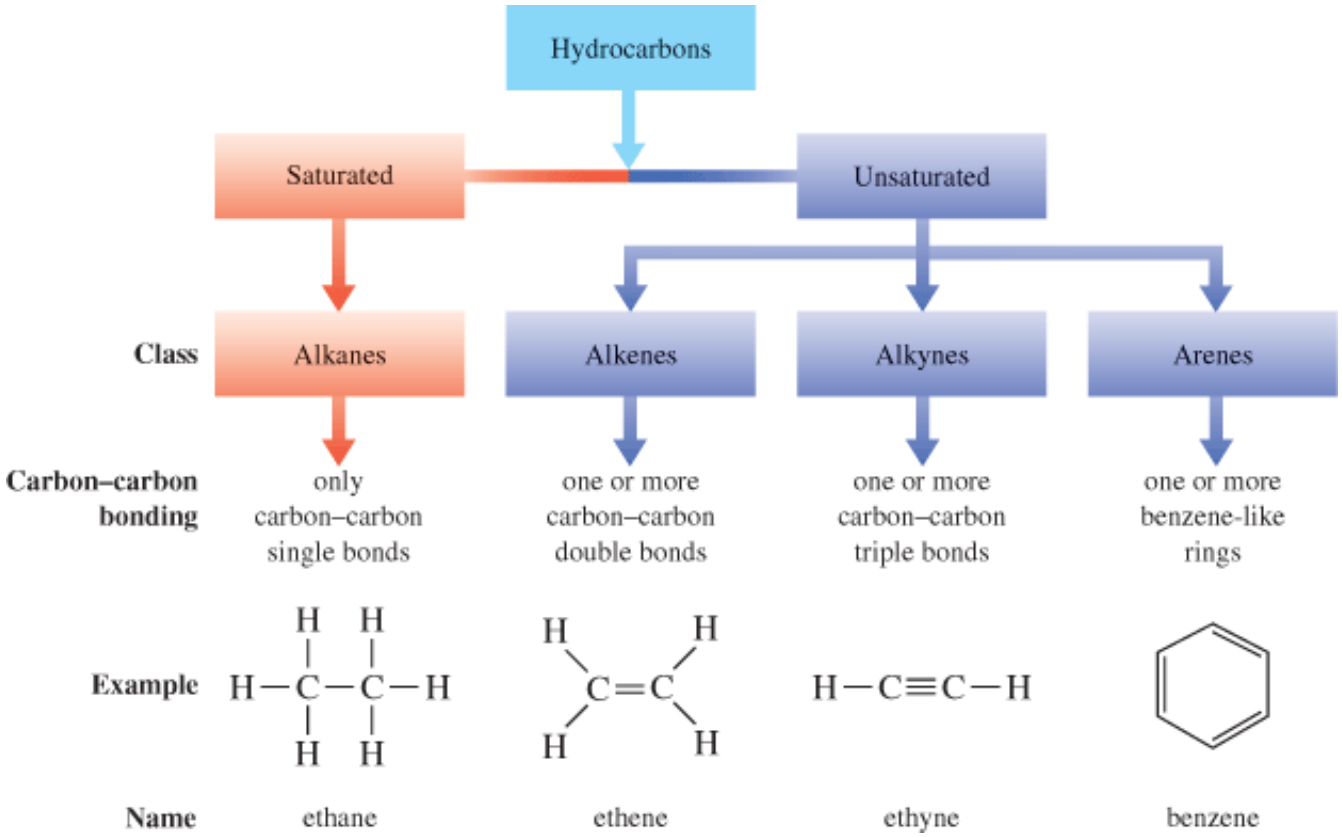


FIGURE 16.1 The four classes of hydrocarbons.

Alkanes are hydrocarbons that contain only carbon–carbon single bonds. Such hydrocarbons are said to be **saturated hydrocarbons**, meaning that each carbon atom has the maximum possible number of atoms (four) bonded to it. We often refer to alkanes as **aliphatic hydrocarbons**, because the physical properties of the higher molecular weight members of this class resemble those of the long-carbon-chain molecules we find in animal fats and plant oils ('aliphatic' is derived from the Greek word *aleiphar* meaning 'fat' or 'oil').

Alkenes are hydrocarbons that contain one or more carbon–carbon double bonds. **Alkynes** are hydrocarbons that contain one or more carbon–carbon triple bonds. **Arenes** are cyclic structures containing carbon–carbon bonds that impart special stability. Alkenes, alkynes and arenes are said to be **unsaturated hydrocarbons**.

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16.2 Alkanes

Recall that alkanes are saturated hydrocarbons; they contain only single bonds and each carbon has the maximum number of atoms (four) bonded to it. Methane, CH_4, and ethane, C_2H_6, are the first two members of the alkane family. Figure 16.2 shows Lewis structures and ball-and-stick models for these molecules. The Lewis structures show the atom connectivity but do not reflect the three-dimensional shapes of the molecules. We learned in section 5.4 that methane is tetrahedral, and all H—C—H bond angles are 109.5°. Each carbon atom in ethane is also tetrahedral, and all bond angles are about 109.5°. Although the three-dimensional shapes of larger alkanes are more complex than those of methane and ethane, the four bonds around each carbon atom are still arranged in a tetra hedral manner, and all bond angles are still approximately 109.5°.

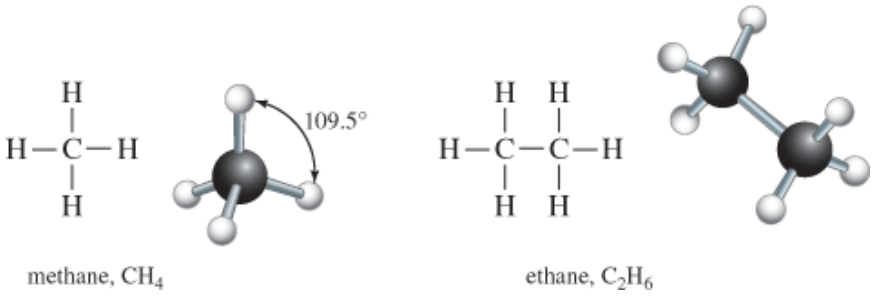


FIGURE 16.2 Structures of methane and ethane.

In chapter 2 we learned various ways to depict chemical structures. In figure 16.3, the next members of the alkane family — propane, butane and pentane — are drawn, first as condensed structural formulae that show all carbons and hydrogens, then as line structures, and then as ball-and-stick models. Recall that, in this type of representation, a line represents a carbon–carbon bond and an angle represents a carbon atom. A line ending represents a — CH_3 group. Although hydrogen atoms are not shown in line structures, they are assumed to be there in sufficient numbers to give each carbon atom four bonds.

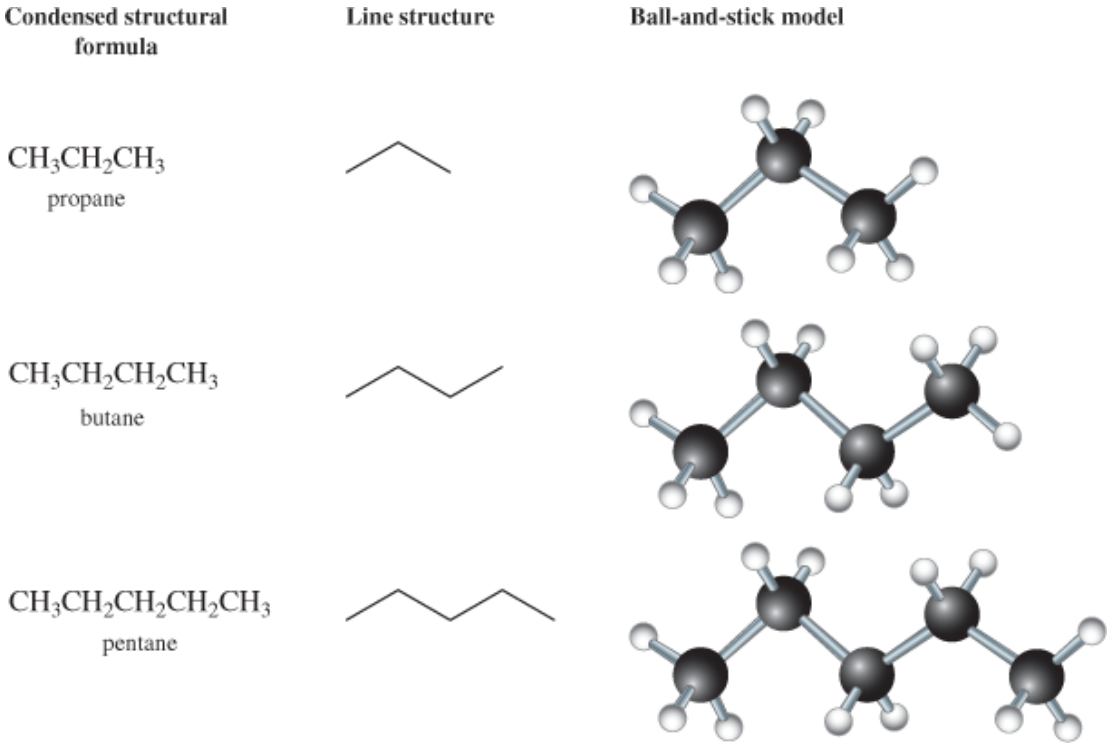


FIGURE 16.3 Structures of propane, butane and pentane.

We can write condensed structural formulae for alkanes in still another abbreviated form. For example, the condensed structural formula of pentane, $CH_3CH_2CH_2CH_2CH_3$, contains three CH_2 (methylene) groups in the middle of the chain. We can collect these groups together and write the condensed structural formula as $CH_3(CH_2)_3CH_3$. Table 16.1 gives the IUPAC names and molecular formulae of the first 10 alkanes. Note that the names of all alkanes end in-*ane*.

TABLE 16.1 Names, molecular formulae and condensed structural formulae for the first 10 straight-chain alkanes.

Molecular	Condensed structural	Melting point	Boiling point	Density of liquid (g mL^{-1} at 0

Name	formula	formula	(°C)	(°C)	°C)[a]	
methane	CH_4	CH_4	-182	-164		(a gas)
ethane	C_2H_6	CH_3CH_3	-183	-88		(a gas)
propane	C_3H_8	$CH_3CH_2CH_3$	-190	-42		(a gas)
butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	-138	0		(a gas)
pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	-130	36		0.626
hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	-95	69		0.659
heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	-90	98		0.684
octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	-57	126		0.703
nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	-51	151		0.718
decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	-30	174		0.730

(a) For comparison, the density of H_2O is 1 g mL^{-1} at 4 °C.

Alkanes have the general molecular formula C_nH_{2n+2} (with the exception of cycloalkanes, which we will deal with later in the chapter). Thus, given the number of carbon atoms in an alkane, it is easy to determine the number of hydrogen atoms in the molecule and also its molecular formula. For example, decane, with 10 carbon atoms, must have $(2 \times 10) + 2 = 22$ hydrogen atoms and a molecular formula of $C_{10}H_{22}$.

Conformation of Alkanes

Even though structural and condensed structural formulae are useful for showing the order of attachment of atoms, they do not show three-dimensional shapes. To recognise the relationships between the structure and properties of molecules, it is crucial to understand the three-dimensional shapes of molecules. Molecules are three-dimensional objects, and it is essential that you become comfortable in dealing with them as such.

Alkanes of two or more carbon atoms can be twisted into a number of different three-dimensional arrangements by rotating around one or more carbon–carbon bonds. Any three-dimensional arrangement of atoms that results from rotation around a single bond is called a **conformer**; the representation of the position of the atoms in the molecule is called its **conformation**. Figure 16.4a shows a ball-and-stick model of a *staggered conformation* of ethane. In this conformation, the three C—H bonds on one carbon atom are as far away as possible from the three C—H bonds on the adjacent carbon atom. Figure 16.4b shows a **Newman projection**, which is a shorthand way of representing the staggered conformation of ethane. In a Newman projection, we view a molecule along the axis of a C—C bond. The three atoms or groups of atoms nearer your eye appear on lines extending from the centre of the circle at angles of 120°. The three atoms or groups of atoms on the carbon atom further from your eye appear on lines extending from the circumference of the circle at angles of 120°. Remember that bond angles around each carbon atom in ethane are approximately 109.5° and not 120°, as this Newman projection might suggest.

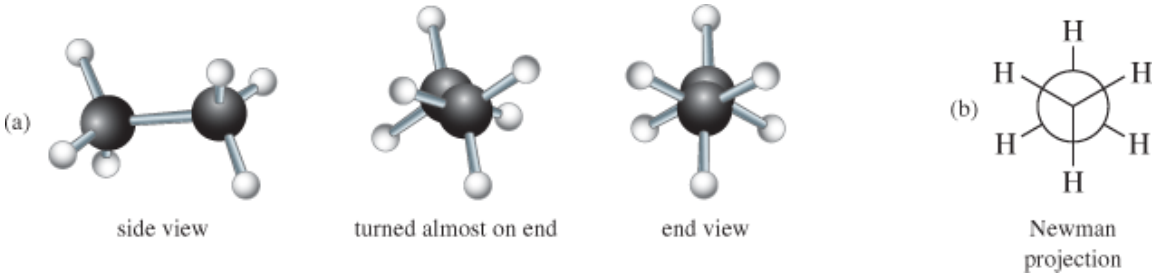


FIGURE 16.4 A staggered conformation of ethane:
(a) ball-and-stick models and
(b) Newman projection.

Figure 16.5 shows a ball-and-stick model and a Newman projection of an *eclipsed conformation* of ethane. In this conformation, the three C—H bonds on one carbon atom are as close as possible to the three C—H bonds on the adjacent

carbon atom. In other words, hydrogen atoms on the back carbon atom are eclipsed by the hydrogen atoms on the front carbon atom. (Note that in the Newman projection the bonds have been offset a little for clarity.)

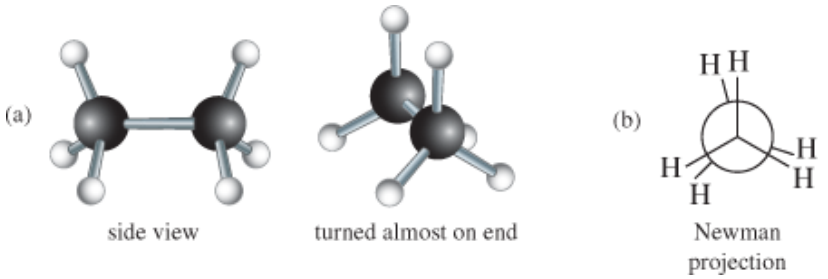


FIGURE 16.5 An eclipsed conformation of ethane:
(a) ball-and-stick models and
(b) Newman projection, with the bonds offset slightly for clarity.

The difference in potential energy between these two conformations is approximately 12.6 kJ mol^{-1} (see figure 16.6), which means that, at room temperature, the ratio of ethane molecules in a staggered conformation to those in an eclipsed conformation is approximately 100 to 1.

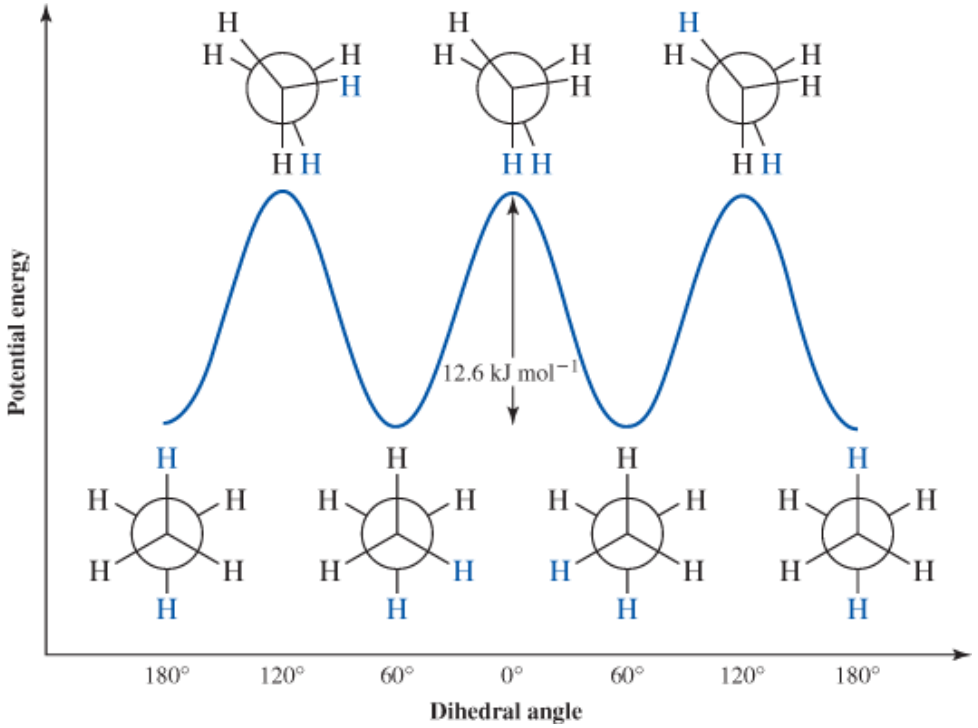


FIGURE 16.6 An energy diagram showing the conformational analysis of ethane.

It is important to realise that molecules are not static like the pictures you see on this page and in figure 16.7 on the next page. At room temperature the bonds can be stretching, shaking, bending and vibrating up to 10^{13} times per second! The groups rotate more slowly, but typical C—C bond rotation is still more than a *billion* revolutions per second. You will learn more about how chemists detect some of these atom movements when we deal with infrared spectroscopy in section 20.3. The key point here is that, at room temperature, movement between the various conformers is constant and occurs *extremely* rapidly, even with the energy barriers that arise from eclipsing interactions. Thus, while you may be able to draw many conformational forms for a molecule, in practical terms, for a typical noncyclic alkane, they do not exist long enough to display the different properties that constitutional isomers possess.

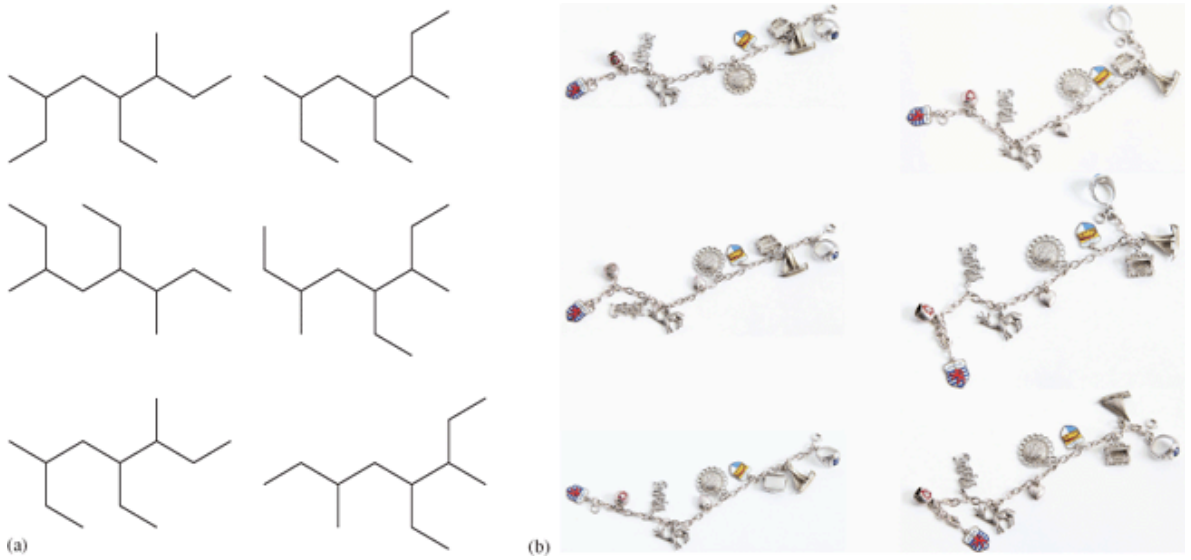


FIGURE 16.7 (a) None of these structures represent different isomers. They are all 4-ethyl-3,6-dimethyloctane drawn in different orientations or conformations.
(b) These photos do not represent different pieces of jewellery. They are all of the same charm bracelet shown in different orientations or conformations.
John Wiley & Sons Australia

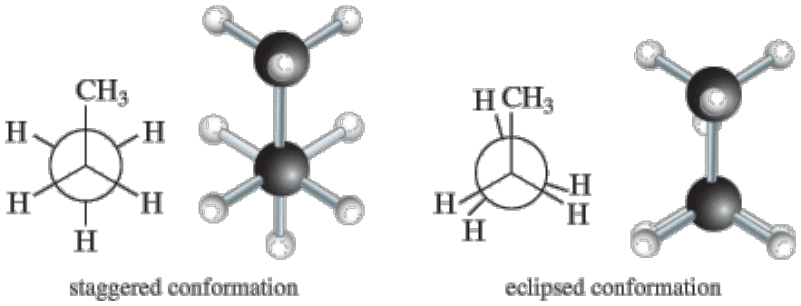
WORKED EXAMPLE 16.1

Drawing Newman Projections

Draw Newman projections for one staggered conformation and one eclipsed conformation of propane.

Solution

The following are Newman projections and ball-and-stick models of these conformations.



Viewed end on along the central carbon–carbon bond, we can see the atoms align in the eclipsed conformation whereas, in the staggered conformation, they are distributed as far apart as possible.

PRACTICE EXERCISE 16.1

Draw Newman projections for two staggered and two eclipsed conformations of butane as viewed down the central C—C bond.

Cycloalkanes

A hydrocarbon that contains carbon atoms joined to form a ring is called a cyclic hydrocarbon. When all carbon atoms of

the ring are saturated, we call the hydrocarbon a **cycloalkane**. Cycloalkanes with ring sizes of three to over 30 abound in nature, but, in principle, there is no limit to ring size. Five-membered (cyclopentane) and six-membered (cyclohexane) rings are especially abundant in nature.

Cycloalkanes contain two fewer hydrogen atoms than an alkane with the same number of carbon atoms. For instance, compare the molecular formula of cyclohexane, C_6H_{12}, with that of hexane, C_6H_{14}. The general formula of a cycloalkane is C_nH_{2n}. Note that cycloalkanes have the same molecular formulae as linear alkenes. However, they have essentially the same chemical reactivity as linear alkanes, so this degree of 'unsaturation' does not provide any chemical functionality.

Figure 16.8 shows the structural formulae of cyclobutane, cyclopentane and cyclohexane. When writing structural formulae for cycloalkanes, chemists rarely show all carbon and hydrogen atoms. Rather, they use line structures to represent cycloalkane rings. Each ring is represented by a regular polygon having the same number of sides as there are carbon atoms in the ring. For example, chemists represent cyclobutane by a square, cyclopentane by a pentagon and cyclohexane by a hexagon.

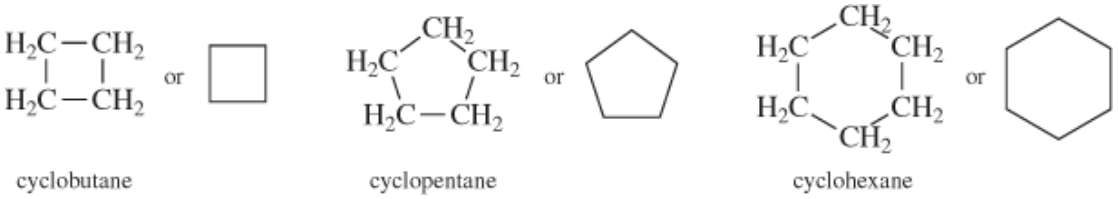


FIGURE 16.8 Examples of cycloalkanes: cyclobutane, cyclopentane and cyclohexane.

To name a cycloalkane, prefix the name of the corresponding open-chain hydrocarbon with *cyclo*-, and name each substituent on the ring. If there is only one substituent, there is no need to give it a number. If there are two substituents, number the ring beginning with the substituent of lower alphabetical order. If there are three or more substituents, number the ring to give them the lowest set of numbers, and then list the substituents in alphabetical order.

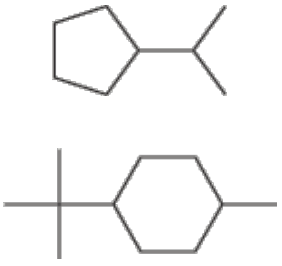
WORKED EXAMPLE 16.2

Naming Cycloalkanes

Write the molecular formula and IUPAC name for each of the following cycloalkanes.

(a)

(b)



Analysis and solution

(a) The molecular formula of this cycloalkane is C_8H_{16}. Because there is only one substituent on the ring, there is no need to number the atoms of the ring. IUPAC accepts two names for this compound: isopropylcyclopentane and 1-methylethylcyclopentane.

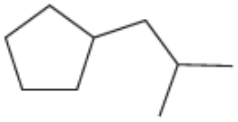
(b) Number the atoms of the cyclohexane ring beginning with *tert*-butyl, the substituent of lower alphabetical order. The compound's name is 1-*tert*-butyl-4-methylcyclohexane and its molecular formula is $C_{11}H_{22}$. IUPAC also accepts 1-(1,1-dimethylethyl)-4-methylcyclohexane.

PRACTICE EXERCISE 16.2

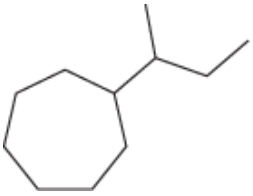
Write the molecular formula and IUPAC name for

each of the following cycloalkanes.

(a)



(b)



(c)



Conformations of cycloalkanes

When using line structure polygons to represent cycloalkane rings, it is important to realise that cycloalkanes are not flat structures. A pentagon possesses angles of 108°, which is close to the ideal tetrahedral angle of 109.5° found in methane (see section 5.4). This implies that the **angle strain** in a flat pentagon would be small. Angle strain results when a bond angle in a molecule differs from the optimal tetrahedral angle. Yet cyclopentane is not flat but in fact forms an 'open envelope' structure.

This structure arises to reduce the eclipsing interactions that would occur if the molecule was a flat structure. Recall from the discussions on the conformation of alkanes (p. 688) that the lowest energy for a molecule arises when bonds are staggered and are not eclipsed in the Newman projection (figure 16.4). A flat pentagon structure for pentane would give rise to 10 eclipsed C—H bonds. This unfavoured interaction produces **torsional strain**. Also called eclipsed interaction strain, torsional strain arises when nonbonded atoms separated by three bonds are forced from a staggered conformation to an eclipsed conformation. For a flat pentagon structure this torsional strain would equate to about 42 kJ mol^{-1}. To relieve some of this strain, the atoms twist into the 'envelope' conformation (figure 16.9) where four carbon atoms are in a plane and the fifth carbon lies above the plane, somewhat like an envelope with the flap folded outward.

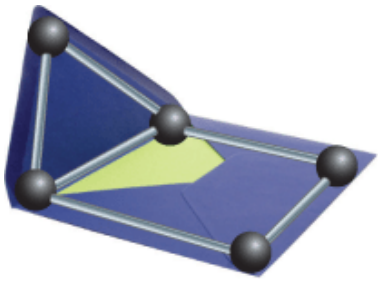


FIGURE 16.9 'Envelope' conformation.

In this envelope conformation the number of eclipsing interactions is reduced, but to attain this shape the C—C—C bond angles are also reduced to 105°, thus indicating an increase in angle strain. The total strain energy in cyclopentane in the envelope conformation is about 23.4 kJ mol^{-1}, which is substantially less than if the molecule was completely flat. It is important to remember, however, that molecules exist in a dynamic situation and these cyclopentane molecules are not rigid and unmoving. Although the envelope conformation represents a preferred lower energy state, at normal temperatures these molecules vibrate and wiggle as bonds stretch and contract. The out-of-plane carbon atom can move to the other side

of the plane, and indeed other carbon atoms in the ring can assume the out-of-plane position. This property is particularly important with other rings, especially cyclohexane.

Cyclohexane can readily adopt a number of puckered conformations, the most stable of which is called the **chair conformation**. In the chair conformation, four carbon atoms lie in a plane with one carbon atom above the plane and another carbon atom on the opposite side of the ring taking a position below the plane. The shape of the chair conformation is somewhat like the low reclining chairs that you might find beside a swimming pool (figure 16.10). The chair conformation for cyclohexane (figure 16.11) is the most stable arrangement because the C—C—C bond angles are all very close to the ideal 109.5° (minimising angle strain) and the C—H bonds can all form a low-energy staggered orientation (minimising torsional strain). The consequence of this is that in the chair conformation there are two sets of C—H bonds, depending on their orientation in space. Six C—H bonds are oriented essentially in the same plane as the four carbon atoms that make up the 'seat' of the chair. The other six C—H bonds point either up or down in the approximate direction of the chair 'back' or 'legs'. Arranging the bonds in this conformation minimises angle and torsional strain, and so cyclohexane in the chair conformation has almost no strain energy; this explains why these six-membered rings of carbon are found so commonly in nature.



FIGURE 16.10 'Chair' conformation.

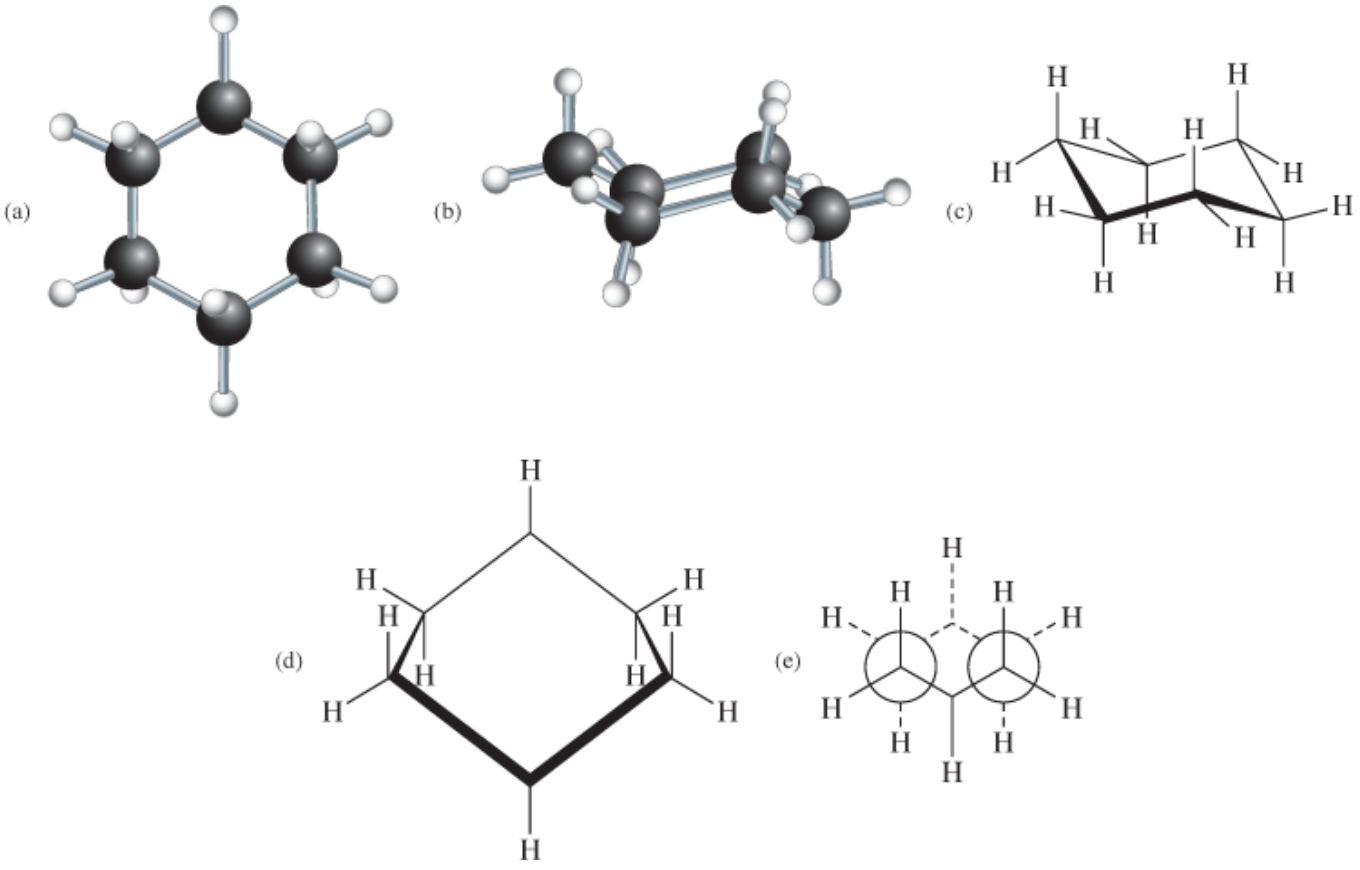


FIGURE 16.11 Cyclohexane. The most stable conformation is the 'chair' conformation:
(a) ball-and-stick model viewed from above,

(b) ball-and-stick model viewed from the side,
(c) skeletal model,
(d) skeletal model viewed from the front of the 'chair' and
(e) Newman projection.

Equatorial bonds are those that are oriented more or less in the plane of the seat of the chair (figure 16.12b) and the hydrogen atoms therefore are called equatorial hydrogen atoms. The other bonds are called **axial bonds** (figure 16.12c) and the hydrogen atoms in this orientation are called axial hydrogen atoms. Three axial bonds are directed upwards and three downwards. Equatorial bonds are aligned approximately in the plane of the seat of the imaginary chair, but close inspection shows that these also involve three bonds that point slightly up and three that point slightly down. Notice also that the orientation of either the axial or the equatorial bonds alternates, first up and then down, as you move from one carbon atom in the ring to the next. If the axial bond on one carbon atom points up then the equatorial bond on that carbon atom points slightly downwards. Conversely, if the axial bond on a particular carbon atom points downwards, then the equatorial bond on that atom points slightly upwards.

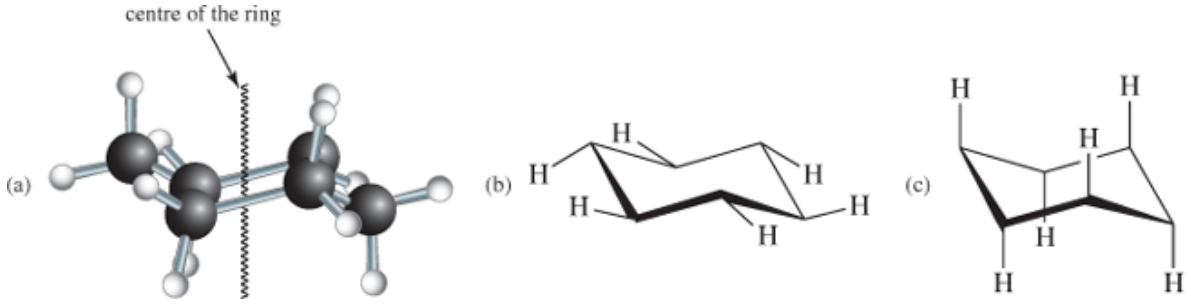


FIGURE 16.12 Chair conformation of cyclohexane showing axial and equatorial C—H bonds:
(a) ball-and-stick model showing all 12 hydrogen atoms,
(b) the six equatorial C—H bonds and
(c) the six axial C—H bonds.

Remember that, like cyclopentane, cyclohexane exists in a dynamic state and there are many other nonplanar conformations that the ring easily attains. Apart from other chair conformations, there is also a 'boat' conformation. The **boat conformation** occurs when both of the out-of-plane carbon atoms are on the same side of the plane made from the other four carbon atoms. This conformation is readily formed from the chair conformation by bending the ring and swinging the carbon atom on the chair 'leg' up so that it reaches the same position as the carbon atom on the chair 'back' (figure 16.13).

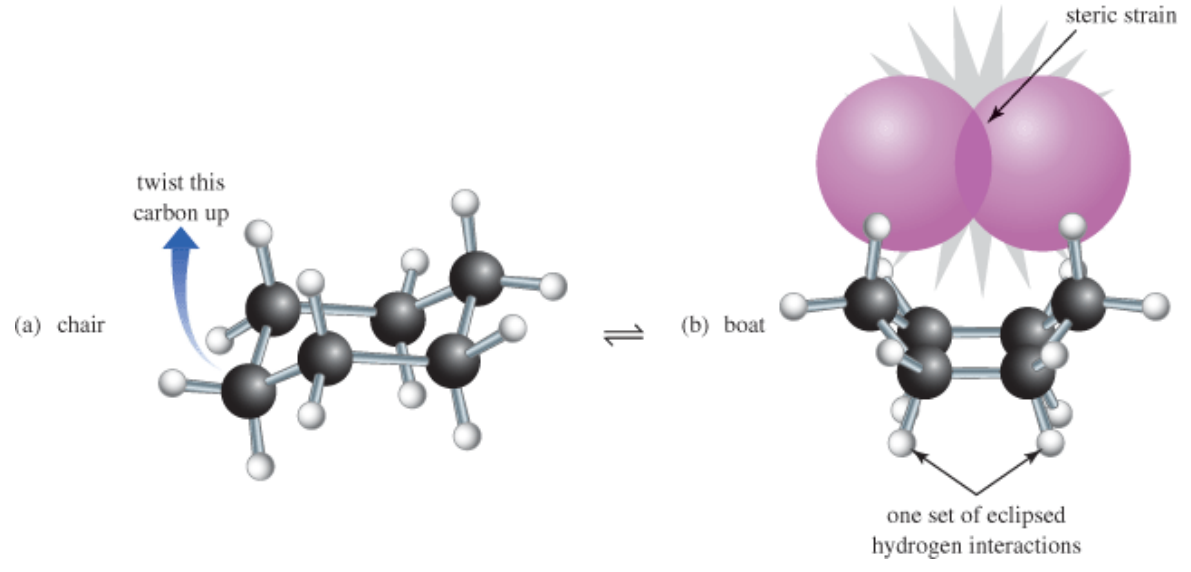


FIGURE 16.13 Conversion of

(a) a chair conformation to

(b) a boat conformation. In the boat conformation, there is both torsional strain, due to the four sets of eclipsed hydrogen interactions, and steric strain. A chair conformation is more stable than a boat conformation.

The boat conformation is less stable than the chair conformation. Torsional strain is present in the boat conformation as four sets of hydrogen atoms become eclipsed. Another type of strain, called **steric strain**, is also generated. Steric strain is also called nonbonded interaction strain, and it involves strain which arises in the molecule when two parts try to occupy the same space. In the case of the boat conformation of cyclohexane, the two axial hydrogen atoms and their attendant electron clouds interact across the ring, and this unfavourable action leads to strain in the molecule. The difference in energy between the chair and the boat conformations is about 27 kJ mol^{-1}. This means that, at room temperature, fewer than 0.001% of the molecules might be found in the boat conformation at any time. In fact, to lower the energy slightly, the boat conformation twists into a structure called the twist boat, which is a few kJ mol^{-1} lower in energy. Nevertheless, the boat conformation is important, as it is through this higher energy orientation that one chair conformation is converted into another. Two equivalent-energy chair conformations interconvert rapidly at room temperature by first twisting into the higher energy boat conformation (figure 16.13) and then relaxing into the lower energy chair conformation. When one chair is converted into another, a change occurs in relative orientations in space of the hydrogen atoms bound to the carbon atoms of the ring. All equatorial hydrogen atoms in one chair become axial hydrogen atoms in the other and vice versa (figure 16.14).

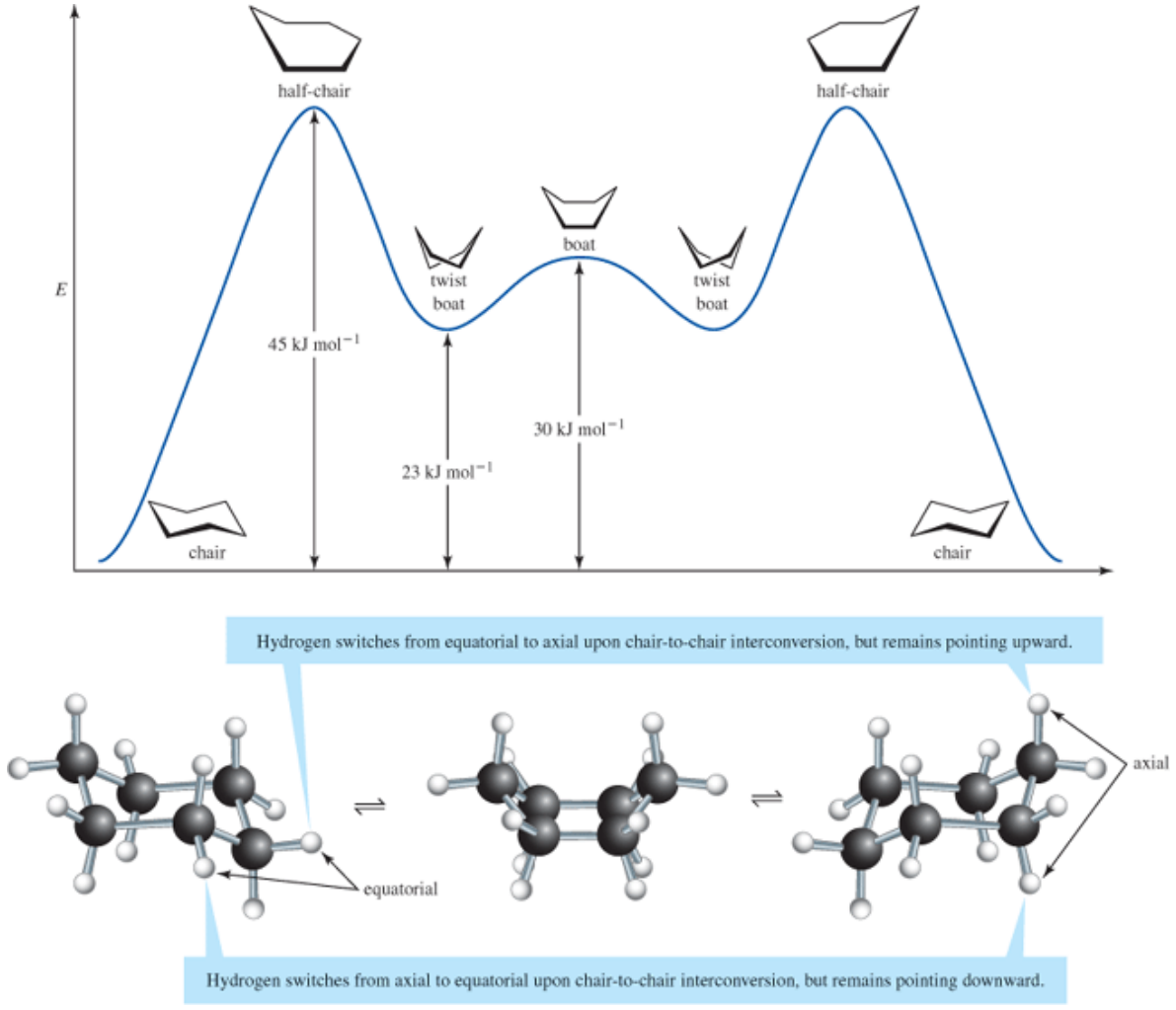


FIGURE 16.14 Interconversion of chair cyclohexanes via a boat conformation. All C—H bonds that are equatorial in one chair are axial in the other chair, and vice versa.

This process becomes much more significant when one of the hydrogen atoms is replaced by another group such as a methyl or other alkyl group. Interconversion of one chair to another now has the consequence of converting the substituted group from an equatorial to an axial orientation (or vice versa) and this now has energy implications. A large group can impose considerable steric strain across the ring when it is in an axial orientation. This type of strain is called an axial–axial (or diaxial) interaction. The presence of such a group on the ring favours the chair conformation where the group is in the equatorial orientation. For a methyl group, this makes the axial orientation about 7.28 kJ mol^{-1} higher in energy and so, at room temperature and at equilibrium, about 95% of these molecules would have the methyl group in the equatorial orientation (figure 16.15). Like the higher energy boat conformation, however, this does not mean that such a conformation is not readily achievable at room temperature but rather that such molecules prefer one conformation over the other.

However, this effect can become very significant when a large group is present on the cyclohexane ring. Large groups can essentially 'lock' the ring into the conformation where the group is equatorial. For a *tert*-butyl group (table 2.9, p. 55), which is considerably larger than a methyl group, this preference means that the equatorial conformer is 4000 times more abundant than the conformer where the *tert*-butyl group is in the axial orientation. In effect, the ring is locked into one conformation, and chemists actually call such molecules conformationally locked isomers.

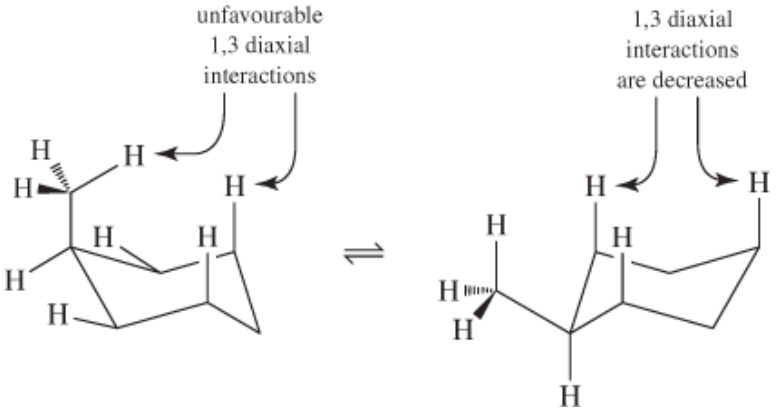
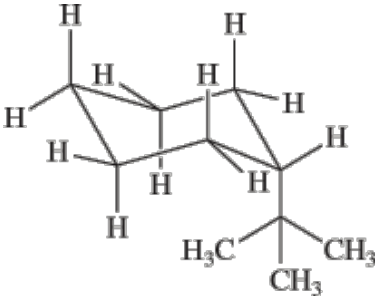


FIGURE 16.15 1,3 diaxial interaction leads to steric strain.

WORKED EXAMPLE 16.3

Cycloalkane Conformational Isomers

Is it possible to draw a lower energy conformation for the following molecule?

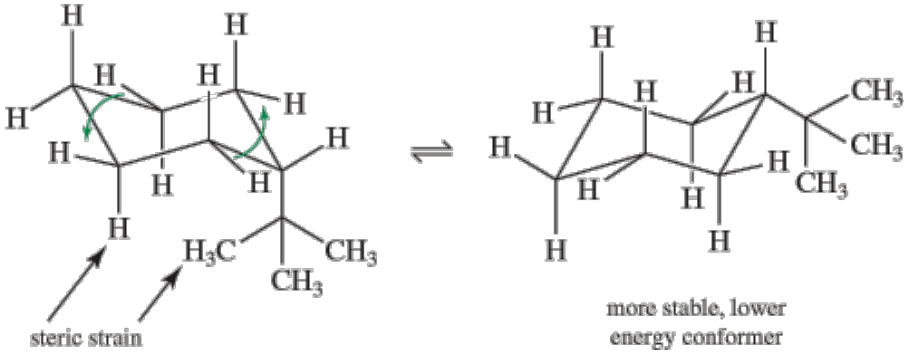


Analysis

In a lower energy conformation, the large *t*-butyl group would not be in an axial position as it interacts with the axial hydrogen atoms on carbons 3 and 5. We know that cyclohexanes can easily flip their orientation from one chair conformer to the other, so we should see what the structure looks like after such a transformation.

Solution

Bringing the left-hand side of the ring downwards and lifting the right-hand side upwards swaps the positions of the current axial groups with the equatorial position.



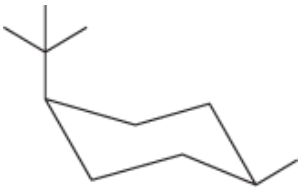
Is our answer reasonable?

The speed at which C—C bonds rotate means that the *t*-butyl group can be thought of as a high-speed fan with the methyl group 'blades', striking the axial hydrogen atoms on carbons 3 and 5. The large *t*-butyl group is now placed further away from the other parts of the cyclohexane, with which it was previously interacting.

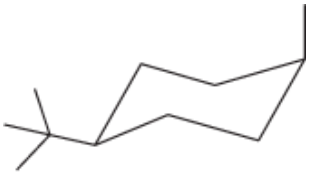
PRACTICE EXERCISE 16.3

For each of the following pairs, which is the lower energy conformation? Explain your answers.

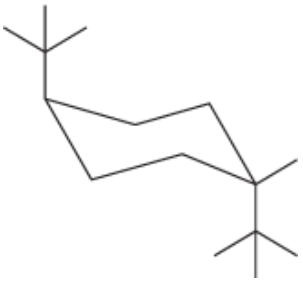
(a) i.



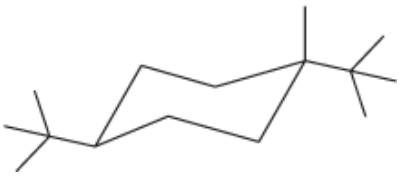
ii.



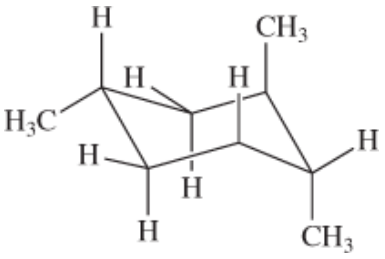
(b) i.



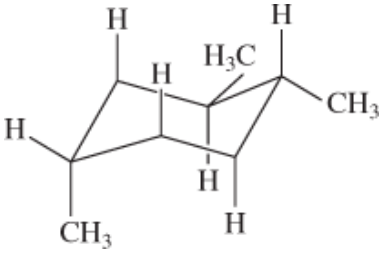
ii.



(c) i.



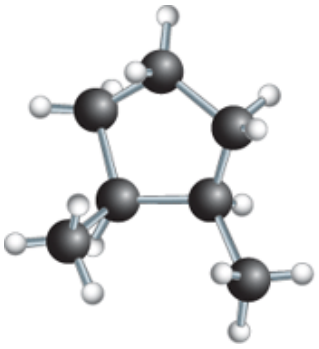
ii.

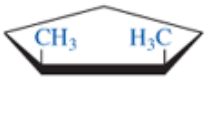


Cis–trans Isomerism in Cycloalkanes

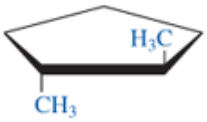
Cycloalkanes with substituents on two or more carbon atoms of the ring are called ***cis–trans* isomers**. All *cis–trans* isomers have (1) the same molecular formula, (2) the same order of attachment of atoms and (3) an arrangement of atoms that cannot be interchanged by rotation around σ bonds under ordinary conditions (see chapter 5). In *cis* isomers, the groups are 'on the same side'; in *trans* isomers, the groups are 'across from each other'.

In chapter 2, we illustrated *cis–trans* isomerism in cycloalkanes using 1,2-dimethylcyclopentane.

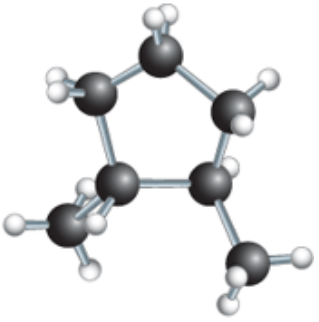




cis-1,2-dimethyl-cyclopentane

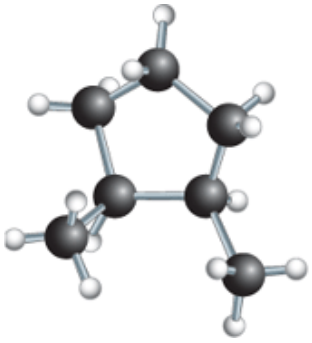


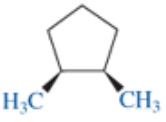
trans-1,2-dimethyl-cyclopentane



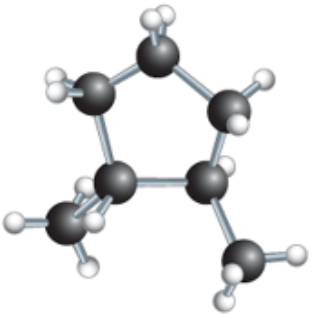
For simplicity, same hydrogen atoms have been omitted and, to add clarity, the cyclopentane ring has been drawn as a planar pentagon viewed edge on. (We know that cyclopentane exists primarily in an 'envelope' conformation shown in the ball-and-stick models above. However, to analyse the structural relationship between the substituents, we can represent this as a pentagonal line drawing.) Carbon–carbon bonds of the ring that project forwards are shown above as heavy lines. When viewed from this perspective, substituents bonded to the cyclopentane ring project above and below the plane of the ring. In the isomer of 1,2-dimethylcyclopentane shown above left, the methyl groups are on the same side of the ring (either both above or both below the plane of the ring) and we call this arrangement *cis*; in the isomer shown on the right, the methyl groups are on opposite sides of the ring (one above and one below the plane of the ring) and we call this arrangement *trans*.

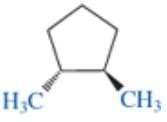
Alternatively, the cyclopentane ring can be viewed from above, with the ring in the plane of the paper. Substituents on the ring then either project towards you (that is, they project above the plane of the page) and are shown by solid wedges, or project away from you (they project below the plane of the page) and are shown by hashed wedges. In the following structural formulae, only the two methyl groups are shown (hydrogen atoms of the ring are not shown).





cis-1,2-dimethyl-cyclopentane





trans-1,2-dimethyl-cyclopentane

WORKED EXAMPLE 16.4

Drawing *Cis–trans* Isomers

Which of the following cycloalkanes show *cis–trans* isomerism? For each that does, draw both forms.

(a) methylcyclopentane

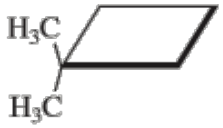
(b) 1,1-dimethylcyclobutane

(c) 1,3-dimethylcyclobutane

Analysis and solution

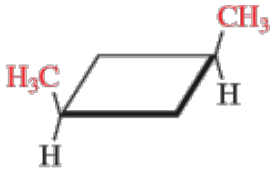
(a) Methylcyclopentane does not show *cis–trans* isomerism. It has only one substituent on the ring.

(b) Only one arrangement is possible for the two methyl groups on the ring, which must be *trans*, so 1,1-dimethylcyclobutane does not show *cis–trans* isomerism.

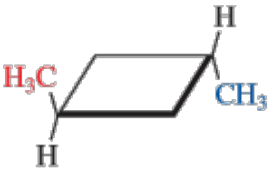


1,1-dimethylcyclobutane

(c) The following diagram shows the *cis–trans* isomerism of 1,3-dimethylcyclobutane. Note that, in these structural formulae, we show only the hydrogen atoms on carbon atoms bearing the methyl groups.



cis-1,3-dimethylcyclobutane



trans-1,3-dimethylcyclobutane

PRACTICE EXERCISE 16.4

Which of the following cycloalkanes show *cis–trans* isomerism? For each that does, draw both isomers.

(a) 1,3-dimethylcyclopentane

(b) ethylcyclopentane

(c) 1-ethyl-2-methylcyclobutane

Physical Properties of Alkanes

The most important property of alkanes is their almost complete lack of polarity. This is illustrated in figure 16.16, which shows the uniform distribution of the outer bonding electrons in pentane. As we saw in chapter 5, the difference in electronegativity between carbon and hydrogen is 2.5 - 2.1 = 0.4 on the Pauling scale and, given this small difference, we classify a C—H bond as a nonpolar covalent bond. Therefore, alkanes are nonpolar compounds, and there are only weak interactions between molecules.

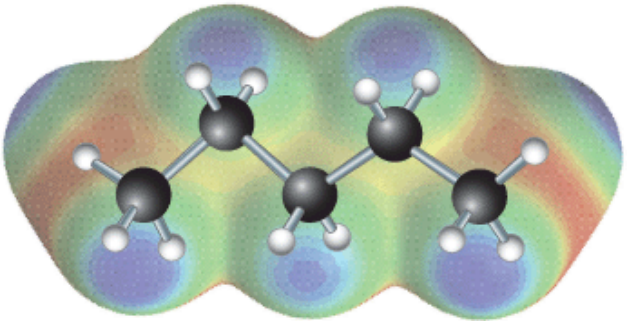


FIGURE 16.16 The electron density model of pentane (like all alkanes) shows no evidence of polarity.

Boiling Points

As we saw in chapter 6 (pp. 241 –2), interactions between alkane molecules consist of only weak dispersion forces. Because of this, the boiling points of alkanes are lower than those of almost any other type of compound of the same molar

mass. As the number of atoms and electrons and, therefore, the molar mass of an alkane increase, the number, and hence total strength, of dispersion forces between alkane molecules increases, thereby increasing the boiling point (see figure 6.34).

Alkanes containing one to four carbon atoms are gases at room temperature and atmospheric pressure, and those containing five to 17 carbon atoms are colourless liquids. High-molar-mass alkanes (those with 18 or more carbon atoms) are white, waxy solids. Several plant waxes are high-molar-mass alkanes. The wax found naturally in apple skins, for example, is an unbranched alkane with the molecular formula $C_{27}H_{56}$. Paraffin wax, a mixture of high-molar-mass alkanes, is used for wax candles, in lubricants and to seal home-made jams and other preserves. Petrolatum, so named because it is derived from petroleum refining, is a liquid mixture of high-molar-mass alkanes. Sold as mineral oil and Vaseline®, petrolatum is used as an ointment base in pharmaceuticals and cosmetics and as a lubricant and rust preventative.

Melting Point and Density

The melting points of alkanes increase with increasing molar mass. The increase, however, is not as regular as that observed for boiling points, because the ability of molecules to pack into ordered patterns of solids changes as the molecular size and shape change.

The average density of the alkanes listed in table 16.1 is about 0.7 g mL^{-1} whereas that of higher molar mass alkanes is about 0.8 g mL^{-1}. All liquid and solid alkanes are less dense than water (1.0 g mL^{-1}) and so float on water.

Isomeric Alkanes

Recall that isomers are molecules with the same molecular formula but different structures, and constitutional isomers are compounds with the same molecular formula but different structures because of different sequences of atom connectivity. Alkanes exhibit constitutional isomerism arising from side chains in the carbon sequence. As we learned in chapter 2 (pp. 55–6), each isomer has a unique name according to a set of rules in which numbers are used to indicate the positions of the side chains.

The ability of carbon atoms to form strong stable bonds with other carbon atoms results in a staggering number of constitutional isomers. As table 16.2 shows, there are three constitutional isomers with the molecular formula C_5H_{12}, 75 constitutional isomers with the molecular formula $C_{10}H_{22}$ and more than 36 million constitutional isomers with the molecular formula $C_{25}H_{52}$.

TABLE 16.2 Constitutional isomers of various C_nH_{2n+2} hydrocarbons.

Molecular formula	No. of constitutional isomers
CH_4	0
C_5H_{12}	3
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4 347
$C_{25}H_{52}$	36 797 588

Thus, for even a small number of carbon and hydrogen atoms, a very large number of constitutional isomers is possible. In fact, the potential for structural and functional group individuality among organic molecules made from just the basic building blocks of carbon, hydrogen, nitrogen and oxygen is practically limitless.

WORKED EXAMPLE 16.5

Hydrocarbon Isomers

How many types of different hydrocarbon molecules are there with the formulae C_4H_{10}, C_5H_{12}, C_6H_{14}, $C_{11}H_{24}$

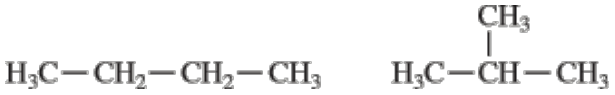
and $C_{30}H_{62}$?

Analysis

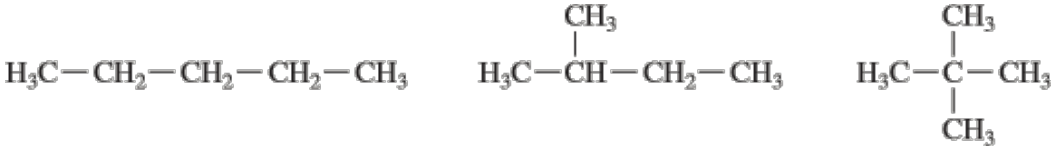
The question seems straightforward and, at least initially, it is. The compounds listed are ordinary hydrocarbons. There are no other elements present so all structural variety arises from the different sequences by which carbon atoms and hydrogen atoms can be assembled. There is no simple shortcut to the answer to this question and, in fact, we are better served by drawing out the possible structures to better understand the nature of the molecules involved.

Solution

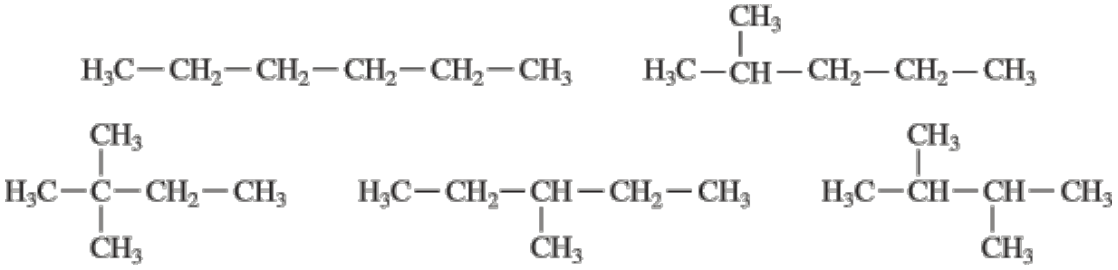
Starting with the simplest, C_4H_{10}, there are two possible structures. The most obvious answer is a simple chain of carbon atoms. There is another possible sequence, however, involving a branch.



With C_5H_{12}, three different molecules are possible:



For C_6H_{14}, there are five different ways to assemble the carbon and hydrogen atoms:



Here you will notice that, for clarity, we have not used line structures. However, even if we did, space precludes drawing all the possible structures for $C_{11}H_{24}$; there are 159!

You will not be surprised to know that there are a lot of isomers of $C_{30}H_{62}$, but you will still no doubt be shocked to know just how many. There are more than 4 billion ways of assembling these 92 atoms. Most organic compounds contain many more than this number of atoms and almost all involve other elements and more complicated bonding than is present in simple hydrocarbons. This is why organic chemistry is such a challenging field of science and why we need to find groupings of similar properties and categories to simplify the topic.

Is our answer reasonable?

To confirm that the structural formulae drawn represent constitutional isomers, write the mol ecular formula of each and check that they are the same, and check each structure to ensure that simple rotation around any bond does not reproduce one of the other structures.

As we learned in chapter 2, constitutional isomers have different physical properties. Table 16.3 lists the boiling points, melting points and densities of the five compounds with the molecular formula C_6H_{14}. The boiling point of each of the branched-chain molecules is lower than that of hexane itself, and the more branching there is the lower the boiling point is. These differences in boiling points are related to molecular shape. The only forces of attraction between alkane molecules are dispersion forces. As branching increases, the shape of an alkane molecule becomes more compact, and its surface area decreases. As the surface area decreases, so too does the area of contact between molecules. This decrease leads to weaker dispersion forces, so boiling points also decrease (see figure 16.17). Thus, for any group of constitutional isomers, it is usually observed that the least branched isomer has the highest boiling point and the most branched isomer has the lowest

boiling point. The trend in melting points is less obvious, but, as previously mentioned, it correlates with a molecule's ability to pack into ordered arrays of solids.

TABLE 16.3 Physical properties of the isomeric alkanes with the molecular formula C_6H_{14}.

Name	Boiling point (°C)	Melting point (°C)	Density (g mL^{-1} at 0 °C)
hexane	69	-95	0.659
3-methylpentane	63	-118	0.664
2-methylpentane	60	-153	0.653
2,3-dimethylbutane	58	-128	0.662
2,2-dimethylbutane	50	-100	0.649

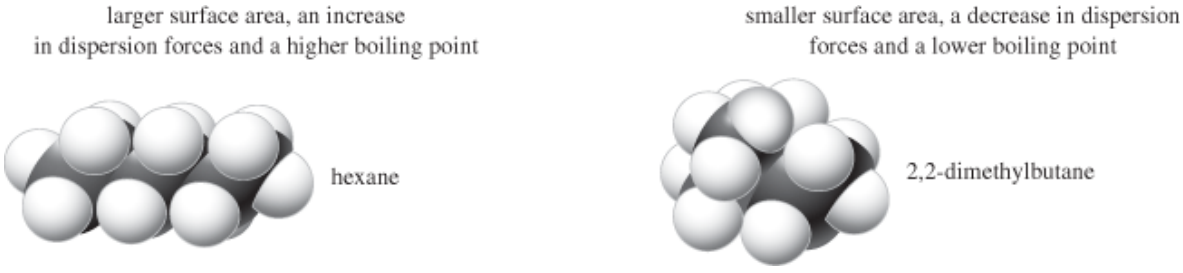


FIGURE 16.17 As branching increases, the shape of an alkane molecule becomes more compact, and its surface area decreases. As the surface area decreases, the strength of the dispersion forces decreases, and the boiling point also decreases.

WORKED EXAMPLE 16.6

Physical Properties of Alkanes

Arrange the alkanes in each of the following sets in order of increasing boiling point.

(a) butane, decane and hexane

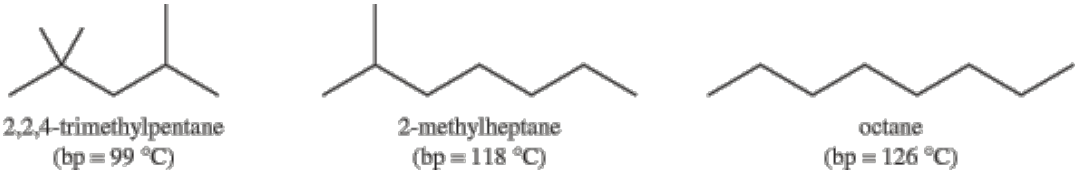
(b) 2-methylheptane, octane and 2,2,4-trimethylpentane

Analysis and solution

(a) All of the compounds are unbranched alkanes. As the number of carbon atoms in the chain increases, the dispersion forces between molecules increase, and the boiling point increases. Decane has the highest boiling point and butane the lowest.



(b) These three alkanes are constitutional isomers with the molecular formula C_8H_{18}. Their relative boiling points depend on the degree of branching. The most highly branched isomer, 2,2,4-trimethylpentane, has the smallest surface area and the lowest boiling point. Octane, the unbranched isomer, has the largest surface area and the highest boiling point.



PRACTICE EXERCISE 16.5

Arrange the alkanes in each of the following sets in order of increasing boiling point.

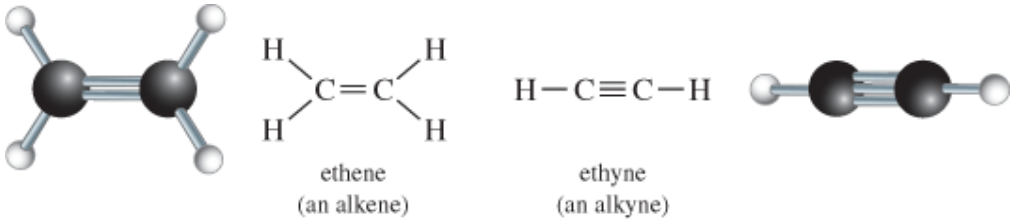
(a) 2-methylbutane, 2,2-dimethylpropane and pentane

(b) 3,3-dimethylheptane, 2,2,4-trimethylhexane and nonane

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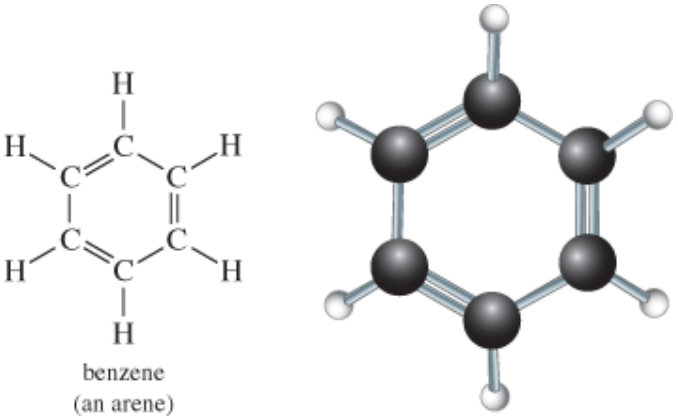
16.3 Alkenes and Alkynes

Some hydrocarbons have double bonds or triple bonds between carbon atoms and, hence, fewer hydrogen atoms than the corresponding alkanes. These are called unsaturated hydrocarbons. There are three classes of unsaturated hydrocarbons: alkenes, alkynes and arenes. Alkenes contain one or more carbon–carbon double bonds, and alkynes contain one or more carbon– carbon triple bonds. Alkenes have the general formula C_nH_{2n}. Alkynes have the general formula C_nH_{2n-2}. Ethene is the simplest alkene, and ethyne is the simplest alkyne:



ethene (an alkene) ethyne (an alkyne)

Arenes are the third class of unsaturated hydrocarbons. The simplest arene is benzene:



benzene (an arene)

Arenes are compounds that contain one or more ‘benzene’ rings. The chemistry of benzene and its derivatives is quite different from that of alkenes and alkynes and will be described later in the chapter. All we need to remember at this point is that a benzene ring is not chemically reactive under any of the conditions we describe for simple alkenes and alkynes.

Compounds containing carbon–carbon double bonds are especially widespread in nature. Many organic compounds found in nature are derived from an alkene called isoprene. Isoprene is a major contributor to the haze and scent that are characteristic of Australian eucalyptus forests (figure 16.18). Furthermore, several low-molar-mass alkenes, including ethene and propene, have enormous commercial importance in our modern, industrialised society. The organic chemical industry produces more ethene worldwide than any other chemical.



FIGURE 16.18 The blue haze that gives the Blue Mountains their name arises from isoprene and other hydrocarbons released from eucalyptus trees on exposure to sunlight and high temperatures.

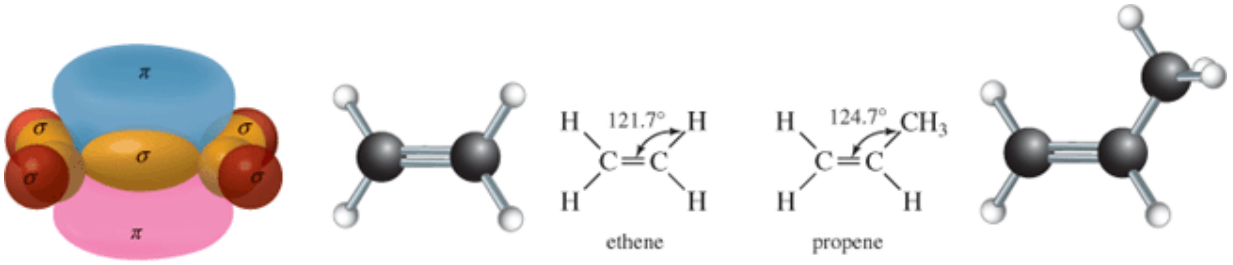
Ethene is unusual among the alkenes in that it occurs only in trace amounts in nature (where it plays an essential role in the process by which fruit ripens). The enormous amounts of it required to meet the needs of the chemical industry are generated from the refining of crude oil into petrol or the conversion of ethane extracted from natural gas as shown below.

$$\underset{\text{ethane}}{CH_3CH_3} \xrightarrow[\text{(thermal craking)}]{800-900\,^\circ C} \underset{\text{ethene}}{CH_2=CH_2} + H_2$$

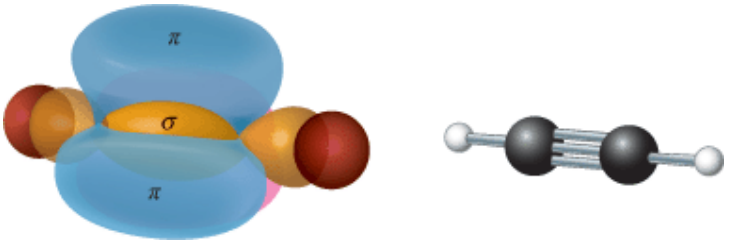
The crucial point to recognise is that ethene and all of the commercial and industrial products made from it (such as plastic shopping bags) are derived from either natural gas or crude oil — both nonrenewable natural resources!

Shapes of Alkenes and Alkynes

Using the valence-shell-electron-pair repulsion (VSEPR) model (see chapter 5), we predict a value of 120° for the bond angles around each carbon atom in a double bond. The observed H—C—C bond angle in ethene is 121.7°, a value close to that predicted by this model. In other alkenes, deviations from the predicted angle of 120° may be somewhat larger as a result of strain between groups bonded to one or both carbon atoms of the double bond. The C—C—C bond angle in propene, for example, is 124.7°.



Using the VSEPR model again, we predict all of the bond angles around each carbon atom in the triple bond to be 180°. The simplest alkyne is ethyne, C_2H_2. Ethyne is indeed a linear molecule; all of its bond angles are 180°. (*Note:* All orbitals, except pink π orbitals, are the same phase. Colours are used for clarity only.)



As we saw in chapter 5, a C≡C triple bond is described in terms of the overlap of *sp* hybrid orbitals of adjacent carbon atoms to form a σ bond, the overlap of parallel $2p_y$ orbitals to form one π bond, and the overlap of parallel $2p_z$ orbitals to form a second π bond. In ethyne, each carbon atom bonds to a hydrogen atom by the overlap of an *sp* hybrid orbital of carbon with a 1*s* atomic orbital of hydrogen.

Cis–trans Isomerism in Alkenes

In chapter 5, we described the formation of a carbon–carbon double bond in terms of the overlap of atomic orbitals. A carbon–carbon double bond consists of one σ bond and one π bond. Each carbon atom of the double bond uses its three sp^2 hybrid orbitals to form σ bonds with three atoms. The unhybridised 2*p* atomic orbitals, which lie perpendicular to the plane created by the axes of the three sp^2 hybrid orbitals, combine to form the π bond of the carbon–carbon double bond.

Whereas rotation around a single bond is relatively free (the energy barrier in ethane is approximately 12.5 kJ mol^{-1}), it takes considerably more energy to rotate a double bond. To break the π bond in ethene (i.e. to rotate one carbon atom by 90° with respect to the other so that no overlap occurs between 2*p* orbitals on adjacent carbon atoms) requires approximately 264 kJ mol^{-1} (figure 16.19). This energy is considerably greater than the thermal energy available at room temperature, so rotation around a carbon–carbon double bond is severely restricted.

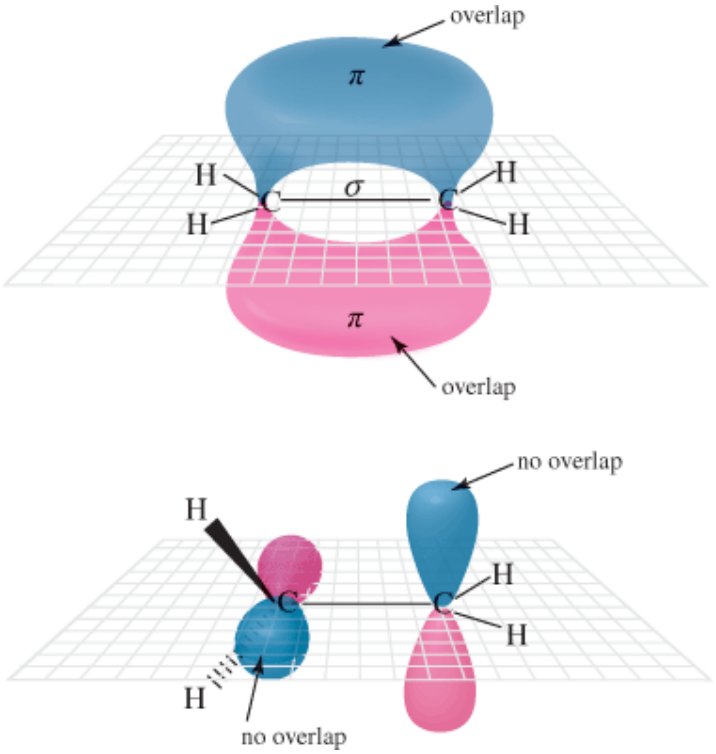
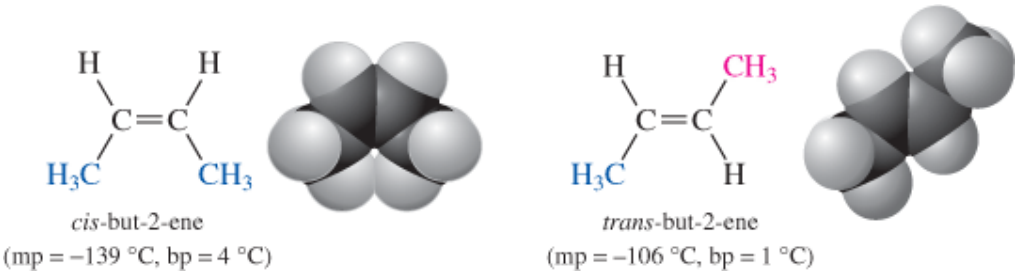


FIGURE 16.19 Restricted rotation around the carbon–carbon double bond in ethene:

(a) Orbital overlap model showing the π bond;

(b) The π bond is broken by rotating the plane of one H—C—H group by 90° with respect to the plane of the other H—C—H group.

Because of restricted rotation around a carbon–carbon double bond, an alkene in which each carbon atom of the double bond has two different groups bonded to it shows *cis–trans* isomerism. Consider, for example, but-2-ene. In *cis*-but-2-ene, the two methyl groups are on the same side of the double bond; in *trans*-but-2-ene, the two methyl groups are on opposite sides of the double bond.



cis-but-2-ene
(mp = –139 °C, bp = 4 °C)

trans-but-2-ene
(mp = –106 °C, bp = 1 °C)

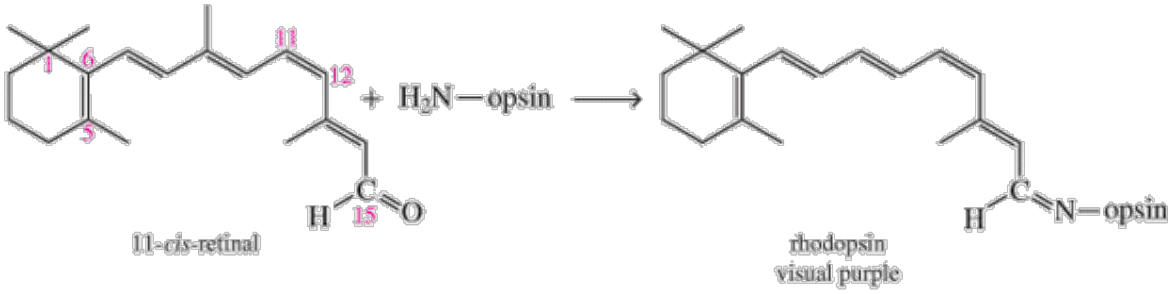
These two compounds cannot be converted into one another at room temperature because of the restricted rotation around the double bond; they are different compounds with different physical and chemical properties and are called **configurational isomers**.

Because of repulsion between alkyl substituents on the same side of the double bond in the *cis* isomer, *cis* alkenes are less stable than their *trans* isomers. This can be seen from the forcing together of the methyl hydrogen atoms in the space-filling model of *cis*-but-2-ene model above.

Chemical Connections

The Chemistry of Vision: From Man to Mollusc

Remarkably, all vertebrates, arthropods and, indeed, some molluscs share aspects of the amazing chemistry that drives the process of vision. To some extent, all of these creatures rely on the same molecule, 11-*cis*-retinal, an unsaturated alkene that strongly absorbs blue-green light (between 450 and 550 nm with a peak absorption at 498 nm). This molecule, when bound to the protein opsin in human eyes, forms rhodopsin — a purple-coloured material that is the basis of how we sense light and convert this to a biological response.



Our eyes are sophisticated organs with two forms of light-sensing cells that, because of their shape, are called rods and cones. About 100 million rod cells are located primarily on the periphery of the retina, and these allow vision in low light. However, this sensitivity does not extend to colour recognition, so the view is monochromatic. To detect colour, there are three types of cone cells, each of which uses retinal bound to proteins, slightly different from opsin, called iodopsins. Variation in a few key amino acids in the iodopsin chain distorts retinal's π bond system to change the position of the peak of maximum light absorption.

In the human eye, there are only about 3 million cone cells, and the photoreceptors in these cells are sensitive to three different portions of the visible spectrum covering from about 380 nm to 750 nm. A ‘green’ apple is perceived by us to be green only because our eye is able to distinguish between different wavelengths. A green apple does not emit green light. Rather, it simply absorbs all the wavelengths of light shining on it except the wavelengths we call green, which are reflected, enter our eye and are detected by our brain as green (figure 16.20).



FIGURE 16.20 A green apple absorbs all wavelengths of light except green, which it reflects. The reflected light enters our eyes and the brain detects it as green.

The signals generated by the rod and cone cells in the retina are converted by our brain to a visual image of the colour and brightness of an object. This process relies on a remarkable fusion of physics, chemistry and biology: the physics of light interacting with matter, the chemistry of how a molecule's shape is controlled by the nature of its bonds and the biology of the way a molecule's shape governs a cellular membrane to create a flow of ions and a nerve response. To interact with light, a molecule must have bonds that allow absorption of the precise energy of the light we see as ‘visible’. Most organic molecules do not absorb any light in this region and so, naturally, cannot form the basis of a chemical light detector. However, when 11-*cis*-retinal is bound to opsin, it absorbs the energy of photons of wavelength around 500 nm — right in the middle of our visible region. This is only the first step in a complicated process, however (see figure 16.21). Absorption of light allows 11-*cis*-retinal to relax from a bent shape (arising from the *cis* double bond) to a lower energy, all-*trans* arrangement. The straighter all-*trans*-retinal can no longer fit in the receptor designed for 11-*cis*-retinal and is ejected. This change leads to differences in cell membrane potential and, as ions are pumped into the cell, this response turns into a nerve impulse that travels to the brain. That is not the end of the matter; the all-*trans*-retinal generated by this process is reconverted to 11-*cis*-retinal by specific enzymes, which can re-bind into the receptor, ready to interact with another photon of light.

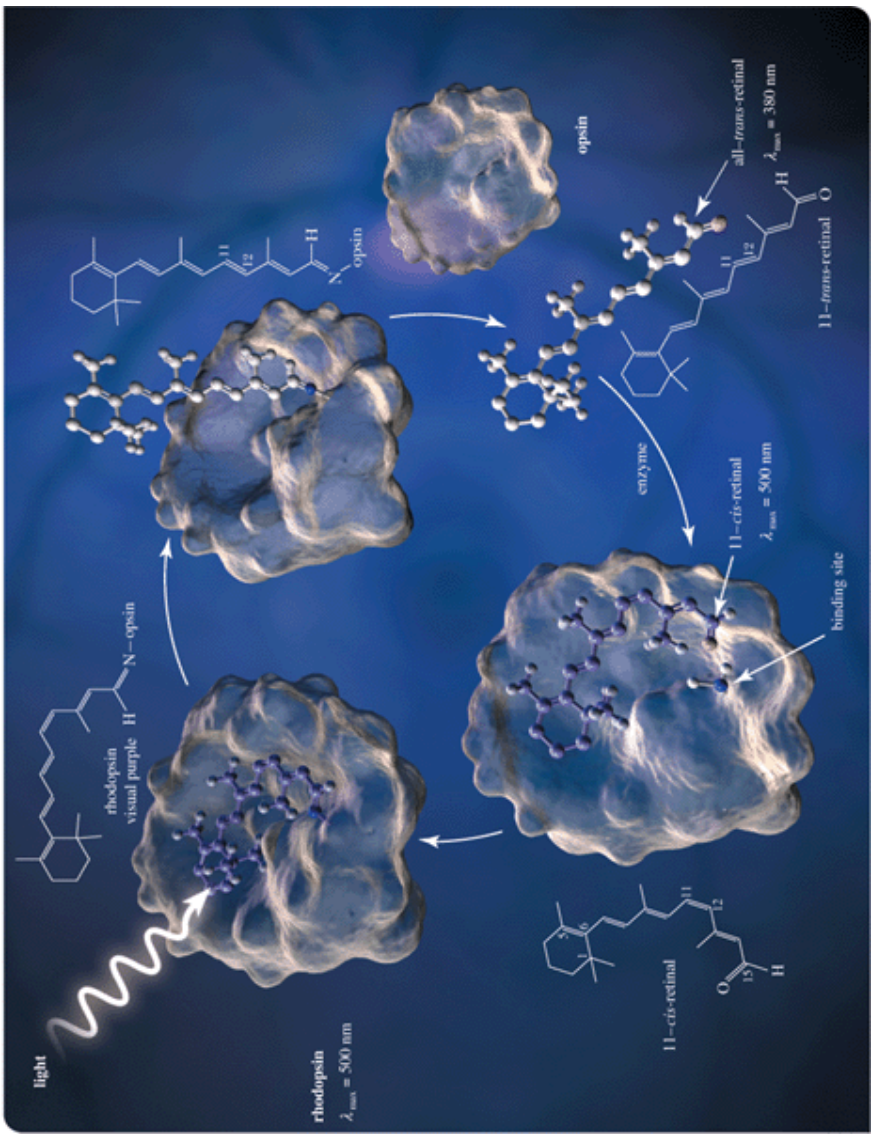


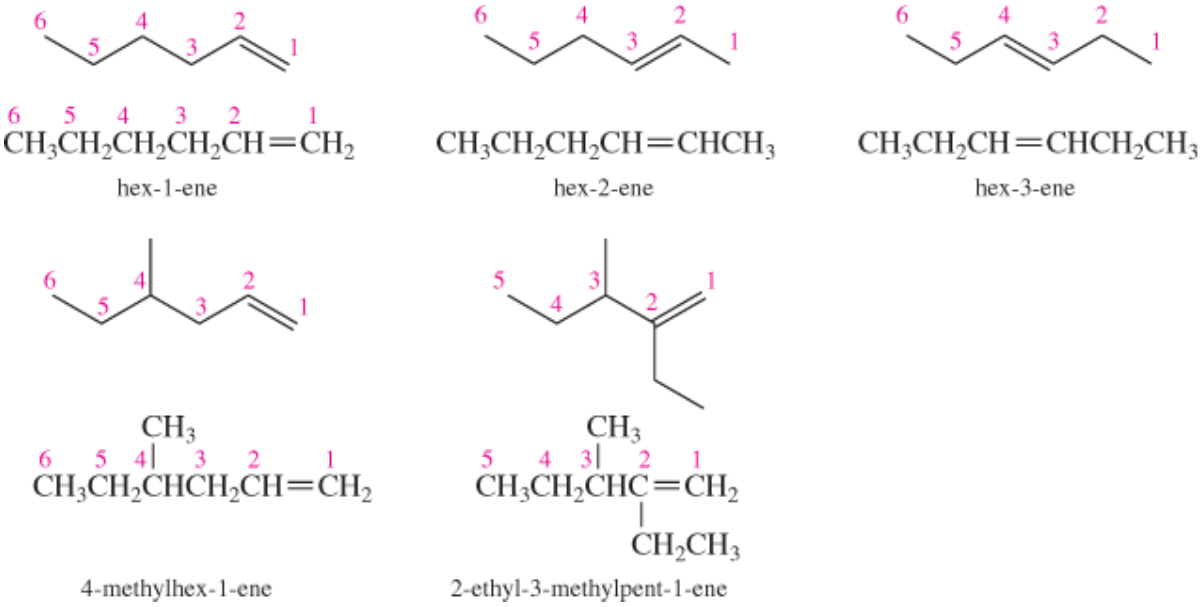
FIGURE 16.21 The chemistry of colour detection in the eye following absorption of a particular wavelength of light by rhodopsin.

Nomenclature of Alkenes and Alkynes

Like alkanes, alkenes are named using the IUPAC system, but, as we shall see, some are still referred to by their common names.

We form IUPAC names of alkenes by changing the *-an-* component of the name of the parent alkane to *-en-*. Hence, $CH_2{=}CH_2$ is named ethene, and $CH_3CH{=}CH_2$ is named propene. In higher alkenes where the location of the double bond differs between isomers, we use a numbering system. We identify the longest carbon chain that contains the double bond and number it in the direction that gives the carbon atoms of the double bond the lower set of

numbers. We then use the number of the first carbon atom of the double bond to show its location. As seen below, hex-1-ene has the double bond at the end of the chain, the double bond in hex-2-ene involves the 2nd and 3rd carbon atoms, and the double bond in hex-3-ene is in the middle of the chain. We name branched or substituted alkenes in a manner similar to the way we name alkanes. We number the carbon atoms, locate the double bond, locate and name substituent groups, and name the main chain.

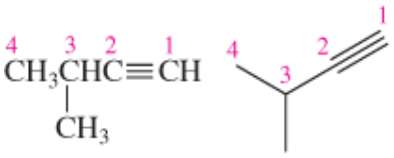


Note that there is a six-carbon chain in 2-ethyl-3-methylpent-1-ene. However, because the longest chain that contains the double bond has only five carbon atoms, the parent hydrocarbon is pentane, and we name the molecule as a disubstituted pent-1-ene.

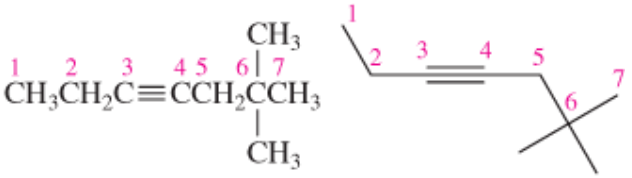
We form IUPAC names of alkynes by changing the *-an-* component of the name of the parent alkane to *-yn-*. Thus, HC≡CH is named ethyne, and $CH_3C{\equiv}CH$ is named propyne. (The IUPAC system retains the name *acetylene*, so there are two acceptable names for ethyne: ethyne and acetylene. Of these two names, acetylene is used much more frequently (figure 16.22).) For larger molecules, such as those shown below, we number the longest carbon chain that contains the triple bond from the end that gives the triple-bonded carbon atoms the lower set of numbers. We indicate the location of the triple bond by the number of the first carbon atom of the triple bond.



FIGURE 16.22 The combustion of ethyne (commonly called acetylene) in an oxyacetylene torch yields energy that produces very high temperatures.



3-methylbut-1-yne



6,6-dimethylhept-3-yne

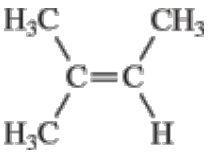
WORKED EXAMPLE 16.7

Naming Alkenes and Alkynes

Write the IUPAC name of each of the following unsaturated hydrocarbons.

(a) $CH_2{=}CH(CH_2)_5CH_3$

(b)



(c) $CH_3(CH_2)_2C{\equiv}CCH_3$

Analysis and solution

(a) As with all nomenclature, the first task is to find the longest chain involving the functional group: in this case, a double bond. The name given to hydrocarbons with double bonds is 'alkene'. The eight carbon atoms in this chain give the parent name, octene. We then number the chain to give the carbon atoms involved in the double bond the smallest numbers: in this case, 1 and 2. Hence the name is oct-1-ene.

(b) Use the same process as for (a). In this case, the functional group is again a double bond and the longest chain is four carbon atoms, so the parent name is butene. The double bond is between carbon atoms 2 and 3, so we have but-2-ene. There is a methyl substituent, also on carbon atom 2. Hence the name is 2-methylbut-2-ene.

(c) In this case, the functional group is a triple bond, which makes the hydrocarbon an alkyne, and the longest chain is six carbon atoms. The triple bond is between carbon atoms 2 and 3, so the name is hex-2-yne.

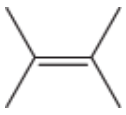
PRACTICE EXERCISE 16.6

Write the IUPAC name of each of the following unsaturated hydrocarbons.

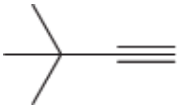
(a)



(b)



(c)



Despite the precision and universal acceptance of IUPAC nomenclature, some alkenes and alkynes — particularly those of low molar mass — are known almost exclusively by their common names, as illustrated below.

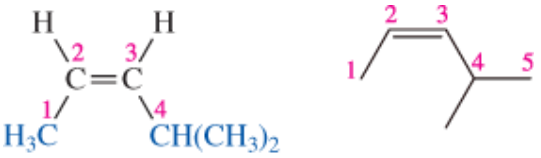
	$CH_2=CH_2$	$CH_3CH=CH_2$	$CH_3C(CH_3)=CH_2$	$H-C\equiv C-H$
IUPAC name	ethene	propene	2-methylpropene	ethyne
Common name	ethylene	propylene	isobutylene	acetylene

Designating Configuration in Alkenes

As we saw previously (p. 701), the physical properties of but-2-ene depend on the orientation of the substituents (or bonds to the substituents) in relation to the double bond. These different orientations represent different molecules (*cis–trans* isomers). We need a precise way of describing the different isomers that can arise when a double bond is present in a hydrocarbon. There are currently two ways of designating the orientation of groups attached to carbon atoms in a double bond: *cis–trans* isomers and *E,Z* isomers.

The *Cis–trans* System

The most common method for specifying the configuration of a disubstituted alkene uses the prefixes *cis* and *trans*. In this system, the orientation of the atoms of the parent chain determines whether the alkene is *cis* or *trans*. The following is the structural formula for the *cis* isomer of 4-methylpent-2-ene.



cis-4-methylpent-2-ene

In this example, carbon atoms of the main chain (carbons 1 and 4) are on the same side of the double bond so the configuration of this alkene is *cis*.

WORKED EXAMPLE 16.8

Describing *Cis–trans* Isomers in Alkenes

Name each of the following alkenes, and, using the *cis–trans* system, specify the configuration around each double bond.

(a)



(b)



Analysis and solution

(a) The chain contains seven carbon atoms and is numbered from the end that gives the lower number to the first carbon atom of the double bond. The carbon atoms of the parent chain are on opposite sides of the double bond. The compound's name is *trans*-hept-3-ene.

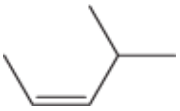
(b) The longest chain contains seven carbon atoms and is numbered from the right, so that the first

carbon atom of the double bond is C(3) of the chain. The carbon atoms of the parent chain are on the same side of the double bond. The compound's name is *cis*-6-methylhept-3-ene.

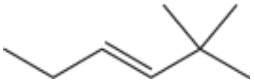
PRACTICE EXERCISE 16.7

Name each of the following alkenes, and, using the *cis–trans* system, specify its configuration.

(a)

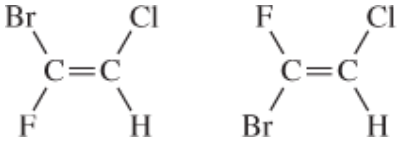


(b)

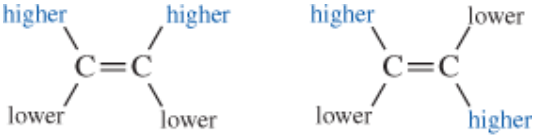


The *E, Z* System

Consider the two possible structures of the molecule 1-bromo-2-chloro-1-fluoroethene.

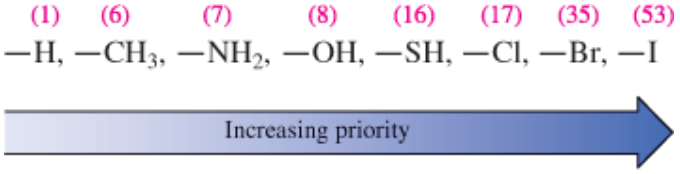


The *cis–trans* convention fails when trying to give a definitive name to each of these isomers. The ***E,Z* system** must be used for tri- and tetrasubstituted alkenes. This system uses a set of rules to assign priorities to the substituents on each carbon atom of a double bond. If the groups of higher priority are on the same side of the double bond, the configuration of the alkene is *Z* (from the German word *zusammen* meaning 'together'). If the groups of higher priority are on opposite sides of the double bond, the configuration is *E* (from the German word *entgegen* meaning 'opposite').

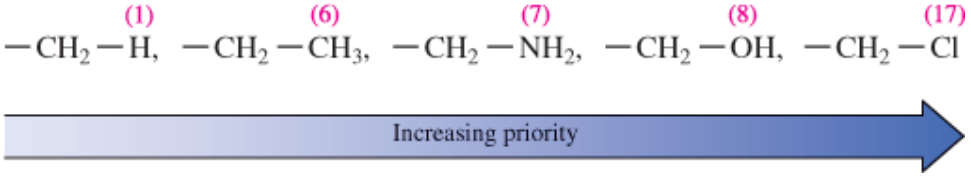


The most important step in determining an *E* or a *Z* configuration is to correctly assign a priority to each of the groups bonded to each carbon atom. The priority rules are shown in figure 16.23. (The priority rules are often called the Cahn–Ingold–Prelog (CIP) rules after the chemists who developed the system.)

1. Priority is based on atomic number. The higher the atomic number, the higher the priority. The following are several substituents arranged in order of increasing priority (the atomic number of the atom determining priority is shown in parentheses):



2. If priority cannot be assigned on the basis of the atoms bonded directly to the double bond, look at the next set of atoms, and continue until a priority can be assigned. Priority is assigned at the first point of difference. The following is a series of groups, arranged in order of increasing priority (again, numbers in parentheses give the atomic number of the atom on which the assignment of priority is based):



3. We treat atoms participating in a double or triple bond as if they were bonded to an equiv alent number of similar atoms by single bonds; that is, atoms of a double bond are replicated. Accordingly:

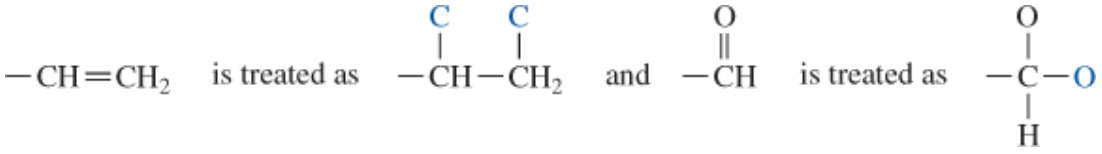


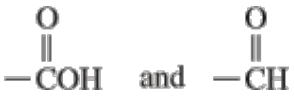
FIGURE 16.23 Priority rules for the *E,Z* system.

WORKED EXAMPLE 16.9

Assigning Priorities in the *E, Z* System

Assign priorities to the groups in each of the following sets.

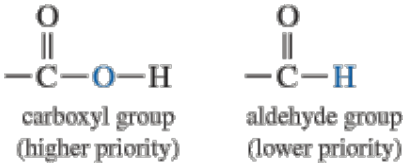
(a)



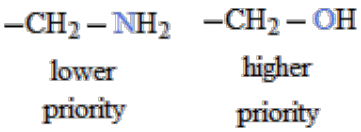
(b) $—CH_2—NH_2$ and $—CH_2—OH$

Analysis and solution

(a) The first point of difference is the O of the —OH in the carboxyl group, compared with the —H in the aldehyde group. The carboxyl group has higher priority.



(b) Oxygen has higher priority (higher atomic number) than nitrogen. Therefore, the carboxyl group has higher priority than the primary amino group.



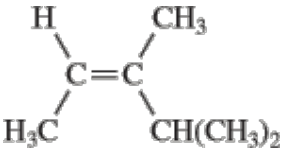
WORKED EXAMPLE 16.10

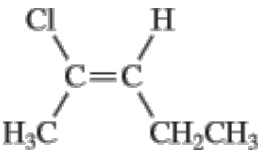
Specifying Configurations of Alkenes Using the *E, Z* System

Name each of the following alkenes and specify its configuration using the *E,Z* system.

(a)

(b)





Analysis and solution

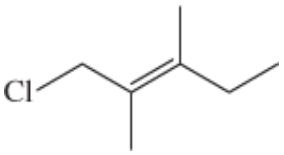
(a) The group of higher priority on C(2) is methyl; that of higher priority on C(3) is isopropyl. Because the groups of higher priority are on the same side of the carbon–carbon double bond, the alkene has the *Z* configuration. Its name is (*Z*)-3,4-dimethylpent-2-ene.

(b) The groups of higher priority on C(2) and C(3) are —Cl and —CH_2CH_3. Because these groups are on opposite sides of the double bond, the configuration of this alkene is *E*, and its name is (*E*)-2-chloropent-2-ene.

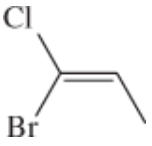
PRACTICE EXERCISE 16.8

Name each of the following alkenes and specify its configuration using the *E*,*Z* system.

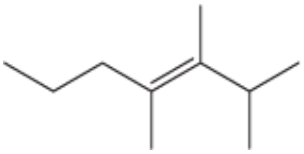
(a)



(b)

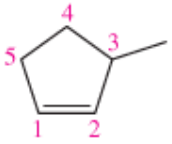


(c)

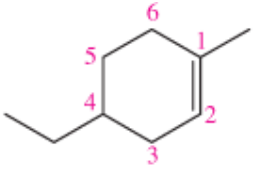


Cycloalkenes

Double bonds can be present in cyclic hydrocarbons and these molecules are called **cycloalkenes**. The rules for naming cycloalkenes follow the same logic we have seen previously. In naming cycloalkenes, we number the carbon atoms of the ring double bond 1 and 2 in the direction that gives the substituents the smallest possible numbers. We name and locate substituents and list them in alphabetical order, as in the following compounds.



3-methylcyclopentene
(not 5-methylcyclopentene)



4-ethyl-1-methylcyclohexene
(not 5-ethyl-2-methylcyclohexene)

Herbal Remedies: a Chemical Basis

Professor James De Voss, University of Queensland

Herbal medicines represent a multibillion-dollar industry. The De Voss research group at the University of Queensland is involved in identifying and synthesising the constituents of various popular herbal medicines in conjunction with a company called Integria Healthcare. Integria, through its brand Mediherb, specialises in developing medicinal products from natural sources (figure 16.24). The chemical make-up of herbs and other natural remedies is remarkably complicated and it is important to assess accurately the levels of active ingredients, some of which may vary from season to season and even from plant to plant. Surprisingly, detailed chemical profiles for many herbal extracts are unavailable, making production of uniform-quality herbal extracts a challenge for companies such as Integria.

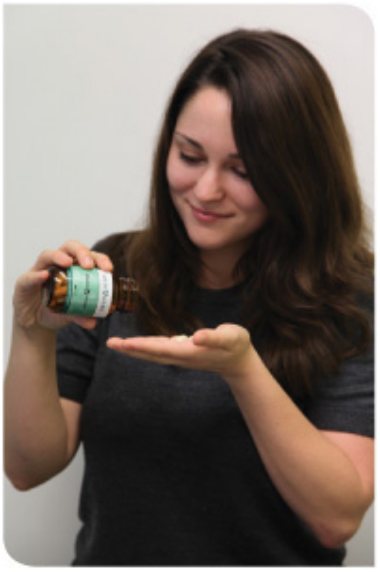
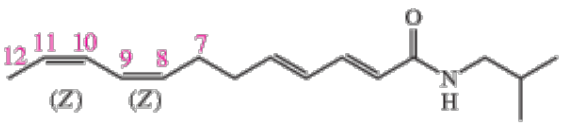


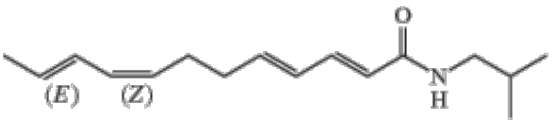
FIGURE 16.24 Medicinal echinacea is produced in tablet and liquid forms from extracts of *Echinacea purpurea* and *E. angustifolia*. Amanda Murfitt

The De Voss research group is tackling this problem by synthesising the complicated active ingredients of herbal remedies using smaller molecules available in the laboratory. This provides accurate standards against which to measure the quality of the extracts. For instance, the active ingredients in echinacea extracts are thought to be mixtures of polyunsaturated compounds such as (a)–(c) (shown below), but determining exactly which of these compounds is present is a challenging task. Recently, the De Voss group has synthesised all four of the *E, Z* isomers possible for the C(8)–C(9) and C(10)–C(11) double bonds present in compounds (a)–(d), thus providing the pure materials required to compare with the actual isomers present in species of *Echinacea* (figure 16.25). The arrangement of the groups around the C═C bonds can have profound effects on the physical and biological properties of these molecules. The key step in the synthesis was the controlled introduction of the double bonds, i.e. either *E* or *Z*. For instance, the *Z* double bonds of compound (a) were introduced by reduction of a compound that had alkynes at the carbon atoms corresponding to the *Z* alkenes in the final product. Although the group explored the use of Lindlar catalysts (p. 722), they finally used a different reagent to reduce the sensitive diyne system employed.

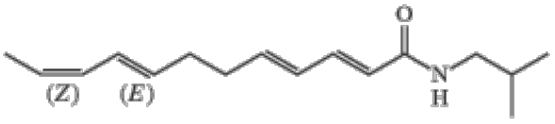
(a)



(b)



(c)



(d)

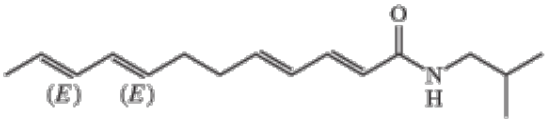




FIGURE 16.25 Flowers of *Echinacea purpurea*. Currently, the species most commonly used for medicinal purposes are *E. purpurea*, *E. angustifolia* and *E. pallida.*

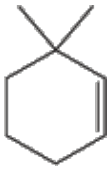
With all four isomers shown above synthesised and characterised, the De Voss group was able to demonstrate that (a) and (b) are the major products present in extracts of species of *Echinacea*, but that their levels varied considerably. They showed for the first time that the *E*, *Z* isomer (c) is also present in echinacea extracts. This specific isomer had been reported in an African plant, *Spilanthes mauritiana*, and was thought to have potential as a natural agent to control mosquito larvae. However, the work of the De Voss group showed that the original report was wrong and that the isolated compound was actually isomer (a).

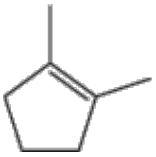
One postulate to explain the biological action of echinacea extracts is that they interact with proteins in the body called cannabinoid type-2 (CB_2) receptors. These are believed to play a role in many processes including those of the cellular immune system. The De Voss group subsequently investigated how well each of the four isomers (a)–(d) binds to CB_2 receptors. It was determined that, while (a) binds tightly, the affinity of (d) is approximately 1500 times lower, with isomers (b) and (c) having intermediate affinity. The arrangement of the groups around a carbon–carbon double bond is important in determining both the reactivity and the shape of such molecules. It is this latter property that influences how these molecules interact with biological receptors and thus governs their biological activity.

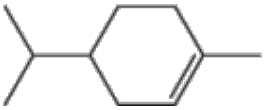
Although the synthesis of such compounds is a difficult task, it is only when the fully characterised compounds are in hand that researchers such as those in the De Voss group can truly understand the nature of the action of herbal remedies.

Naming Cycloalkenes

Write the IUPAC names for the following cycloalkenes.

(a) 

(b) 

(c) 

Analysis

We number the carbon atoms of the double bond 1 and 2 in the direction that gives the substituents the smallest possible numbers. We name and locate substituents and list them in alphabetical order.

Solution

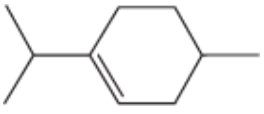
(a) 3,3-dimethylcyclohexene

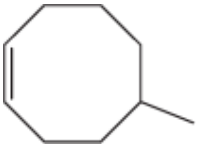
(b) 1,2-dimethylcyclopentene

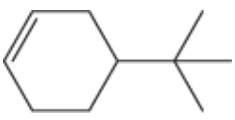
(c) 4-isopropyl-1-methylcyclohexene

PRACTICE EXERCISE 16.9

Write the IUPAC names for the following cycloalkenes.

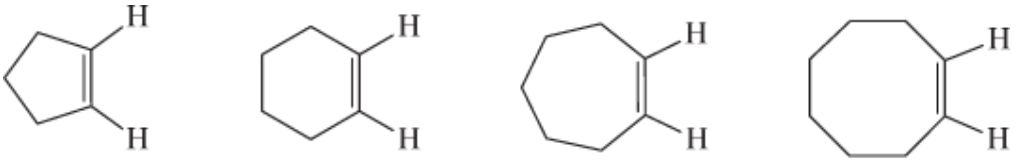
(a) 

(b) 

(c) 

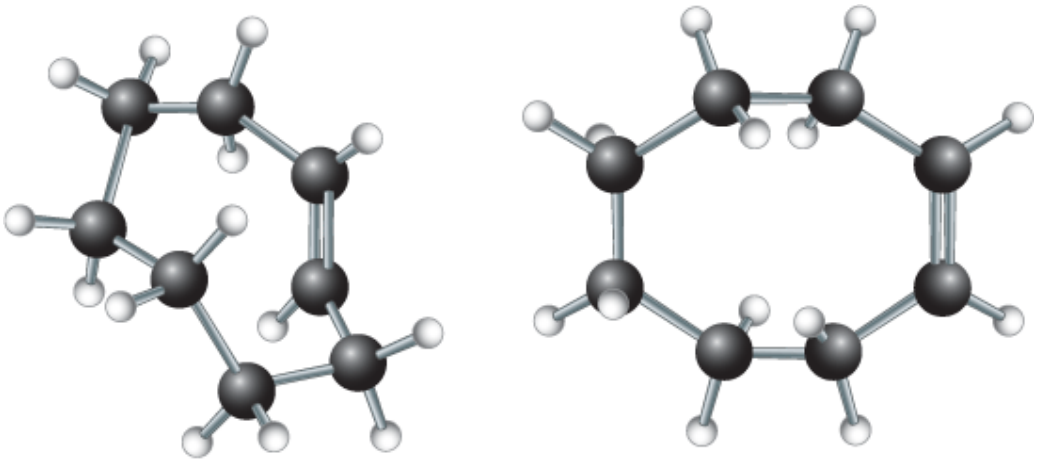
Cis–trans Isomerism in Cycloalkenes

The following are structural formulae for four cycloalkenes.



cyclopentene cyclohexene cycloheptene cyclooctene

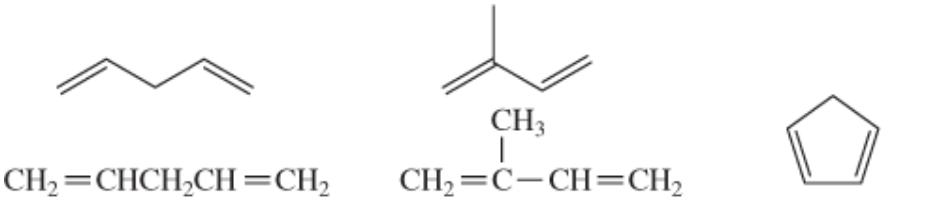
In these representations, the configuration around each double bond is *cis*. Because of angle strain, it is not possible to have a *trans* configuration in cycloalkenes of seven or fewer carbon atoms. To date, *trans*-cyclooctene (shown below) is the smallest *trans*-cycloalkene that has been prepared in pure form and that is stable at room temperature. Yet, even in this *trans*-cycloalkene, there is considerable intramolecular strain. The isomer *cis*-cyclooctene is more stable than its *trans* isomer by 38 kJ mol^{-1}.



trans-cyclooctene *cis*-cyclooctene

Dienes, Trienes, and Polyenes

We name alkenes that contain more than one double bond as alkadienes (two double bonds), alka trienes (three double bonds) and so on. We refer to those that contain several double bonds more generally as polyenes (from the Greek word *poly* meaning 'many'). Three examples of dienes are shown on the next page.



$CH_2=CHCH_2CH=CH_2$ penta-1,4-diene

$CH_2=C(CH_3)-CH=CH_2$ 2-methylbuta-1,3-diene (isoprene)

cyclopenta-1,3-diene

Thus far, we have considered *cis–trans* isomerism in alkenes containing only one carbon– carbon double bond. For an alkene with one carbon–carbon double bond that can show *cis–trans* isomerism, there are two isomers: one *cis* and one *trans*. For an alkene with *n* carbon–carbon double bonds, each of which can show *cis–trans* isomerism, a maximum of 2^n *cis–trans* isomers are possible.

WORKED EXAMPLE 16.12

Cis–trans Isomerism in Polyenes

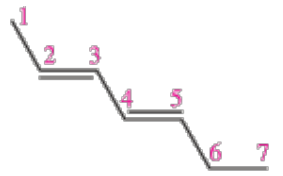
(a) How many *cis–trans* isomers are possible for hepta-2,4-diene?

(b) Name these isomers using the *E,Z* nomenclature.

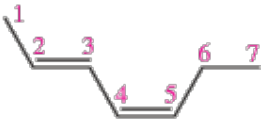
Analysis and solution

(a) This molecule has two carbon–carbon double bonds, each of which exhibits *cis–trans* iso merism. As the following table shows, $2^2 = 4$ *cis–trans* isomers are possible (to the right of the table are line structures for two of these isomers).

Double bond	
$C_2{=}C_3$	$C_4{=}C_5$
trans	*trans*
trans	*cis*
cis	*trans*
cis	*cis*



trans,trans-hepta-2,4-diene



trans,cis-hepta-2,4-diene

(b) All of these isomers are disubstituted alkenes and therefore *cis* can be replaced with *Z* and *trans* can be replaced with *E*. So, for instance, the names of the two isomers shown become (*E,E*)-hepta-2,4-diene and (*E,Z*)-hepta-2,4-diene, respectively.

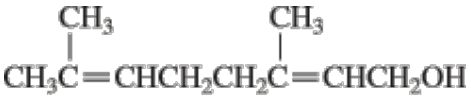
PRACTICE EXERCISE 16.10

Draw structural formulae for the two *cis–trans* isomers of hepta-2,4-diene not shown in worked example 16.12.

WORKED EXAMPLE 16.13

Drawing *Cis–trans* Isomers of Polyenes

Draw all possible *cis–trans* isomers for the following unsaturated alcohol.

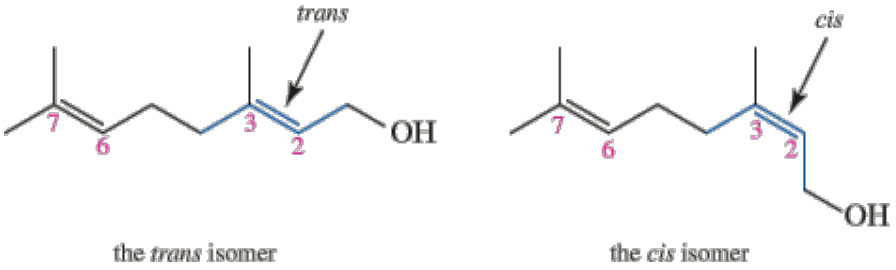


Analysis and solution

It is possible to have *cis–trans* isomerism only around the double bond between C(2) and C(3) of the chain. It is not possible for the other double bond, because C(7) has two identical groups on it. Thus, $2^1 = 2$ *cis–trans* isomers are possible. The *trans* isomer of this alcohol, named geraniol, is a major component of the oils of rose, citronella and lemongrass (figure 16.26).



FIGURE 16.26 Geraniol is a major component of the oils of citronella, rose and lemongrass. Kari-Ann Tapp

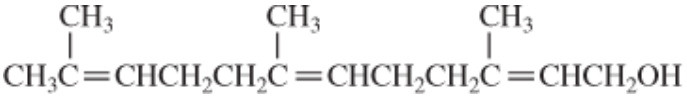


the *trans* isomer

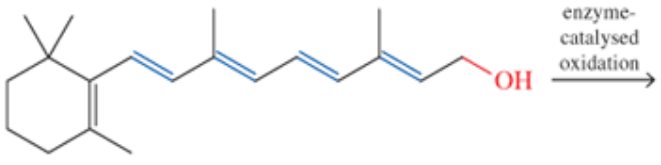
the *cis* isomer

PRACTICE EXERCISE 16.11

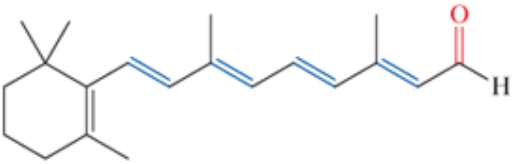
How many *cis*–*trans* isomers are possible for the following unsaturated alcohol?



Vitamin A is an example of a biologically important compound for which a number of *cis*– *trans* isomers are possible. There are four carbon–carbon double bonds (highlighted in blue) in the chain of carbon atoms bonded to the substituted cyclohexene ring, and each has the potential for *cis*–*trans* isomerism. Thus, $2^4 = 16$ *cis*–*trans* isomers are possible for a molecule with this structural formula. Vitamin A is the all-*trans* isomer. The enzyme-catalysed oxidation of vitamin A converts the primary hydroxyl group (highlighted in red) to an aldehyde group (red) to give retinal, the biologically active form of the vitamin.



vitamin A (retinol)



vitamin A aldehyde (retinal)

Physical Properties of Alkenes and Alkynes

Alkenes and alkynes are nonpolar compounds, and the only attractive forces between their molecules are dispersion forces. Therefore, their physical properties are similar to those of alkanes with the same carbon skeletons. Alkenes and

alkynes that are liquid at room temperature have densities less than 1.0 g mL^{-1}, so they are less dense than water. Like alkanes, alkenes and alkynes are soluble in each other. Because of their contrasting polarity with water, they do not dissolve. Instead, they form a separate layer when mixed with water or another polar organic liquid such as methanol.

WORKED EXAMPLE 16.14

Physical Properties of Alkenes and Alkynes

Describe what happens when non-1-ene is mixed each of with the following compounds.

(a) water

(b) 8-methylnon-1-yne

Analysis and solution

(a) Because non-1-ene is an alkene, it is nonpolar. It will not dissolve in a polar solvent such as water. Water and non-1-ene will form two layers; water has the higher density and so will be the lower layer, and non-1-ene will be the upper layer.

(b) Because alkenes and alkynes are both nonpolar, they will dissolve in one another.

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16.4 Reactions of Alkanes

For completeness, we should start with the reactions of alkanes, yet alkanes actually have very little reactivity. It is for this reason that chemists describe alkanes as unfunctionalised. They are quite unreactive with most reagents, a behaviour consistent with the fact that they are nonpolar compounds containing only strong σ bonds.

Under certain conditions, however, alkanes and cycloalkanes react with oxygen, O_2. By far their most important reaction with oxygen is oxidation (combustion) to form carbon dioxide and water. The oxidation of saturated hydrocarbons is the basis for their use as energy sources for heat (natural gas, liquefied petroleum gas (LPG) and fuel oil) and power (petrol, diesel fuel and aviation fuel). The following are balanced equations for the complete combustion of methane, the major component of natural gas, and for propane, the major component of LPG.

$$\underset{\text{mathane}}{CH_4} + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta_c H^{\ominus} = -886\ \text{KJ mol}^{-1}$$

$$\underset{\text{propane}}{CH_3CH_2CH_3} + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad \Delta_c H^{\ominus} = -2220\ \text{KJ mol}^{-1}$$

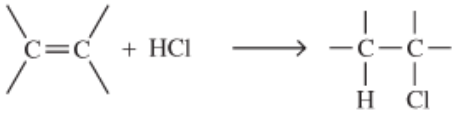
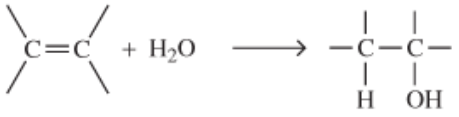
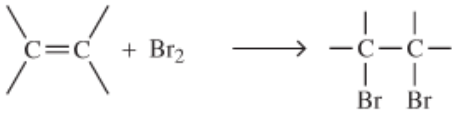
Another reaction of alkanes involves a substitution reaction where halogens replace hydrogen atoms, and this will be discussed in chapter 18.

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16.5 Reactions of Alkenes

The most characteristic reaction of alkenes is **addition to the carbon–carbon double bond** so that the π bond is broken and, in its place, σ bonds are formed to two new atoms or groups of atoms. Several examples of reactions at the carbon–carbon double bond are shown in table 16.4, along with the descriptive name(s) associated with each.

TABLE 16.4 Characteristic addition reactions of alkenes.

Reaction	Descriptive name(s)
	hydrochlorination (an example of hydrohalogenation)
	hydration
	bromination (an example of halogenation)
	hydrogenation (reduction)

From the perspective of the chemical industry, the most important reaction of low-molar-mass alkenes is the production of polymers (e.g. polyethylene and polystyrene). Polymers arise from the sequential addition of many low-molar-mass molecules to create very large molecules of high molar mass, as illustrated here by the formation of polyethylene from ethene (ethylene):



To achieve such an addition, alkenes first react with a specific reagent called an initiator and then with each other to form a steadily growing chain. In alkene-derived polymers of industrial and commercial importance, *n* is a large number, typically several thousand. We discuss the formation of polymers from alkenes in more detail in chapter 26.

Another reaction of alkenes is reduction to alkanes, which is essentially the addition of H_2 across the double bond. We will discuss this after we look at the addition reactions.

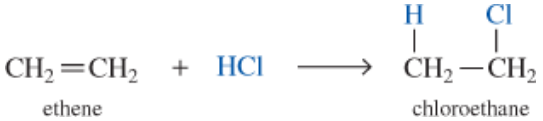
Electrophilic Addition Reactions

The basis of reactivity is the attraction between positive and negative species. The double bond in alkenes is an electron-rich (i.e. negative) target for positive species. These positive species are called **electrophiles** (which literally means 'attracted to electrons'). Alkenes undergo addition reactions with electrophiles to produce saturated compounds.

In this section we examine the three most important types of electrophilic addition reactions: the addition of hydrogen halides (HCl, HBr, and HI), water (H_2O) and halogens (Br_2, Cl_2). We first study some of the experimental observations about each addition reaction and then its mechanism. By examining these particular reactions, we develop a general understanding of how alkenes undergo addition reactions.

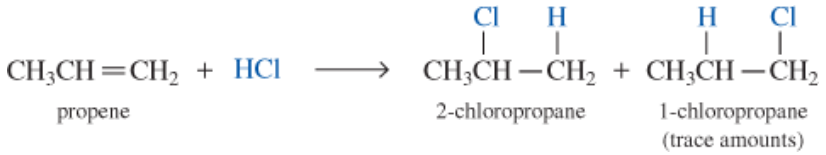
Addition of Hydrogen Halides

The hydrogen halides HCl, HBr and HI (commonly abbreviated HX) add to alkenes to give halo-alkanes (alkyl halides). These additions may be carried out either with the pure reagents or in the presence of a polar solvent such as acetic acid. The addition of HCl to ethene gives chloroethane:



The addition of HCl to propene gives 2-chloropropane; hydrogen adds to C(1) of propene, and chlorine adds to C(2). If the orientation of addition were reversed, 1-chloropropane would be formed.

The observed result is that 2-chloropropane is formed to the virtual exclusion of 1-chloropropane:



We say that the addition of HCl to propene is highly regioselective and that 2-chloropropane is the major (indeed almost exclusive) product of the reaction. A **regioselective reaction** is one in which one direction of bond forming or breaking occurs in preference to all other directions.

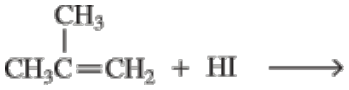
Nineteenth century Russian chemist Vladimir Markovnikov observed this regioselectivity and made the generalisation, known as **Markovnikov's rule**, that, in the addition of HX to an alkene, hydrogen adds to the double-bonded carbon atom with the greater number of hydrogen atoms already bonded to it.

WORKED EXAMPLE 16.15

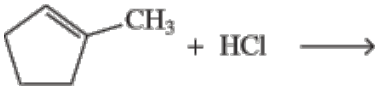
Alkene Addition Reactions

Name and draw a structural formula for the major product of each of the following alkene addition reactions.

(a)



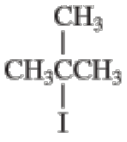
(b)



Analysis and solution

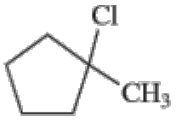
Using Markovnikov's rule, we predict that 2-iodo-2-methylpropane is the product in (a) and 1-chloro-1-methylcyclopentane is the product in (b).

(a)



2-iodo-2-methylpropane

(b)



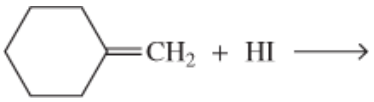
1-chloro-1-methylcyclopentane

PRACTICE EXERCISE 16.12

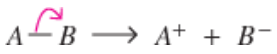
Name and draw the structural formula of the major product of each of the following alkene addition reactions.

(a) $CH_3CH{=}CH_2 + HI \rightarrow$

(b)



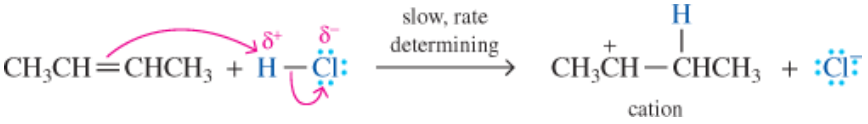
Although Markovnikov's rule provides a way to predict the product of many alkene addition reactions, it does not explain why one product predominates over other possible products. To do this, we need to understand the mechanism of the process. As we saw in chapter 15, mechanisms provide a complete description of the bond-breaking and bond-forming processes that occur in the transformation of starting materials to intermediate species and, then, to products. We represent the movement of the two electrons involved in these bond-breaking and bond-forming steps with a curved arrow. For example, we can represent the breaking of the single bond in the hypothetical *AB* molecule by using curved arrows:



Note that the arrow begins at the bond that is being broken and the head of the arrow shows the destination of the pair of electrons. We use arrows to show the movement of electrons in each bond-forming and bond-breaking step in a mechanism. Once we have a complete mechanistic description for a particular reaction, it is possible to make generalisations and then predict how other similar reactions might occur.

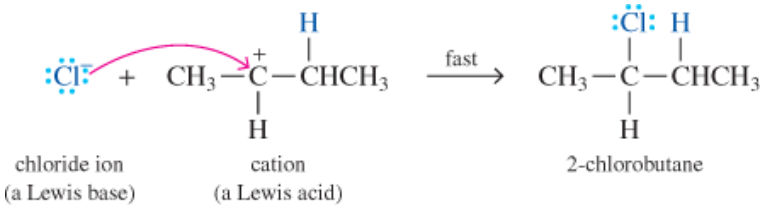
Chemists account for the addition of HX to an alkene by a two-step mechanism, which we illustrate by the reaction of but-2-ene with hydrogen chloride to give 2-chlorobutane. Let us first look at this two-step mechanism in general and then go back and study each step in detail.

Step 1: The reaction begins with the transfer of a proton from HCl to but-2-ene, as shown by the two curved arrows on the left side of the following equation:



The first curved arrow shows the breaking of the π bond of the alkene and its electron pair now forming a new covalent bond with the hydrogen atom of HCl. The second curved arrow shows the breaking of the polar covalent bond in HCl and this electron pair being given entirely to chlorine, forming a chloride ion. Step 1 in this mechanism results in the formation of an organic cation and a chloride ion. It is important to remember that, even though we described this process as a proton transfer, a mechanistic arrow always shows the movement of electrons, not protons. A mechanistic arrow should *never* start from a hydrogen atom in an organic molecule.

Step 2: The reaction of the cation (a Lewis acid) with a chloride ion (a Lewis base) completes the valence shell of carbon and gives 2-chlorobutane:



Now let us look at the individual steps in more detail. There is a great deal of important organic chemistry embedded in these two steps, and it is crucial that you understand it now.

Step 1 results in the formation of an organic cation. One carbon atom in this cation has only six electrons in its valence shell and carries a charge of +1. A species containing a positively charged carbon atom is called a **carbocation** (*carbon + cation*). Carbocations are classified as primary (1°), secondary (2°) or tertiary (3°), depending on the number of carbon atoms bonded to the carbon atom bearing the positive charge. The cation in the reaction given above is a 2° carbocation. All carbocations are Lewis acids (chapter 11). They are also electrophiles.

In a carbocation, the carbon atom bearing the positive charge is bonded to three other atoms, and, as predicted by the valence-shell-electron-pair repulsion (VSEPR) model, the three bonds around that carbon atom are coplanar and form bond angles of approximately 120°. According to the valence bond theory, the electron-deficient carbon atom of a carbocation uses its sp^2 hybrid orbitals to form σ bonds to the three attached groups. The unhybridised 2*p* orbital lies perpendicular to the σ bond framework and contains no electrons. A Lewis structure and an orbital overlap diagram for a common tertiary carbocation ($C_4H_9^+$) are shown in figure 16.27. This carbocation is given the common name *tertiary* butyl cation or *tert*-butyl cation.

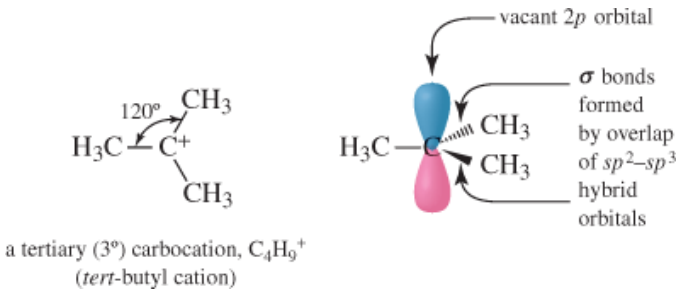


FIGURE 16.27 Representations of the structure of a tertiary (3°) carbocation:
(a) Lewis structure and
(b) an orbital picture.

Recall from chapter 15 that the process of a reaction can also be depicted by the energy changes from starting material to intermediate species through to products. Figure 16.28 shows such an energy diagram for the two-step reaction of but-2-ene with HCl. The slower, rate-determining step (that has to pass over the higher energy barrier) is step 1 (i.e. E_{a1} is greater than E_{a2}), which leads to the formation of the 2° carbocation intermediate. This intermediate lies in an energy minimum between the transition states for steps 1 and 2. As soon as the carbocation intermediate (a Lewis acid) forms, it reacts with a chloride ion (a Lewis base) in a Lewis acid–base reaction to give 2-chlorobutane. Note that the energy of 2-chlorobutane (the product) is less than the energy of but-2-ene and HCl (the reactants). Thus, in this alkene addition reaction, heat is released so the reaction is exothermic.

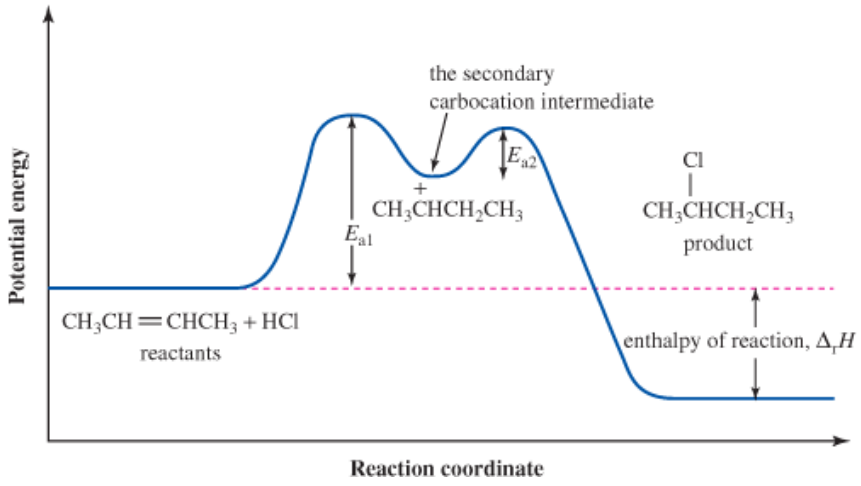


FIGURE 16.28 Energy diagram for the two-step addition of HCl to but-2-ene. The reaction is exothermic.

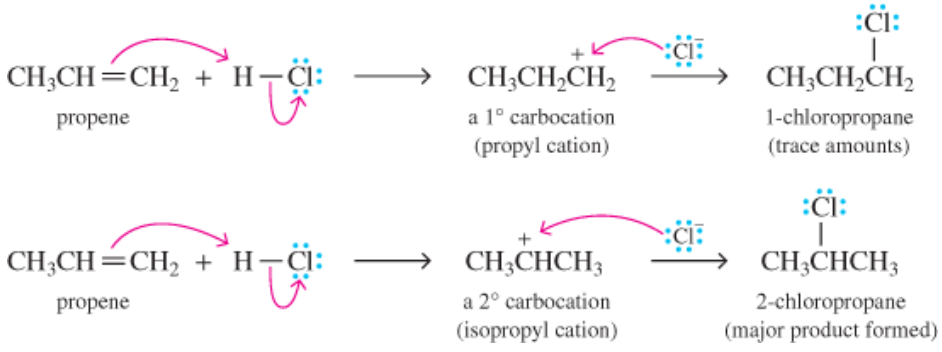
Given that the rate-determining step of the reaction in figure 16.28 involves both but-2-ene and HCl as reactants, we would expect the rate law for this reaction to have the form:

$$\text{rate of reaction} = k[\text{but} - 2 - \text{ene}]\,[\text{HCl}]$$

and the reaction should display second-order kinetics (see chapter 15).

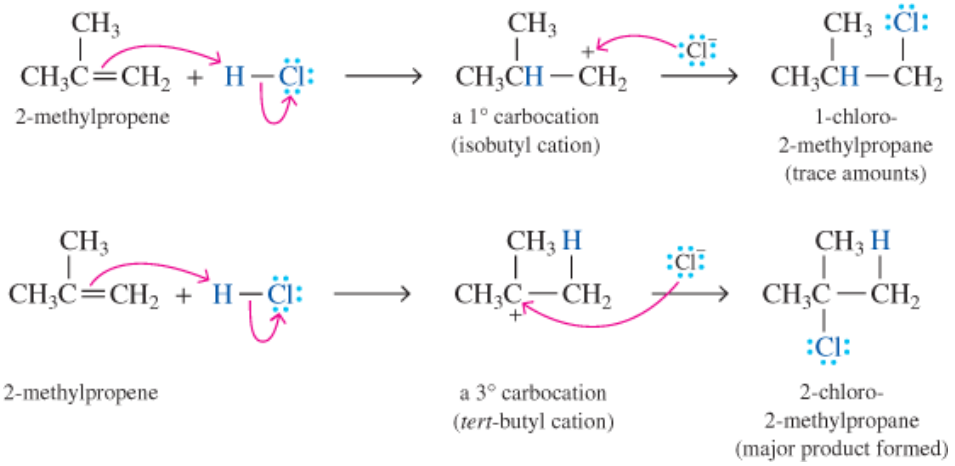
Relative Stabilities of Carbocations: Regioselectivity and Markovnikov's Rule

The reaction of HX with an asymmetrical alkene can, at least in principle, give two different carbocation intermediates, depending on which of the double-bonded carbon atoms has H^+ added to it, as illustrated by the reaction of HCl with propene.



The major product formed is 2-chloropropane, and 1-chloropropane is formed in only trace amounts. Because carbocations react very quickly with chloride ions, the virtual absence of 1-chloropropane as a product tells us that the 2° carbocation is formed in preference to the 1° carbocation.

Similarly, in the reaction of HCl with 2-methylpropene, the transfer of a proton to the carbon– carbon double bond might form either a 1° carbocation (isobutyl cation) or a 3° carbocation *(tert*-butyl cation).



In this reaction, the observed product is 2-chloro-2-methylpropane, indicating that the 3° carbocation forms in preference to the 1° carbocation.

From such experiments and a great amount of other experimental evidence, we learn that a 3° carbocation is more stable and has a lower activation energy for its formation than a 2° carbocation. A 2° carbocation, in turn, is more stable and has a lower activation energy for its formation than a 1° carbocation. It follows that a more stable carbocation intermediate forms more rapidly than a less stable carbocation intermediate. Figure 16.29 shows the order of stability of four types of alkyl carbocations.

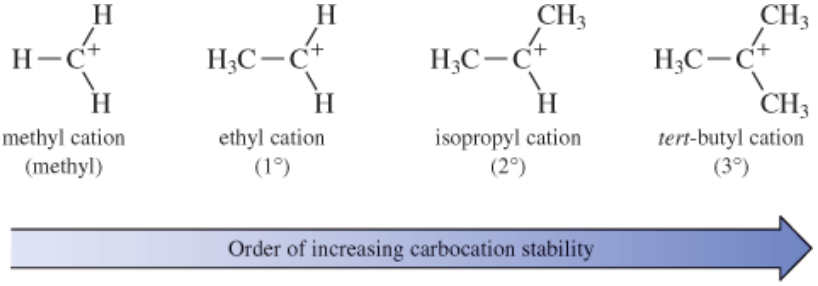


FIGURE 16.29 The order of stability of four types of alkyl carbocations.

Although the concept of the relative stabilities of carbocations had not been developed in Markovnikov's time, it is the underlying basis for his rule; that is, the proton of H—X adds to the less substituted carbon atom of a double bond, because this mode of addition produces the more stable carbocation intermediate.

Now that we know the order of stability of carbocations, how do we account for it? The principles of physics teach us that a system bearing a charge (either positive or negative) is more stable if the charge is distributed over the system rather than localised at a particular point within the system. If we assume that alkyl groups bonded to a positively charged carbon atom release electrons towards the cationic carbon atom, thereby distributing the charge of the cation over the structure, this explains the order of stability of carbocations. The electron-releasing ability of alkyl groups bonded to a cationic carbon atom is accounted for by the **inductive effect**.

The inductive effect operates in the following way: the electron deficiency of the carbon atom bearing a positive charge exerts an electron-withdrawing inductive effect that polarises electrons from adjacent σ bonds towards it. Thus, the positive charge of the cation is not localised on the trivalent carbon atom, but rather is partially distributed over nearby atoms. As the number of alkyl groups bonded to the cationic carbon atom increases, the positive charge can be distributed over more atoms and the stability of the cation increases.

The inductive effect is not the only factor that influences the stability of carbocations. In future studies in chemistry, you may learn about the principle of hyperconjugation, which also affects carbocation stability. Hyperconjugation involves that interaction of adjacent *p* orbitals of alkyl groups, helping to stabilise the carbocation. Again, as with the inductive effect, the more alkyl groups

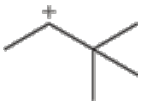
bound to the carbocation, the greater is its stability.

WORKED EXAMPLE 16.16

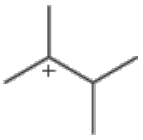
Relative Stabilities of Carbocations

Arrange the following carbocations in order of increasing stability.

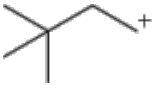
(a)



(b)



(c)



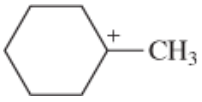
Solution

Carbocation (a) is secondary, (b) is tertiary and (c) is primary. In order of increasing stability, they are (c), (a) and (b).

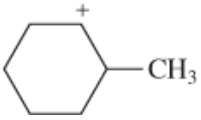
PRACTICE EXERCISE 16.13

Arrange the following carbocations in order of increasing stability.

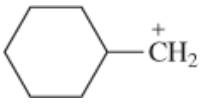
(a)



(b)



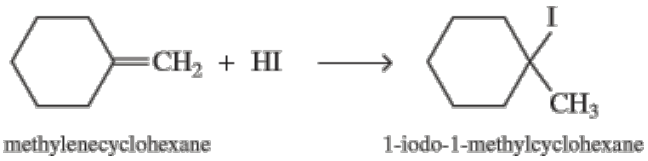
(c)



WORKED EXAMPLE 16.17

The Mechanism of Addition

Propose a mechanism for the addition of HI to methylenecyclohexane, which gives 1-iodo-1-methylcyclohexane.



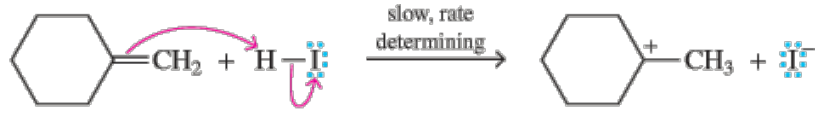
methylenecyclohexane — 1-iodo-1-methylcyclohexane

Which step in your mechanism is rate determining?

Analysis and solution

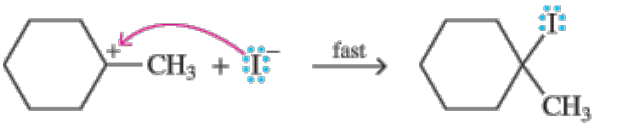
Propose a two-step mechanism similar to that proposed for the addition of HCl to propene.

Step 1: A rate-determining proton transfer from HI to the carbon–carbon double bond gives a 3° carbocation intermediate.



methylenecyclohexane — a 3° carbocation intermediate

Step 2: Reaction of the 3° carbocation intermediate (a Lewis acid) with an iodide ion (a Lewis base) completes the valence shell of carbon and gives the product.



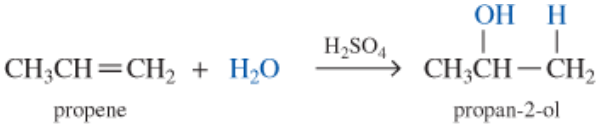
1-iodo-1-methylcyclohexane

PRACTICE EXERCISE 16.14

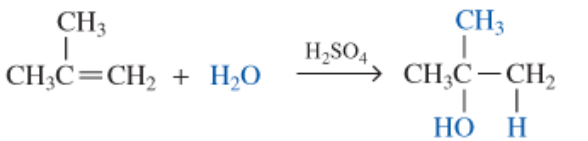
Propose a mechanism for the addition of HI to 1-methylcyclohexene, which gives 1-iodo-1-methylcyclohexane. Which step in your mechanism is rate determining?

Addition of Water: Acid-catalysed Hydration

In the presence of an acid catalyst — most commonly, sulfuric acid — water adds to the carbon– carbon double bond of an alkene to give an alcohol. The addition of water is called **hydration**. The precise mechanism of this hydration is given below but, in effect, for simple alkenes, H is added to the carbon atom of the double bond with the greater number of hydrogen atoms, and OH is added to the carbon atom with the lower number of hydrogen atoms. Thus, H—OH adds to alkenes in accordance with Markovnikov's rule:



propene — propan-2-ol



2-methylpropene — 2-methylpropan-2-ol

WORKED EXAMPLE 16.18

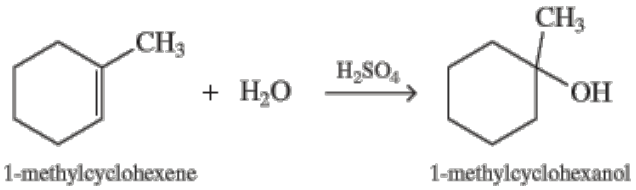
Acid-catalysed Hydration

Draw the structural formula of the product of the acid-catalysed hydration of 1-methylcyclohexene.

Analysis

We know that a hydrogen atom from water will add to the carbon atom of the double bond bearing more attached hydrogen atoms. This then means that the — OH will add to the carbon atom bearing the methyl group. We can therefore write the structural formula of the product.

Solution

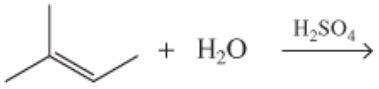


1-methylcyclohexene 1-methylcyclohexanol

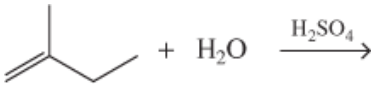
PRACTICE EXERCISE 16.15

Draw structural formulae of the products of the following alkene hydration reactions.

(a)

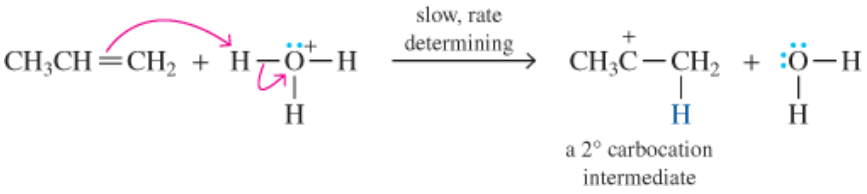


(b)



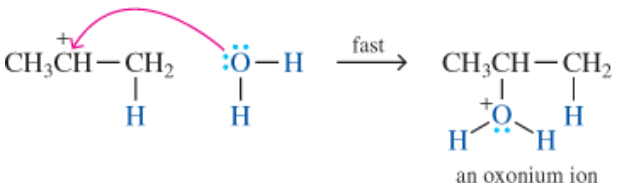
The mechanism of the acid-catalysed hydration of alkenes is similar to the mechanism we have described for the addition of HCl, HBr and HI to alkenes and is illustrated by the hydration of propene to propan-2-ol. This mechanism is consistent with the fact that acid is a catalyst. For every H_3O^+ consumed in step 1, another is generated in step 3.

Step 1: Proton transfer from the acid catalyst to propene gives a 2° carbocation intermediate (a Lewis acid):



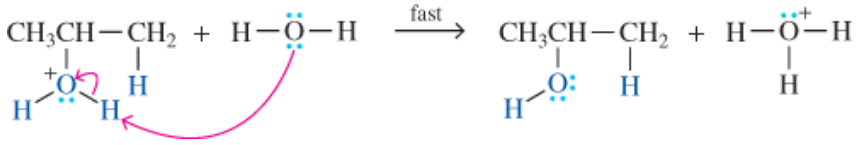
a 2° carbocation intermediate

Step 2: Reaction of the carbocation intermediate (a Lewis acid) with water (a Lewis base) completes the valence shell of carbon and gives an **oxonium ion**:



an oxonium ion

Step 3: Proton transfer from the oxonium ion to water gives the alcohol and generates a new molecule of the catalyst:



WORKED EXAMPLE 16.19

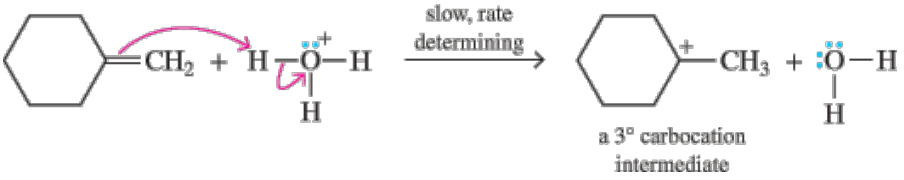
The Mechanism of Acid-catalysed Hydration

Propose a mechanism for the acid-catalysed hydration of methylenecyclohexane to give 1-methylcyclohexanol. Which step in your mechanism is rate determining?

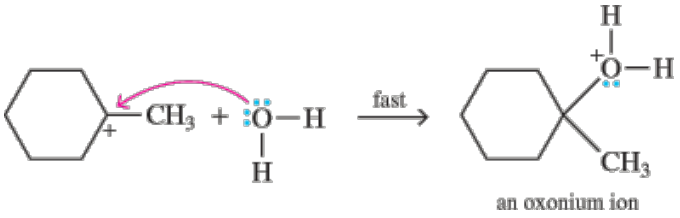
Solution

The mechanism involves three steps, similar to those for the acid-catalysed hydration of propene. The formation of the 3° carbocation intermediate in step 1 is rate determining.

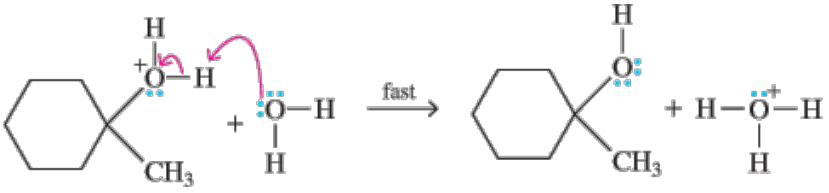
Step 1: Proton transfer from the acid catalyst to the alkene gives a 3° carbocation intermediate (a Lewis acid):



Step 2: Reaction of the carbocation intermediate (a Lewis acid) with water (a Lewis base) completes the valence shell of carbon and gives an oxonium ion:



Step 3: Proton transfer from the oxonium ion to water gives the alcohol and generates a new molecule of the catalyst:



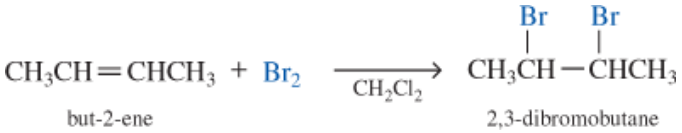
PRACTICE EXERCISE 16.16

Propose a mechanism for the acid-catalysed hydration of 1-methylcyclohexene to give 1-methylcyclohexanol. Which step in your mechanism is rate determining?

Addition of Bromine and Chlorine

Chlorine, Cl_2, and bromine, Br_2, react with alkenes at room temperature by the addition of halogen atoms to the two carbon atoms

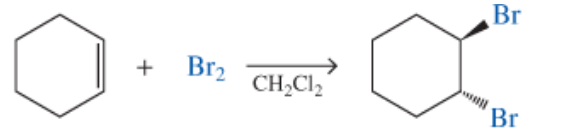
of the double bond, forming two new carbon–halogen bonds:



but-2-ene 2,3-dibromobutane

Fluorine, F_2, also adds to alkenes, but, because its reactions are very fast and difficult to control, addition of fluorine is not a useful laboratory reaction. Iodine, I_2, also adds to alkenes, but the products of the reaction can in some cases be unstable and subsequently degrade, generating other products.

The addition of bromine and chlorine to a cycloalkene gives a *trans*-dihalocycloalkane. For example, the addition of bromine to cyclohexene gives *trans*-1,2-dibromocyclohexane; the *cis* isomer is not formed. Thus, the addition of a halogen to a cycloalkene is stereospecific. A **stereospecific reaction** is a reaction in which one stereoisomer is formed or destroyed in preference to all others that might be formed or destroyed. Addition of bromine to a cycloalkene is highly stereospecific; the halogen atoms always add *trans* to each other.



cyclohexene *trans*-1,2-dibromocyclohexane

The reaction of bromine with an alkene is a particularly useful qualitative test for the presence of a carbon–carbon double bond. If we dissolve bromine in dichloromethane, CH_2Cl_2, the solution becomes red due to the presence of the red-coloured bromine (figure 16.30). Both alkenes and dibromoalkanes are colourless. If we now mix a few drops of the bromine solution with an alkene, the bromine is consumed, a dibromoalkane is formed and, with the removal of the bromine, the solution becomes colourless.



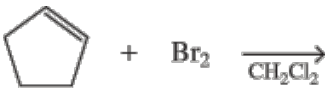
FIGURE 16.30 A solution of bromine in dichloromethane, CH_2Cl_2, is red (left). Add a few drops of an alkene and the red colour disappears (right). Charles D Winters

WORKED EXAMPLE 16.20

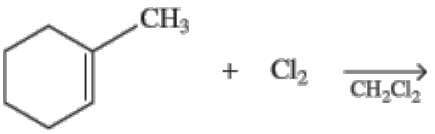
Addition of Bromine and Chlorine

Complete the following reactions, showing the relative orientations of the substituents in the products.

(a)



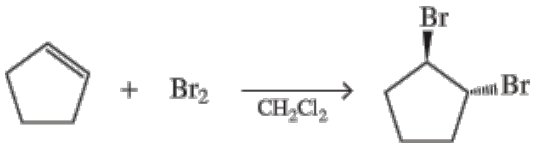
(b)



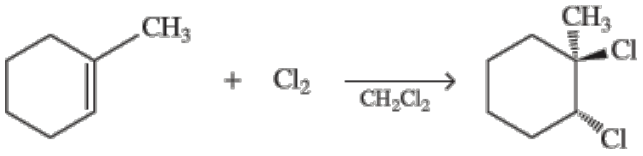
Solution

The halogen atoms are *trans* to each other in each product.

(a)



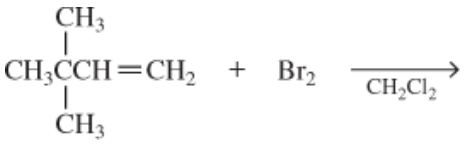
(b)



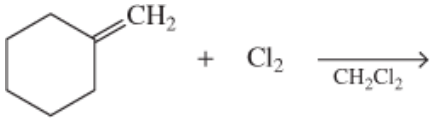
PRACTICE EXERCISE 16.17

Complete the following reactions.

(a)



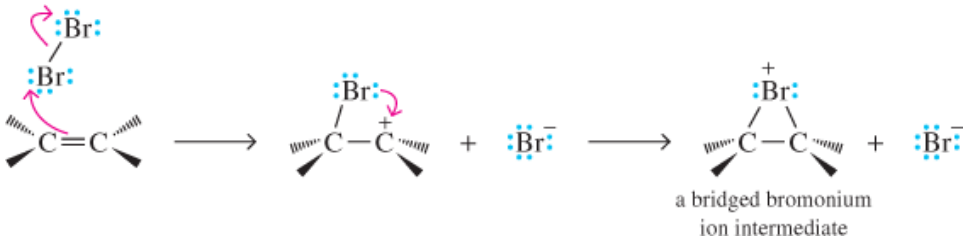
(b)



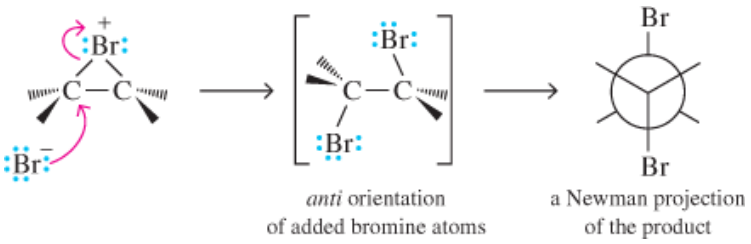
Bridged Halonium Ion Intermediates and *Anti* Selectivity

We explain the addition of bromine and chlorine to cycloalkenes, as well as their selectivity (they always add *trans* to each other), by a two-step mechanism that involves a halogen bearing a positive charge, called a **halonium ion**. The cyclic structure of which this ion is a part is called a **bridged halonium ion**. The bridged bromonium ion shown in step 1 of the mechanism below may look odd to you, but it is an acceptable Lewis structure. A calculation of formal charge places a positive charge on bromine. Then, in step 2, a bromide ion reacts with the bridged intermediate from the side opposite that occupied by the bromine atom, giving the dibromoalkane. Thus, bromine atoms add from opposite faces of the carbon–carbon double bond. We say that this addition occurs with ***anti* selectivity**. Alternatively, we say that the addition of halogens is stereospecific involving ***anti* addition** of the halogen atoms.

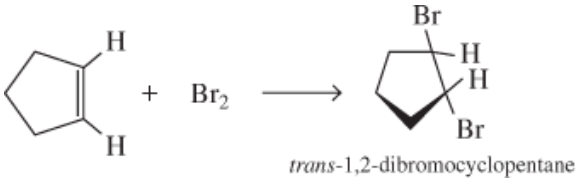
Step 1: Reaction of the π electrons of the carbon–carbon double bond with bromine forms a bridged bromonium ion intermediate in which bromine bears a positive formal charge:



Step 2: A bromide ion (a Lewis base) attacks a carbon atom of the three-membered ring (a Lewis acid) from the side opposite the bridged bromonium ion, opening the three-membered ring:

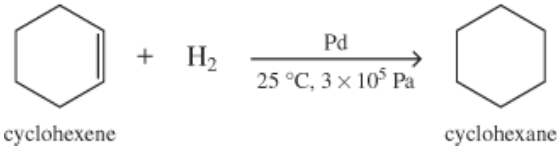


As we can see from the Newman projection above, these bromine atoms are *trans* to each other but, in open-chain alkanes, this relative position is rapidly scrambled by normal bond rotation around the carbon–carbon bonds. On the other hand, such rotation is not possible in a cycloalkene so the bromine atoms remain on opposite sides of the ring.



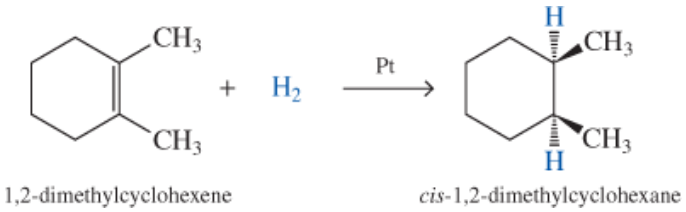
Reduction of Alkenes: Formation of Alkanes

Most alkenes react quantitatively with molecular hydrogen, H_2, in the presence of a transition metal catalyst to give alkanes. Commonly used transition metal catalysts include platinum, palladium, ruthenium and nickel. Yields are usually quantitative or nearly so. Because the conversion of an alkene to an alkane involves reduction by hydrogen in the presence of a catalyst, the process is called **catalytic reduction** or **catalytic hydrogenation**.



The metal catalyst is used as a finely powdered solid, which may be supported on some inert material such as powdered charcoal or alumina. The reaction is carried out by dissolving the alkene in ethanol or another nonreacting organic solvent, adding the solid catalyst, and exposing the mixture to hydrogen gas at pressures ranging from 1×10^5 to 100×10^5 Pa (i.e. up to 100 times normal atmospheric pressure). Alternatively, the metal may be bound to certain organic molecules and used in the form of a soluble complex.

Catalytic reduction is stereospecific, the most common pattern being the ***syn* addition** of hydrogen atoms to the carbon–carbon double bond (meaning the hydrogen atoms are added to the same side of the carbon–carbon double bond). The catalytic reduction of 1,2-dimethylcyclohexene, for example, yields *cis*-1,2-dimethylcyclohexane:



The transition metals used in catalytic reduction can adsorb large quantities of hydrogen onto their surfaces, probably by forming metal–hydrogen σ bonds. Similarly, these transition metals adsorb alkenes on their surfaces, forming carbon–metal bonds (figure 16.31). Hydrogen atoms are added to the alkene in more than one step.

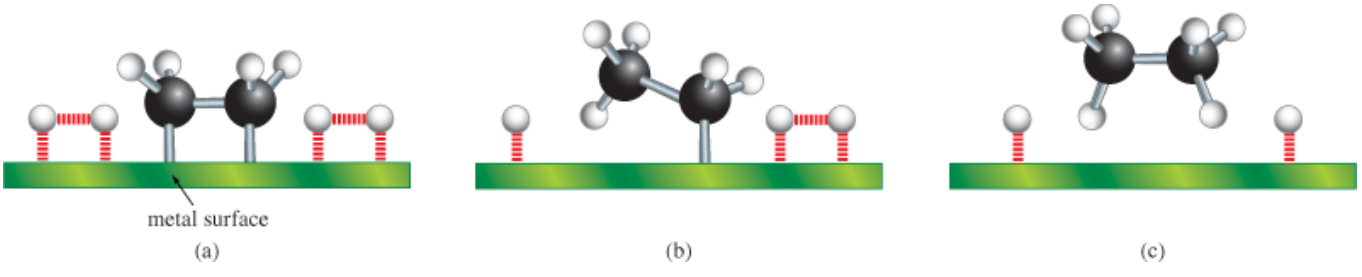


FIGURE 16.31 *syn* addition of hydrogen to an alkene involving a transition metal catalyst.

(a) Hydrogen and the alkene are adsorbed on the metal surface, and

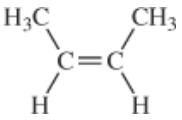
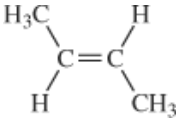
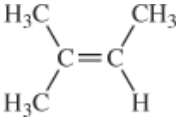
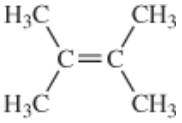
(b) one hydrogen atom is transferred to the alkene, forming a new C—H bond. The other carbon atom remains adsorbed on the metal surface.

(c) A second C—H bond forms and the alkane is desorbed.

Enthalpies of Hydrogenation and the Relative Stabilities of Alkenes

The **enthalpy of hydrogenation** of an alkene is defined as its enthalpy of reaction, $\Delta_r H^\ominus$, with hydrogen to form an alkane. Table 16.5 lists the enthalpies of hydrogenation of several alkenes.

TABLE 16.5 Enthalpies of hydrogenation of several alkenes.

Name	Structural formula	$\Delta_r H^\ominus \{kJ\ mol^{-1}\}$
ethene	$CH_2{=}CH2$	-137
propene	$CH_3CH{=}CH_2$	-126
but-1-ene	$CH_3CH_2CH{=}CH_2$	-127
cis-but-2-ene		-120
trans-but-2-ene		-116
2-methylbut-2-ene		-113
2,3-dimethylbut-2-ene		-111

Three important points follow from the information in table 16.5.

1. The reduction of an alkene to an alkane is an exothermic process. This observation is consistent with the fact that, during hydrogenation, there is net conversion from weaker π bonding to stronger σ bonding; that is, one σ bond (H—H) and one π bond (C═C) are broken, and two new σ bonds (C—H) are formed.
2. The enthalpies of hydrogenation depend on the degree of substitution of the carbon–carbon double bond: the greater the substitution, the lower the enthalpy of hydrogenation. Compare, for example, the enthalpies of hydrogenation of ethene (no substituents), propene (one substituent), but-1-ene (one substituent) and the *cis* and *trans* isomers of but-2-ene (two substituents each).
3. The enthalpy of hydrogenation of a *trans* alkene is less than that of the isomeric *cis* alkene. Compare, for example, the enthalpies of hydrogenation of *cis*-but-2-ene and *trans*-but-2-ene. Because the reduction of both alkenes gives butane, any difference in their enthalpies of hydrogenation must be due to a difference in relative energy between the two alkenes (figure 16.32). The alkene with the lower (less negative) value of $\Delta_r H^\ominus$ is the more stable alkene. We explain the greater stability of *trans* alkenes relative to *cis* alkenes in terms of nonbonded interaction strain. In *cis*-but-2-ene, the two —CH_3 groups are sufficiently close to each other that there is repulsion between their electron clouds. This repulsion is reflected in the larger enthalpy of hydrogenation (decreased stability) of *cis*-but-2-ene compared with that of *trans*-but-2-ene.

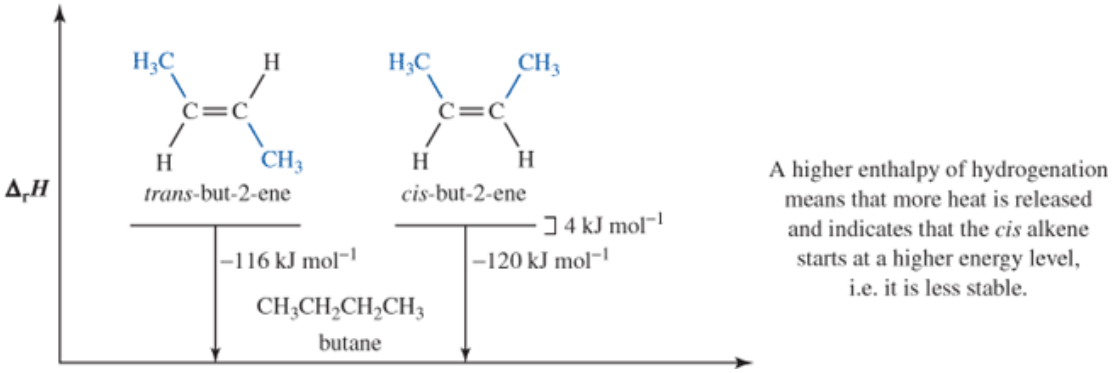


FIGURE 16.32 Enthalpies of hydrogenation of *cis*-but-2-ene and *trans*-but-2-ene; *trans*-but-2-ene is more stable than *cis*-but-2-ene by 4 kJ mol^{-1}.

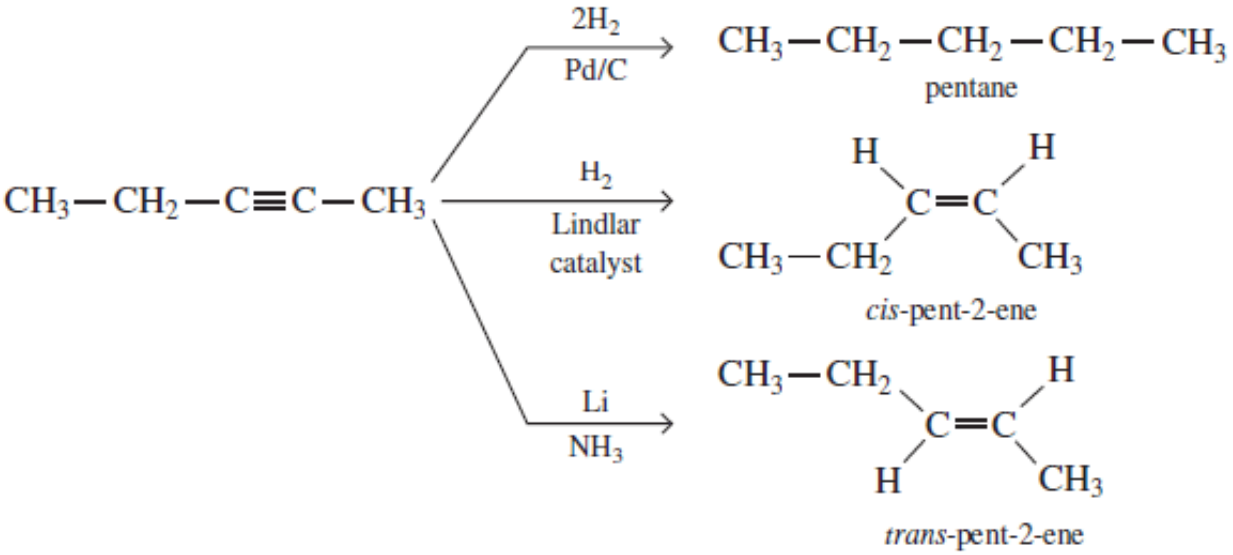
We have looked at molecules with one double bond. Molecules with more than one carbon– carbon double bond undergo the same addition reactions. However, there is a class of unsaturated molecules that do not undergo any of these addition reactions. These molecules are called aromatic compounds and are covered in section 16.7.

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16.6 Reactions of Alkynes

Much of the chemistry of alkynes mirrors the chemistry of alkenes; they undergo the same reduction reactions, as well as hydrogen halide addition and halogen addition reactions. Alkynes also undergo hydration, but unlike alkenes the synthetic outcome is a ketone and this is covered in chapter 21.

Reduction of alkynes is particularly important in the synthesis of complicated molecules used in making pharmaceuticals. Alkynes are easily reduced to alkanes by addition of hydrogen gas using a metal catalyst. The significant differences from the reduction of alkenes are that this reduction occurs in stages and the choice of catalyst can control the synthetic outcome. Complete reduction of the alkyne occurs when palladium coated onto carbon is used as the catalyst. Another catalyst involving deactivated palladium, called Lindlar catalyst, produces the *cis* alkene from the triple bond. The *trans* alkene can be generated using sodium or lithium dissolved in liquid ammonia.



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16.7 Aromatic Compounds

The simplest example of an aromatic compound is benzene, C_6H_6. Benzene, a colourless liquid, was first isolated by Michael Faraday in 1825 from the oily residue that collected in the gas pipes of London. Benzene's molecular formula, C_6H_6, suggests a high degree of unsaturation. Remember, C_nH_{2n+2} is the formula for alkanes, so an alkane with six carbon atoms has a molecular formula of C_6H_{14} and a cycloalkane with six carbon atoms has a molecular formula of C_6H_{12}. Con sidering benzene's high degree of *un*saturation, it might be expected to show many of the reactions characteristic of alkenes. Yet, benzene is remarkably unreactive! It does not undergo the addition, oxidation and reduction reactions characteristic of alkenes. For example, benzene does not undergo addition reactions with bromine, hydrogen chloride or other reagents that usually add to carbon–carbon double bonds. When benzene reacts, it does so by substitution (see chapter 18) in which a hydrogen atom is replaced by another atom or a group of atoms.

The term ‘aromatic’ was originally used to classify benzene and its derivatives because many of them have distinctive odours. It became clear, however, that a better classification for these compounds would be one based on structure and chemical reactivity, rather than aroma. As it is now used, the term **aromatic** refers instead to the fact that benzene and its derivatives are highly unsaturated compounds that are stable towards reagents that react with alkenes.

We use the term ‘arene’ to describe aromatic hydrocarbons, by analogy with alkane and alkene. Benzene is the parent arene. Just as we call a group derived by the removal of an H from an alkane an alkyl group and give it the symbol R— (chapter 2), we call a group derived by the removal of an H from an arene an **aryl group** and give it the symbol Ar—.

The Structure of Benzene

Let us imagine ourselves in the mid-nineteenth century and examine the evidence on which chemists attempted to build a model for the structure of benzene. First, because the molecular formula of benzene is C_6H_6, it seemed clear that the molecule must be highly unsaturated. Yet benzene does not show the chemical properties of alkenes, the only unsaturated hydrocarbons known at that time. Benzene does undergo chemical reactions, but its characteristic reaction is substitution rather than addition. When benzene is treated with bromine in the presence of iron(III) chloride as a catalyst, for example, only one compound, with molecular formula C_6H_5Br, forms:

$$\underset{\text{benzene}}{C_6H_6} + Br_2 \xrightarrow{FeCl_3} \underset{\text{bromobenzene}}{C_6H_5Br} + HBr$$

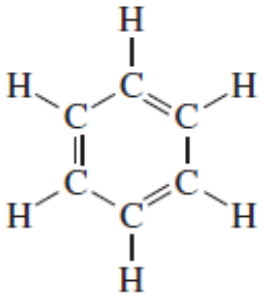
Chemists concluded, therefore, that all six carbon atoms and all six hydrogen atoms of benzene must be equivalent. When bromobenzene is treated with bromine in the presence of iron(III) chloride, three isomeric dibromobenzenes are formed:

$$\underset{\text{bromobenzene}}{C_6H_5Br} + Br_2 \xrightarrow{FeCl_3} \underset{\substack{\text{dibromobenzene}\\ \text{(formed as a mixture of}\\ \text{three constitutional isomers)}}}{C_6H_4Br_2} + HBr$$

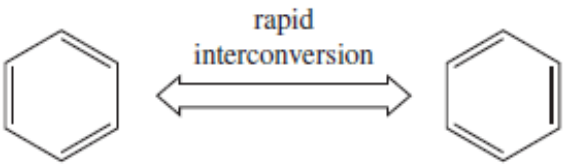
For chemists in the mid-nineteenth century, the problem was to incorporate these observations, along with the accepted tetravalence of carbon, into a structural formula for benzene. Before we examine their proposals, we should note that the problem of the structure of benzene and other aromatic hydrocarbons occupied the efforts of chemists for over a century. It was not until the 1930s that chemists developed a general understanding of the unique chemical properties of benzene and its derivatives.

Kekulé's Model of Benzene

The structure for benzene proposed by August Kekulé in 1872 consisted of a six-membered ring with alternating single and double bonds and with one hydrogen atom bonded to each carbon atom. Kekulé further proposed that the ring contains three double bonds that shift back and forth so rapidly that the two forms cannot be separated. Each structure has become known as a **Kekulé structure**.



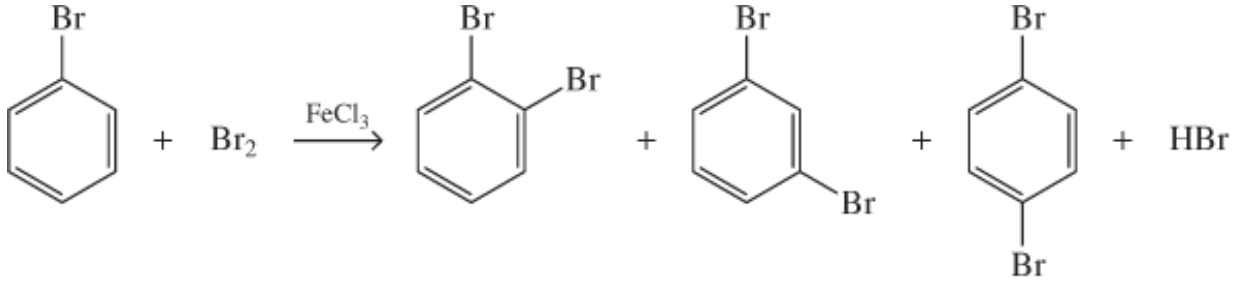
a Kekulé structure, showing all atoms



Kekulé structures as line structures

Because all of the carbon atoms and hydrogen atoms of Kekulé's structure are equivalent, substituting bromine for any one of the hydrogen atoms gives the same compound. Thus, Kekulé's proposed structure was consistent with the fact that treating benzene with bromine in the presence of iron(III) chloride gives only one compound, with molecular formula C_6H_5Br.

His proposal also accounted for the fact that the bromination of bromobenzene gives three (and only three) isomeric dibromobenzenes:



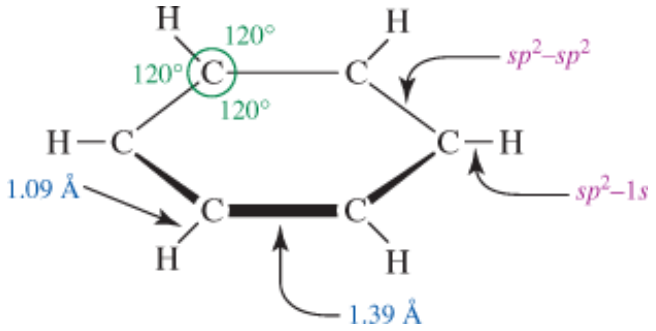
the three isomeric dibromobenzenes

Although Kekulé's proposal was consistent with many experimental observations, it was contested for years. The major objection was that it did not account for the unusual chemical behaviour of benzene. If benzene contains three double bonds, why, his critics asked, doesn't it show the reactions typical of alkenes? Why doesn't it add 3 moles of bromine to form 1,2,3,4,5, 6-hexabromocyclohexane? Why, instead, does benzene react by substitution rather than addition?

The Valence Bond Model of Benzene

The concepts of the **hybridisation of atomic orbitals** and the **theory of resonance**, both components of valence bond theory (see chapter 5) developed by Linus Pauling in the 1930s, provided the first adequate description of the structure of benzene. The carbon skeleton of benzene forms a regular hexagon with C—C—C and H—C—C bond angles of 120°. For this type of bonding, carbon uses sp^2 hybrid orbitals. Each carbon atom forms σ bonds to two adjacent carbon atoms by the overlap of sp^2–sp^2 hybrid orbitals and one σ bond to hydrogen by the overlap of sp^2–1*s* orbitals. As determined experimentally, all carbon–carbon bonds in benzene are the same length, 1.39 Å, a value between the length of a single bond between sp^3

hybridised carbons (1.54 Å) and that of a double bond between sp^2 hybridised carbons (1.33 Å):



Each carbon atom also has a single unhybridised 2*p* orbital that contains one electron. These six 2*p* orbitals lie perpendicular to the plane of the ring and overlap to form a continuous π cloud encompassing all six carbon atoms. The electron density of the π system of a benzene ring lies in one torus (a doughnut-shaped region) above the plane of the ring and in a second torus below the plane (figure 16.33).

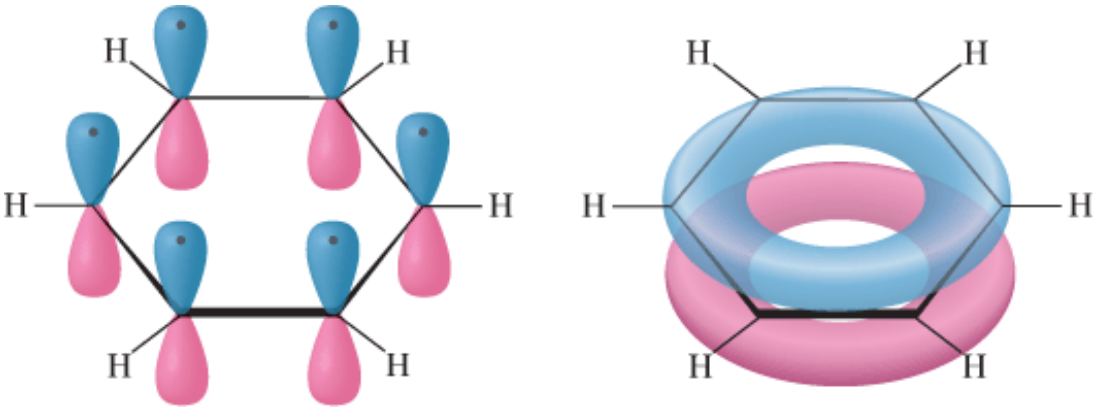


FIGURE 16.33 Orbital overlap model of bonding in benzene:

(a) The carbon–hydrogen framework. The six 2*p* orbitals, each with one electron, are shown uncombined.

(b) The overlap of parallel 2*p* orbitals forms a continuous π cloud, shown by one torus above the plane of the ring and a second below the plane of the ring.

The Resonance Model of Benzene

The concept of resonance introduced in chapter 5 tells us that, if we can represent a molecule or ion by two or more contributing structures, that molecule cannot be adequately represented by any single contributing structure. We represent benzene as a hybrid of two equivalent contributing structures, often referred to as Kekulé structures and we indicate the relationship between the two by the use of a double-headed arrow:



benzene as a hybrid of two equivalent contributing structures

Each Kekulé structure makes an equal contribution to the hybrid; thus, the C—C bonds are neither single nor double bonds, but something intermediate. We recognise that neither of these contributing structures exists (they are merely alternative ways to pair 2*p* orbitals, with no reason to prefer one over the other) and

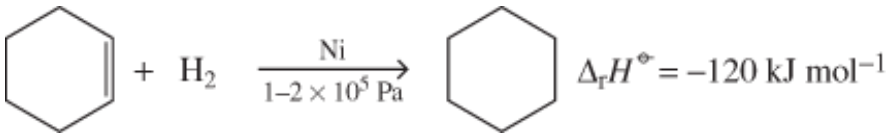
that the actual structure is something in between. An alternative means of representing the benzene ring that highlights the special nature of the aromatic structure is to show a circle within the six-membered ring of carbon atoms:



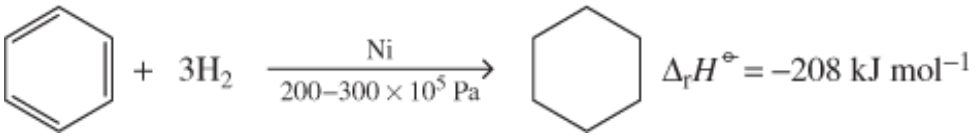
Nevertheless, we continue to use a single contributing structure, also called a resonance structure, to represent this molecule because it serves to remind us of the tetravalence of the carbon atoms involved and allows us to more easily represent the movement of electrons in reaction mechanisms.

The Resonance Energy of Benzene

Resonance energy is the difference in energy between a resonance hybrid and its most stable hypothetical contributing structure. One way to estimate the resonance energy of benzene is to compare the enthalpies of hydrogenation of cyclohexene and benzene. In the presence of a transition metal catalyst, hydrogen readily reduces cyclohexene to cyclohexane (p. 721):



By contrast, benzene is reduced only very slowly to cyclohexane under these conditions. It is reduced more rapidly when heated and under very high pressures of hydrogen:



The catalytic reduction of an alkene is an exothermic reaction (p. 304). The enthalpy of hydrogenation per double bond varies somewhat with the degree of substitution of the double bond; for cyclohexene, $\Delta_r H^\ominus = -120 \text{kJ mol}^{-1}$. If we consider benzene to be 1,3,5-cyclohexatriene, a hypothetical compound with alternating single and double bonds, we might expect its enthalpy of hydrogenation to be 3 × -120 = -360 kJ mol^{-1}. Instead, the enthalpy of hydrogenation of benzene is only -208 kJ mol^{-1}. The difference of 152 kJ mol^{-1} between the expected value and the experimentally observed value is the resonance energy of benzene. Figure 16.34 shows these experimental results in the form of a graph.

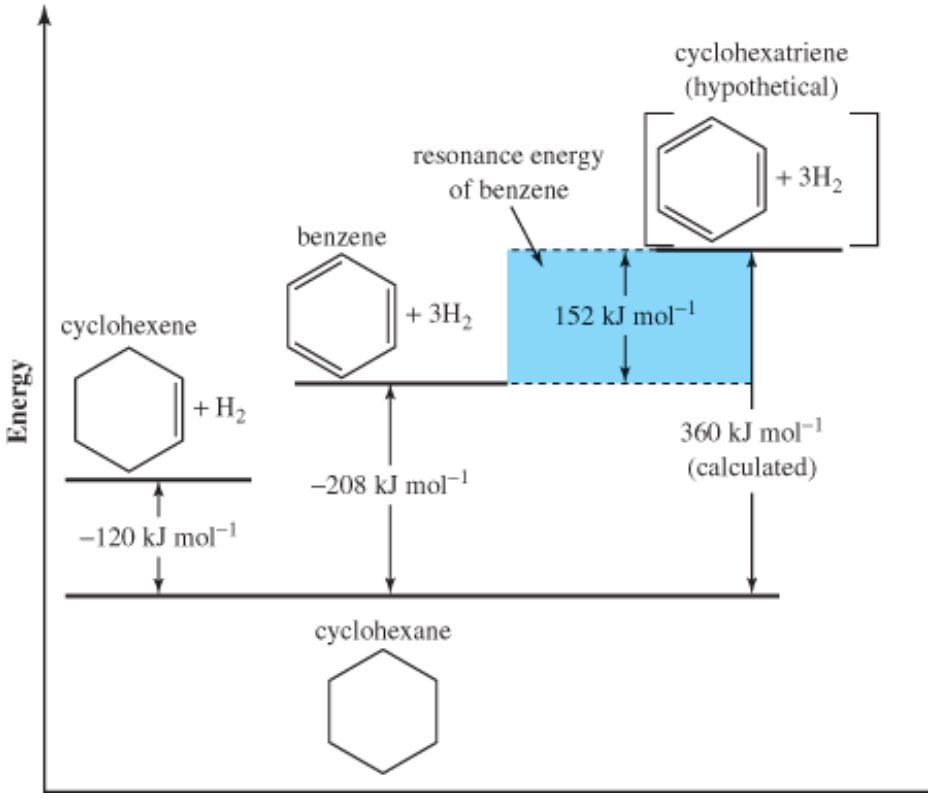
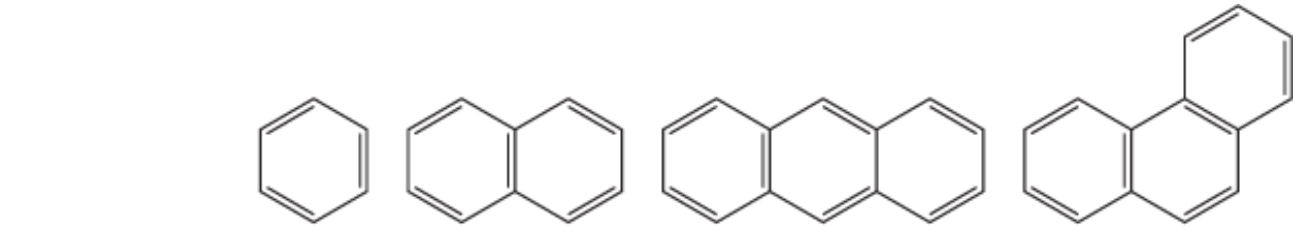


FIGURE 16.34 The resonance energy of benzene, as determined by a comparison of the enthalpies of hydrogenation of cyclohexene, benzene and the hypothetical 1,3,5-cyclohexatriene.

For comparison, the strength of a carbon–carbon single bond is about 333– 418 kJ mol^{-1}, and that of hydrogen bonding in water and low-molar-mass alcohols is about 8.4 –21 kJ mol^{-1}. Thus, although the resonance energy of benzene is less than the strength of a carbon–carbon single bond, it is considerably greater than the strength of hydrogen bonding in water and alcohols. In section 19.1, we will see that hydrogen bonding has a greater effect on the physical properties of alcohols and little impact on those of alkanes. Figure 16.34 shows that the resonance energy of benzene and other aromatic hydrocarbons has a dramatic effect on their chemical reactivity.

The following diagram shows resonance energies for benzene and several other aromatic hydrocarbons.



The Concept of Aromaticity

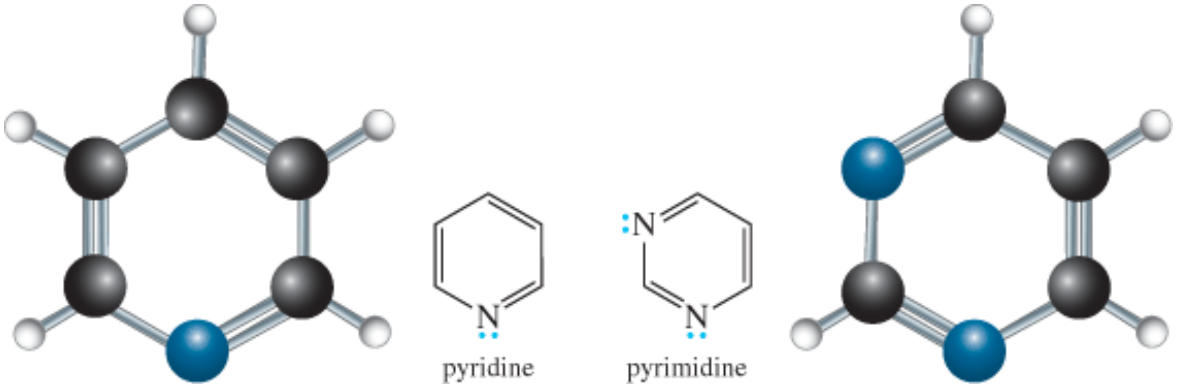
Many types of molecules other than benzene and its derivatives show aromatic character; that is, they contain high degrees of unsaturation, yet fail to undergo characteristic alkene addition and oxidation–reduction reactions. What chemists had long sought to understand were the principles underlying aromatic character. German chemical physicist Erich Hückel solved this problem in the 1930s.

Hückel's criteria are summarised as follows. To be aromatic, a ring must:

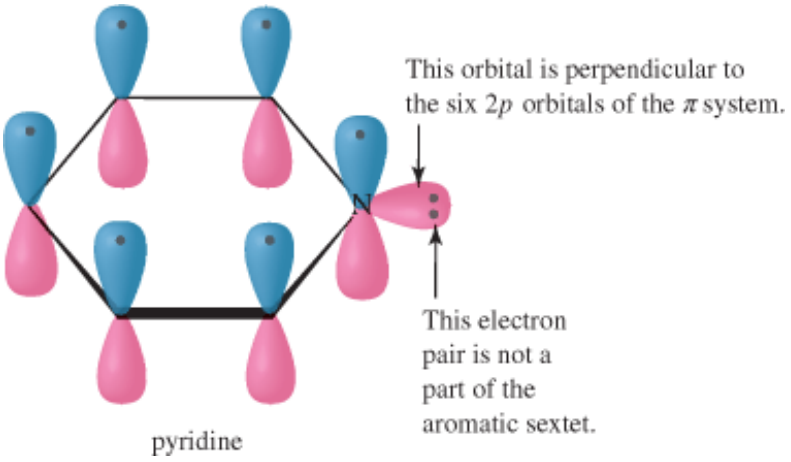
1. have one 2*p* orbital on each of its atoms
2. be planar or nearly planar, so that there is continuous overlap or nearly continuous overlap of all 2*p* orbitals of the ring
3. have 2, 6, 10, 14, 18, and so on, π electrons in the cyclic arrangement of 2*p* orbitals. (Note that these numbers are solutions to the equation $4n + 2$, where n is equal to 0, 1, 2, 3, 4 and so on.)

Benzene meets these criteria. It is cyclic, planar, has one 2*p* orbital on each carbon atom of the ring, and has six π electrons (an aromatic sextet) in the cyclic arrangement of its 2*p* orbitals. If structures with more than one ring meet these criteria, they are also aromatic and some examples of these appear above.

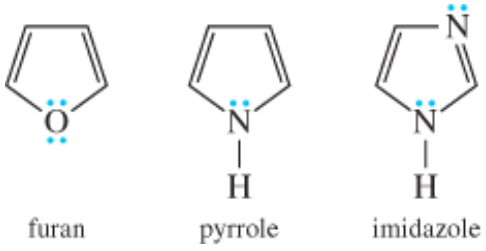
The unsaturated rings may also contain atoms other than carbon, and these molecules are called **heterocyclic compounds**. For example, pyridine and pyrimidine are analogues of benzene. In pyridine, one CH group of benzene is replaced by a nitrogen atom and, in pyrimidine, two CH groups are replaced by nitrogen atoms.



Both the pyridine and pyrimidine molecules meet the Hückel criteria for aromaticity. They are both cyclic and planar, have one 2*p* orbital on each atom of the ring, and have six electrons in the π system. In pyridine, nitrogen is sp^2 hybridised; its unshared pair of electrons occupies an sp^2 orbital perpendicular to the 2*p* orbitals of the π system and so is not a part of the π system. In pyrimidine, neither unshared pair of electrons of nitrogen is part of the π system. The resonance energy of pyridine is 134 kJ mol^{-1}, slightly less than that of benzene. The resonance energy of pyrimidine is 109 kJ mol^{-1}.



The five-membered-ring compounds furan, pyrrole and imidazole are also aromatic:



In these planar compounds, each heteroatom (non-carbon atom) is sp^2 hybridised, and its unhybridised 2*p* orbital is part of a continuous cycle of five 2*p* orbitals. In furan, one unshared pair of electrons of the heteroatom lies in the unhybridised 2*p* orbital and is a part of the π system (figure 16.35). The other unshared pair of electrons lies in an sp^2 hybrid orbital, perpendicular to the 2*p* orbitals, and is not a part of the π system. In pyrrole, the unshared pair of electrons on nitrogen is part of the aromatic sextet. In imidazole, the unshared pair of electrons on one nitrogen is part of the aromatic sextet; the unshared pair on the other nitrogen is not.

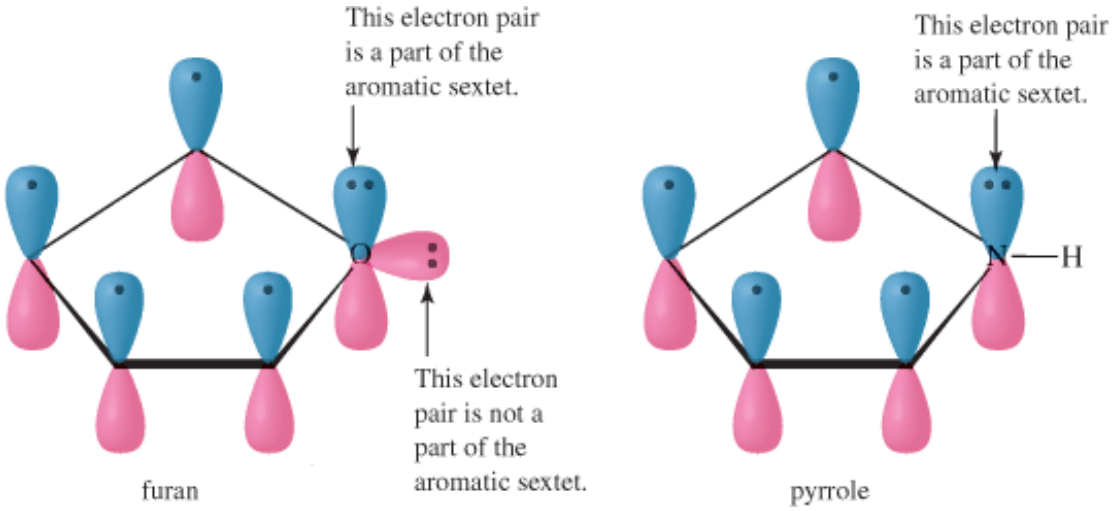
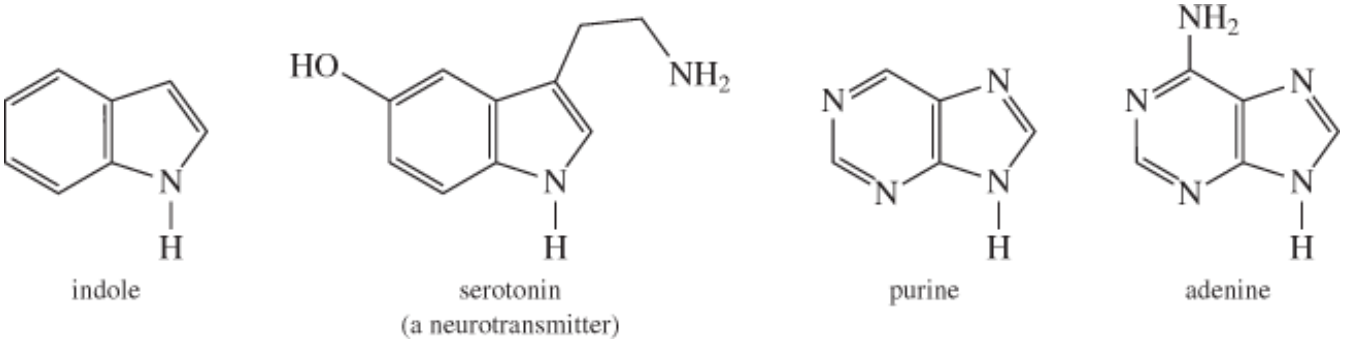


FIGURE 16.35 Origin of the six π electrons (the aromatic sextet) in furan and pyrrole. The resonance energy of furan is 67 kJ mol^{-1} and that of pyrrole is 88 kJ mol^{-1}.

Nature abounds with compounds having a heterocyclic ring fused to one or more other rings. Two such compounds especially important in the biological world are indole and purine.



Indole contains a pyrrole ring fused to a benzene ring. Compounds derived from indole include the amino acid l-tryptophan (section 24.1) and the neurotransmitter serotonin. Purine contains a six-membered pyrimidine ring fused to a five-membered imidazole ring. Adenine is one of the building blocks of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), as described in chapter 25. It is also a component of the biological oxidising agent nicotinamide adenine dinucleotide, abbreviated NAD^+.

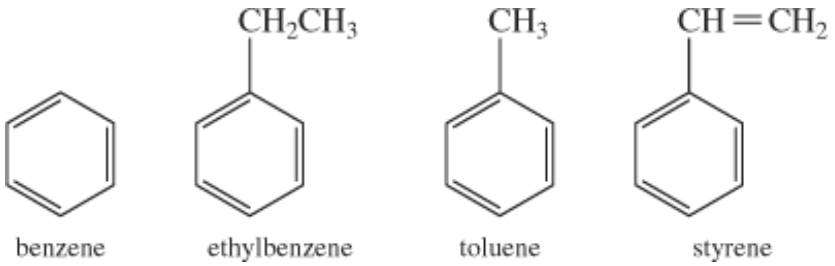
Nomenclature

The simplest aromatic hydrocarbon is benzene, which contains only hydrogen atoms bound to the aromatic

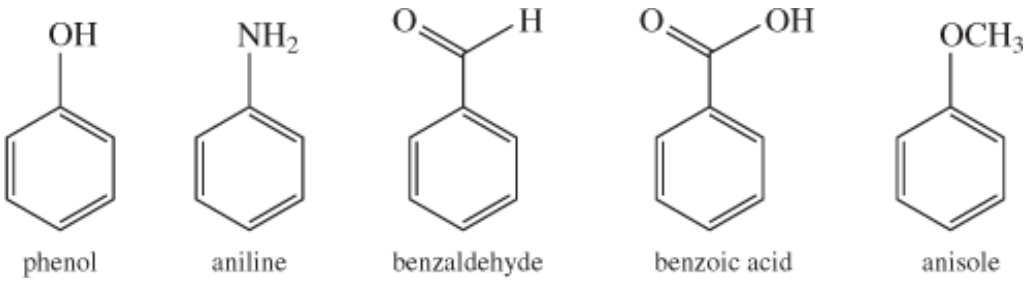
ring. Of course, there are many aromatic hydrocarbons with numerous different substitu ents in various positions around the ring. As always, we need to have a clear means to describe each of these individual molecules.

Monosubstituted Benzenes

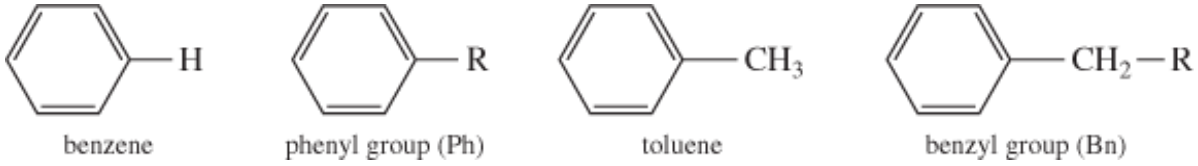
Monosubstituted alkylbenzenes are named as derivatives of benzene; an example is ethylbenzene. The IUPAC system retains certain common names for several of the simpler monosubstituted alkylbenzenes. Examples are **toluene** (rather than methylbenzene) and **styrene** (rather than phenylethene):



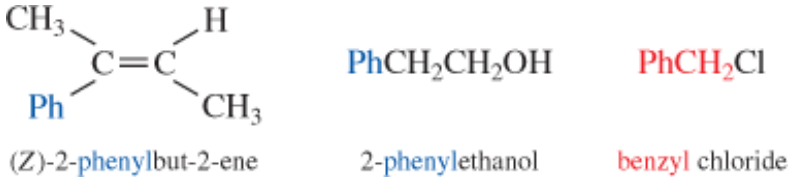
The common names **phenol**, **aniline**, **benzaldehyde**, **benzoic acid** and **anisole** are also retained by the IUPAC system:



The substituent group derived by the loss of an H from benzene is a **phenyl group** (Ph); that derived by the loss of an H from the methyl group of toluene is a **benzyl group** (Bn):



In molecules containing other functional groups, phenyl groups and benzyl groups are often named as substituents:

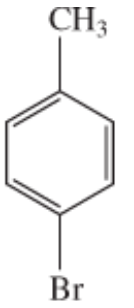


Disubstituted Benzenes

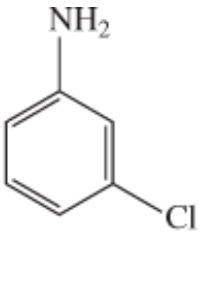
When two substituents occur on a benzene ring, three constitutional isomers are possible. We locate substituents either by numbering the atoms of the ring or by using the locators ***ortho***, ***meta*** and ***para***, which are abbreviated to *o*, *m* and *p* respectively. The numbers 1,2- are equivalent to *ortho* (Greek word meaning

‘straight’), 1,3- to *meta* (Greek word meaning ‘after’) and 1,4- to *para* (Greek word meaning ‘beyond’).

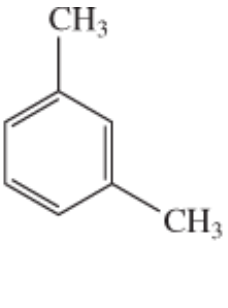
When one of the two substituents on the ring imparts a special name to the compound, such as toluene, phenol and aniline, we name the compound as a derivative of that parent molecule. In this case, the special substituent occupies ring position number 1. The IUPAC system retains the common name **xylene** for the three isomeric dimethylbenzenes. When neither group imparts a special name, we locate the two substituents and list them in alphabetical order before the word ‘benzene’. The carbon atom of the benzene ring with the substituent that comes first in alphabetical order is numbered C(1).



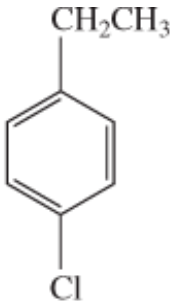
4-bromotoluene
(*p*-bromotoluene)



3-chloroaniline
(*m*-chloroaniline)



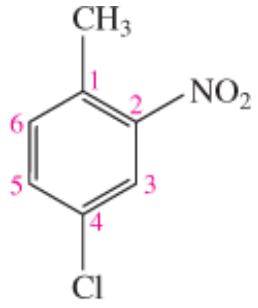
1,3-dimethylbenzene
(*m*-xylene)



1-chloro-4-ethylbenzene
(*p*-chloroethylbenzene)

Polysubstituted Benzenes

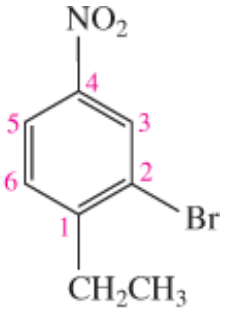
When three or more substituents are present on a ring, we specify their locations by numbers. If one of the substituents imparts a special name, the molecule is named as a derivative of that parent molecule. If none of the substituents imparts a special name, we number them to give the smallest set of numbers and list them in alphabetical order before the word ‘benzene’. In the following examples, the first compound is a derivative of toluene, and the second is a derivative of phenol. Because there is no special name for the third compound, we number the carbon atoms using the smallest possible set of numbers, then list its three substituents in alphabetical order, followed by the word ‘benzene’:



4-chloro-2-nitrotoluene



2,4,6-tribromophenol



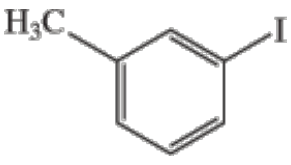
2-bromo-1-ethyl-
4-nitrobenzene

WORKED EXAMPLE 16.21

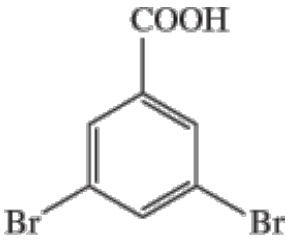
Nomenclature of Substituted Benzenes

Write names for the following compounds.

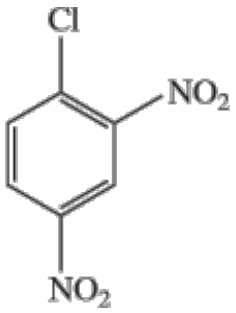
(a)



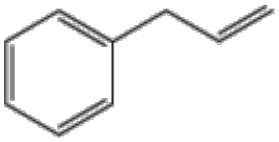
(b)



(c)



(d)



Analysis

We look for the important functional groups that may govern the parent name. For example, the presence of a methyl group bound to benzene generates the parent name toluene; a carboxyl group, benzoic acid. When the substituent becomes complicated we name the benzene ring as the substituent *phenyl*.

Solution

(a) 3-iodotoluene or *m*-iodotoluene

(b) 3,5-dibromobenzoic acid

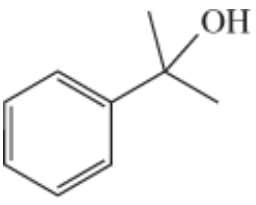
(c) 1-chloro-2,4-dinitrobenzene

(d) 3-phenylpropene

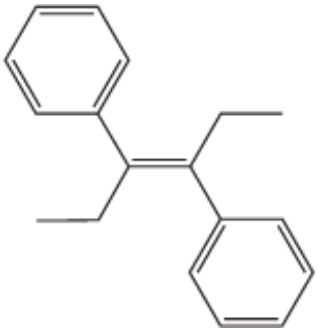
PRACTICE EXERCISE 16.18

Write names for the following compounds.

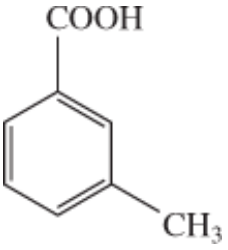
(a)



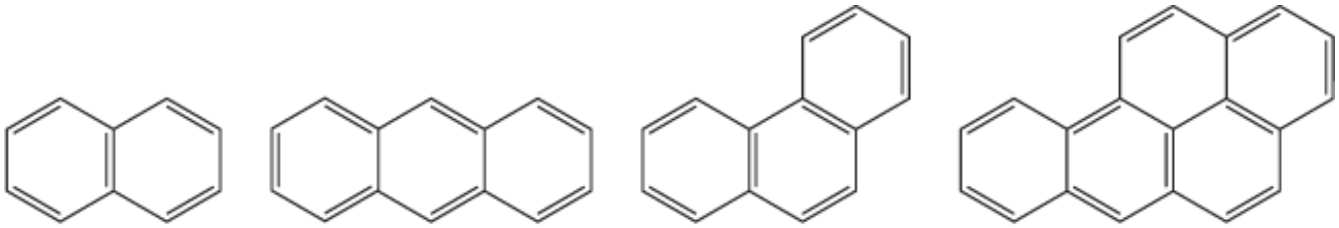
(b)



(c)



Polycyclic aromatic hydrocarbons (PAHs) contain two or more aromatic rings, and each pair of rings shares two carbon atoms. Naphthalene, anthracene and phenanthrene, the most common PAHs, and substances derived from them are found in coal tar and high-boiling-point petroleum residues. At one time, naphthalene was used as a moth repellent and insecticide in preserving woollens, but its use has decreased due to the introduction of chlorinated hydrocarbons such as *p*-dichlorobenzene. Also found in coal tar are lesser amounts of a compound called benzo[*a*]pyrene. This compound is also found in the exhausts of petrol-powered internal combustion engines (such as car engines) and in cigarette smoke. Benzo[*a*]pyrene is a very potent carcinogen and mutagen.

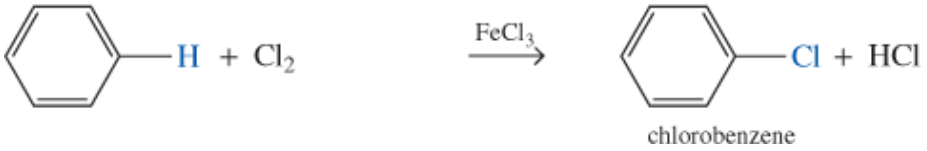


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16.8 Reactions of Aromatic Compounds: Electrophilic Aromatic Substitution

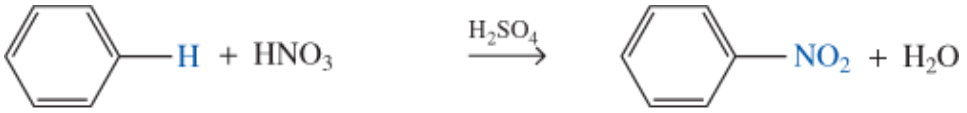
By far the most characteristic reaction of aromatic compounds is substitution at a ring carbon atom. Some groups that can be introduced directly onto the ring are the halogens (—X), the nitro (—NO_2) group, the sulfonic acid (—SO_3H) group, alkyl (—R) groups and acyl (RCO —) groups.

Halogenation:



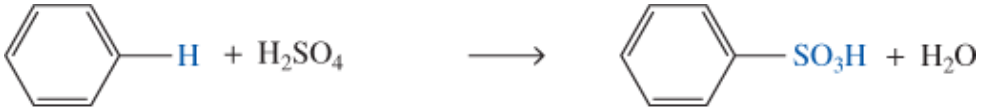
chlorobenzene

Nitration:



nitrobenzene

Sulfonation:



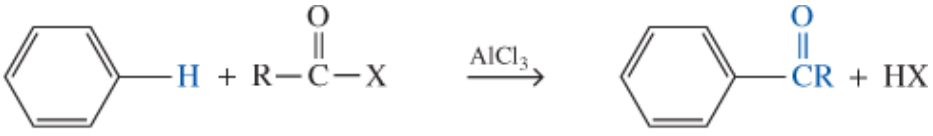
benzenesulfonic acid

Alkylation:



an alkylbenzene

Acylation:



an acyl halide

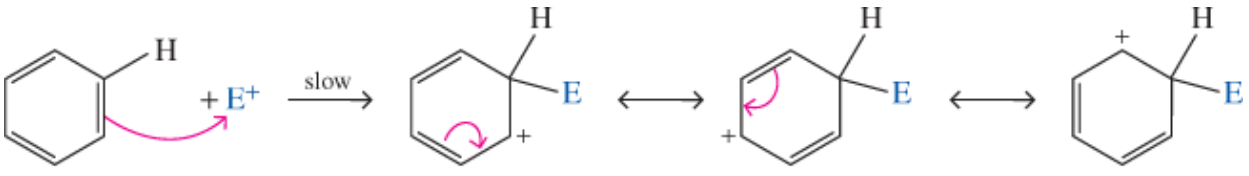
an acylbenzene

There are several types of **electrophilic aromatic substitution** reactions; that is, reactions in which a hydrogen of an aromatic ring is replaced by an electrophile, E^+. The mechanisms of these reactions are actually very similar. In fact, they can be broken down into three common steps.

Step 1: Formation of the electrophile:

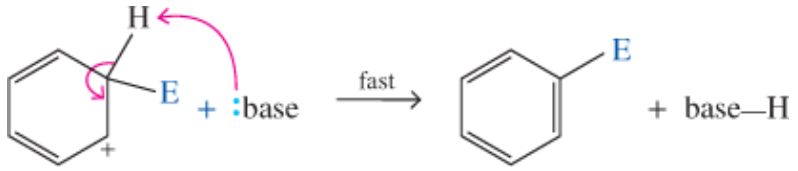
$$\text{reagent(s)} \rightarrow E^+$$

Step 2: Reaction of the electrophile with the aromatic ring to give a resonance-stabilised cation intermediate:



resonance-stabilised cation intermediate

Step 3: Proton transfer to a base to regenerate the aromatic ring:

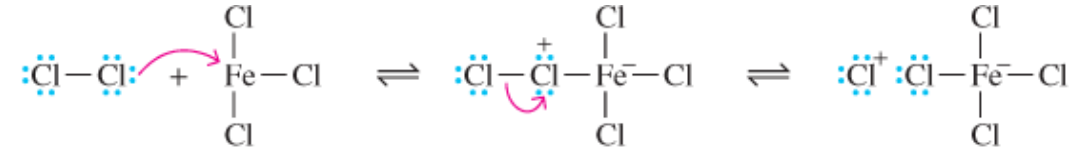


The reactions we are about to study differ only in the way the electrophile is generated and in the base that removes the proton to re-form the aromatic ring. You should keep this principle in mind as we explore the details of each reaction.

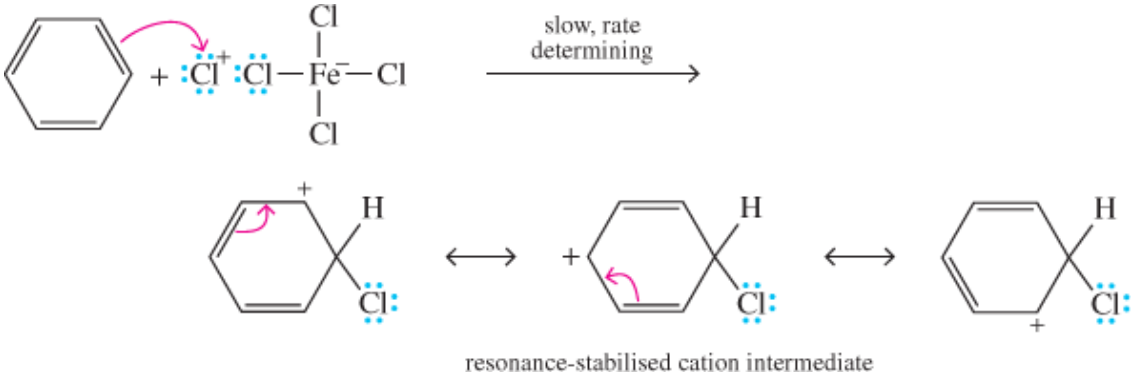
Chlorination and Bromination

Chlorine alone does not react with benzene, in contrast to its instantaneous addition to cyclohexene (section 16.5). However, in the presence of a Lewis acid catalyst, such as iron(III) chloride or aluminium chloride, chlorine reacts to give chlorobenzene and HCl. Chemists account for this type of electrophilic aromatic substitution by the following three-step mechanism.

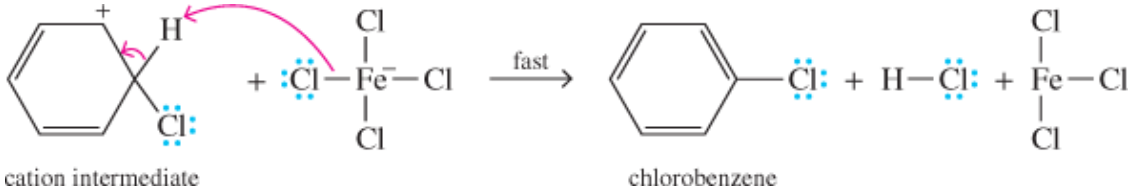
Step 1: Formation of the electrophile by reaction between chlorine (a Lewis base) and $FeCl_3$ (a Lewis acid), giving an ion pair containing a chloronium ion (an electrophile):



Step 2: Reaction of the Cl_2–$FeCl_3$ ion pair with the π electron cloud of the aromatic ring, forming a resonance-stabilised cation intermediate, represented here as a hybrid of three contributing structures:



Step 3: Proton transfer from the cation intermediate to $FeCl_4^-$, forming HCl, regenerating the Lewis acid catalyst and giving chlorobenzene:



Treatment of benzene with bromine in the presence of a Lewis acid gives bromobenzene and HBr. The mechanism for this reaction is the same as that for the chlorination of benzene.

The major difference between the addition of a halogen to an alkene and substitution by a halogen on an aromatic

ring is the fate of the cation intermediate formed in the first step of each reaction (figure 16.36). Recall that the addition of chlorine (or bromine) to an alkene is a two-step process; the first and slower step is the formation of a bridged chloronium ion intermediate. This intermediate then reacts with a chloride ion to complete the addition. With aromatic compounds, the cation intermediate loses H^+ to regenerate the aromatic ring and regain its large resonance stabilisation. There is no such resonance stabilisation to be regained in the case of an alkene.

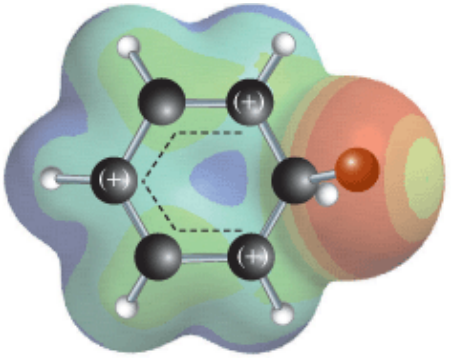
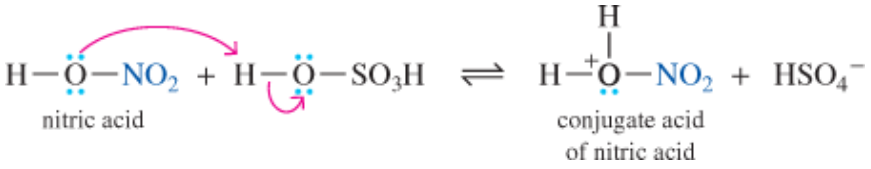


FIGURE 16.36 The positive charge on the resonance-stabilised intermediate is distributed approximately equally on carbon atoms 2, 4 and 6 of the ring relative to the point of substitution.

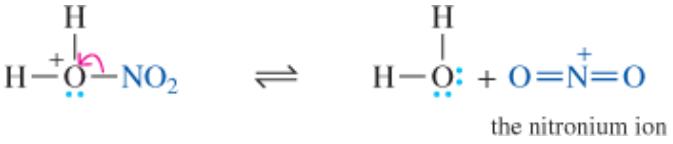
Nitration and Sulfonation

The sequence of steps for the nitration and sulfonation of benzene is similar to that for chlorination and bromination. For *nitration*, the electrophile is the **nitronium ion**, NO_2^+, generated by the reaction of nitric acid with sulfuric acid. In the following equations nitric acid is written $HONO_2$ to show more clearly the origin of the nitronium ion.

Step 1: Formation of the electrophile by (a) proton transfer from sulfuric acid to the —OH group of nitric acid, giving the conjugate acid of nitric acid:



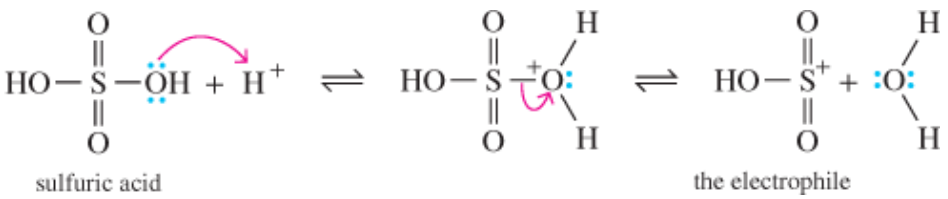
and (b) loss of water from this conjugate acid, giving the nitronium ion, NO_2^+:



Steps 2 and 3 of the nitration are given in worked example 16.22.

The *sulfonation* of benzene is carried out using hot, concentrated sulfuric acid. The electrophile under these conditions is either SO_3 or HSO_3^+, depending on the experimental conditions. The HSO_3^+ electrophile is formed from sulfuric acid in the following way.

Step 1: Formation of the electrophile by acid-catalysed dehydration:



Steps 2 and 3 of sulfonation follow the same mechanism as for nitration.

WORKED EXAMPLE 16.22

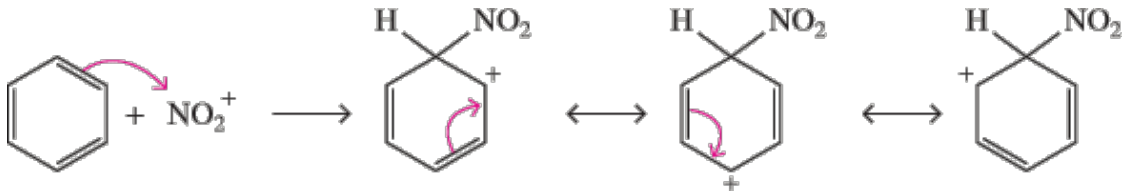
Electrophilic Aromatic Substitution of Benzene

Write a stepwise mechanism for the nitration of benzene.

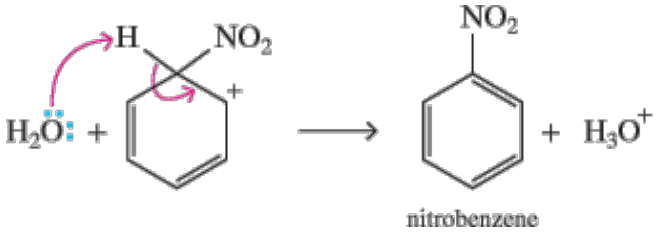
Analysis and solution

Step 1: Formation of the electrophile, as given above

Step 2: Reaction of the nitronium ion (an electrophile) with the benzene ring (a nucleophile), giving a resonance-stabilised cation intermediate:



Step 3: Proton transfer from this intermediate to H_2O regenerating the aromatic ring and giving nitrobenzene:

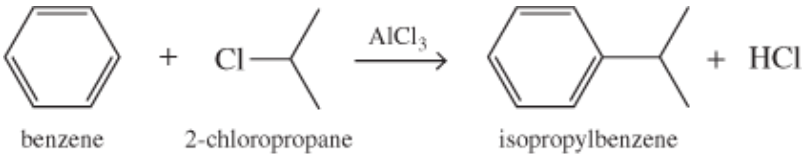


PRACTICE EXERCISE 16.19

Write a stepwise mechanism for the sulfonation of benzene. Use HSO_3^+ as the electrophile.

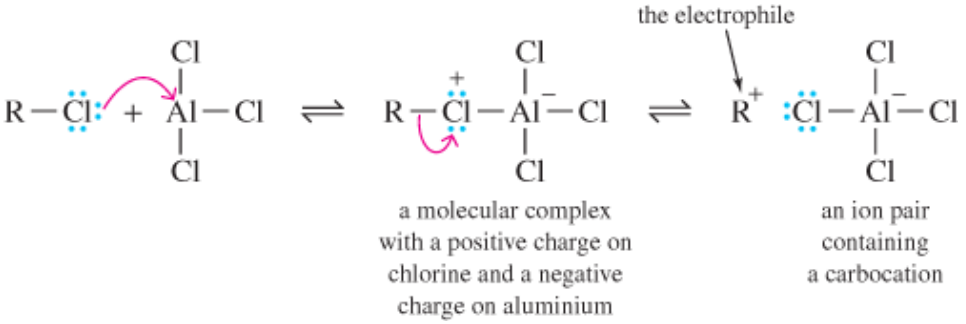
Alkylation

Alkylation is a very important synthetic outcome as the new carbon–carbon bond between benzene and an alkyl group builds up the complexity of the molecule. This is illustrated by the reaction of benzene with 2-chloropropane in the presence of aluminium chloride:

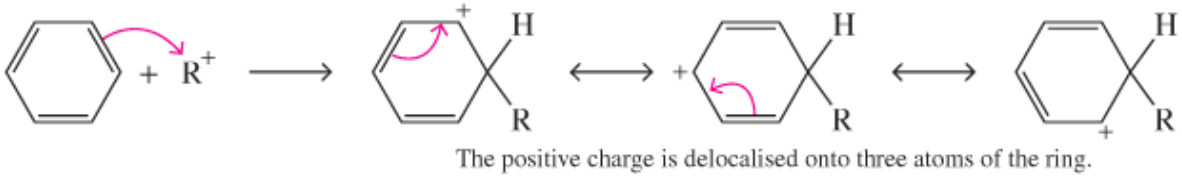


This form of alkylation, often called **Friedel–Crafts alkylation** after the two chemists who discovered it in 1877, is among the most important methods for adding new carbon–carbon bonds to aromatic rings. The reaction involves the following steps.

Step 1: Formation of the electrophile by reaction of a haloalkane (a Lewis base) with aluminium chloride (a Lewis acid), giving a molecular complex in which aluminium has a negative formal charge and the halogen of the haloalkane has a positive formal charge. Redistribution of electrons in this complex then gives an alkyl carbocation as part of an ion pair:

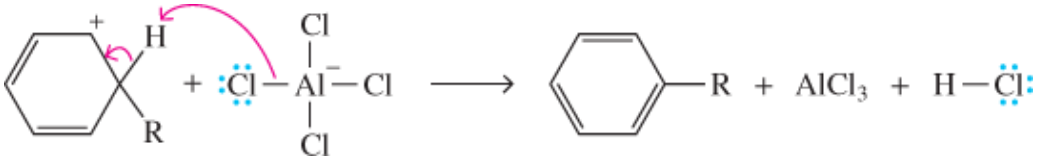


Step 2: Reaction of the alkyl carbocation with the π electrons of the aromatic ring, giving a resonance-stabilised cation intermediate:



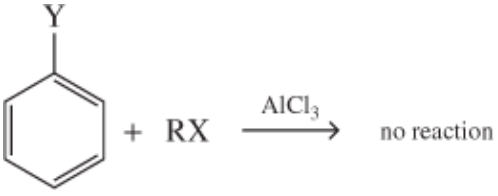
The positive charge is delocalised onto three atoms of the ring.

Step 3: Proton transfer regenerating the aromatic character of the ring and the Lewis acid catalyst:

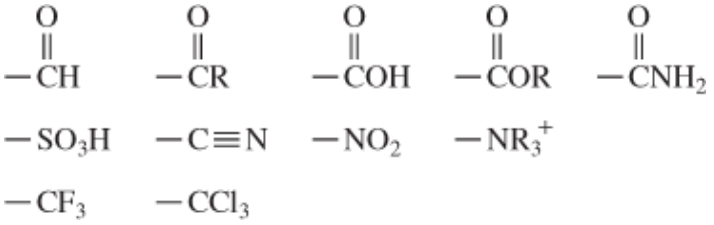


There are two major limitations on Friedel–Crafts alkylations. The first is that it is practical only with stable carbocations, such as 3° and 2° carbocations. You might explore the reasons for this in subsequent chemistry χ α β χ δ ε φ γ η ι φ κ λ μ ν ο π θ ρ σ τ υ ϖ ω ξ ψ ζ

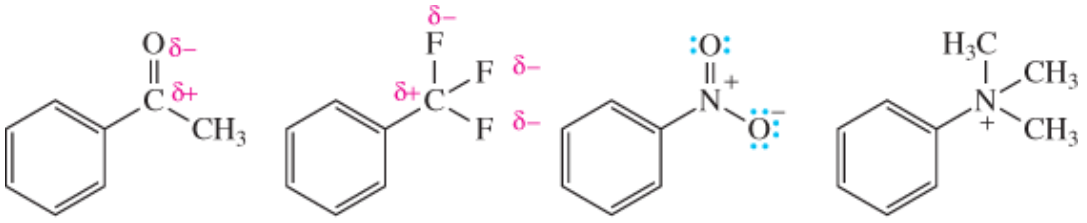
The second limitation on Friedel–Crafts alkylation is that it fails altogether on benzene rings bearing one or more strongly electron-withdrawing groups (indicated by the letter Y):



When any of the following groups is present on the aromatic ring, the benzene ring does not undergo Friedel–Crafts alkylation.



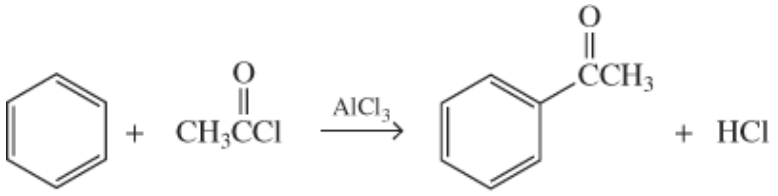
A common characteristic of these groups is that each has either a full or partial positive charge on the atom bonded to the benzene ring (see examples on the next page). For carbonyl-containing compounds, this partial positive charge arises because of the difference in electronegativity between the carbonyl oxygen and carbon atoms. For the —CF_3 and —CCl_3 groups, the partial positive charge on carbon arises because of the difference in electronegativity between the carbon atom and the halogens bonded to it. In both the nitro group, —NO_2, and the trialkylammonium group, such as —$N(CH_3)_3^+$ below, there is a positive charge on nitrogen:



the carbonyl group of a ketone | a trifluoro-methyl group | a nitro group | a trimethyl-ammonium group

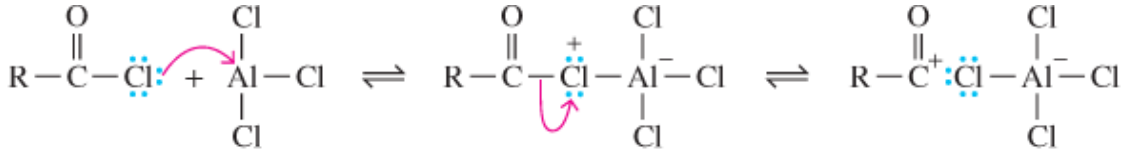
Acylation

Treating an aromatic hydrocarbon with an acyl halide in the presence of aluminium chloride forms a carbon–carbon bond and gives a ketone in a process known as **acylation**. An acyl halide is a derivative of a carboxylic acid in which the —OH of the carboxyl group is replaced by a halogen, most commonly chlorine (see chapter 23). Acyl halides are also referred to as acid halides. An RCO—group is known as an acyl group. The reaction of an acyl halide with an aromatic hydrocarbon is illustrated below by the reaction of benzene and acetyl chloride in the presence of aluminium chloride to give acetophenone.



benzene | acetyl chloride (an acyl halide) | acetophenone (a ketone)

This reaction is related to the Friedel–Crafts alkylation in that aluminium chloride is used to generate the electrophile, which in this case is called an acylium ion. This reaction was also discovered by Friedel and Crafts so is often called the **Friedel–Crafts acylation**. The mechanism is shown below.



an acyl chloride (a Lewis base) | aluminium chloride (a Lewis acid) | a molecular complex with a positive charge on chlorine and a negative charge on aluminium | an ion pair containing an acylium ion

WORKED EXAMPLE 16.23

Forming Carbon–carbon Bonds to Aromatic Rings

Write a structural formula for the product formed by Friedel–Crafts alkylation or acylation of benzene with each of the following.

(a) $C_6H_5CH_2Cl$
benzyl chloride

(b)

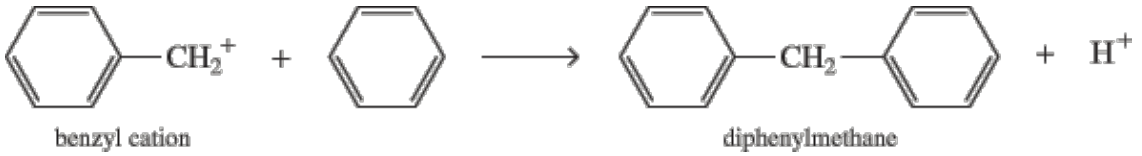


benzoyl chloride

Analysis and solution

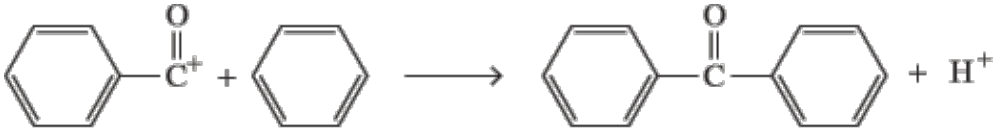
Benzene is unsubstituted so can undergo both alkylations and acylations.

(a) Treatment of benzyl chloride with aluminium chloride gives the resonance-stabilised benzyl cation. Reaction of this cation with benzene, followed by loss of H^+, gives diphenylmethane:



benzyl cation diphenylmethane

(b) Treatment of benzoyl chloride with aluminium chloride gives an acyl cation. Reaction of this cation with benzene, followed by loss of H^+, gives benzophenone:



benzoyl cation benzophenone

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SUMMARY

Introduction to Hydrocarbons

A hydrocarbon is a compound that contains only carbon and hydrogen atoms. The four classes of hydrocarbons are alkanes, alkenes, alkynes and arenes.

Alkanes

A saturated hydrocarbon contains only single bonds. Alkanes have the general formula C_nH_{2n+2}. Constitutional isomers have the same molecular formula but a different connectivity (a different order of attachment of their atoms). Alkanes are named according to a set of rules developed by IUPAC.

An alkane that contains carbon atoms bonded to form a ring is called a cycloalkane. To name a cycloalkane, prefix the name of the open-chain hydrocarbon with '*cyclo*-'. Compounds with the same molecular formula and the same order of attachment of atoms, but arrangements of atoms in space that cannot be interconverted by rotation around single bonds, are called *cis–trans* isomers. The term *cis* means that substituents are on the same side of the ring; *trans* means that they are on opposite sides of the ring. Most cycloalkanes with substituents on two or more carbon atoms of the ring show *cis–trans* isomerism.

Alkanes are nonpolar compounds, and the only forces of attraction between their molecules are dispersion forces, which are weak electrostatic interactions between temporary partial positive and negative charges on atoms or molecules.

Alkenes and Alkynes

An alkene is an unsaturated hydrocarbon that contains a carbon– carbon double bond. Alkenes have the general formula C_nH_{2n}. An alkyne is an unsaturated hydrocarbon that contains a carbon– carbon triple bond. Alkynes have the general formula C_nH_{2n-2}. We show the presence of a carbon–carbon double bond by changing the naming component of the parent hydrocarbon from *-an-* to *-en-*. We show the presence of a carbon–carbon triple bond by changing the naming component of the parent alkane from *-an-* to *-yn-*.

The structural feature that makes *cis–trans* isomerism possible in alkenes is restricted rotation around the two carbon atoms of the double bond. If atoms of the parent chain are on the same side of the double bond, the configuration of the alkene is *cis*; if they are on opposite sides, the configuration is *trans*. Using a set of priority rules, we can also specify the configuration of a carbon–carbon double bond by the *E*,*Z* system. If the two groups of higher priority are on the same side of the double bond, the configuration of the alkene is *Z*; if they are on opposite sides, it is *E*.

Reactions of Alkanes

Alkanes have very limited reactivity. The most important reaction of alkanes is combustion with oxygen, which is the basis of their use as energy sources.

Reactions of Alkenes

A characteristic reaction of alkenes is addition, during which a π bond is broken and σ bonds to two new atoms or groups of atoms are formed. This process is described as *syn* addition or *anti* addition depending on whether the atoms appear on the same or opposite sides of the original carbon–carbon bond.

An electrophile is any molecule or ion that can accept a pair of electrons to form a new covalent bond. All electrophiles are Lewis acids. The rate-determining step in electrophilic addition to an alkene is the

reaction of an electrophile with a carbon–carbon double bond to form a carbocation — an ion that contains a carbon atom with only six electrons in its valence shell and that has a positive charge. Carbocations are planar, with bond angles of 120° around the positive carbon atom. The order of stability of carbocations is 3° > 2° > 1° > methyl.

Reactions of Alkynes

Alkynes can undergo similar reactions to alkenes: addition, reduction and oxidation. Of particular importance is reduction using hydrogen gas where the choice of catalyst determines whether an alkene or an alkane is produced.

Aromatic Compounds

Benzene and its alkyl derivatives are classified as aromatic hydro-carbons, or arenes. The concepts of hybridisation of atomic orbitals and the theory of resonance are used to describe the structure of benzene. The resonance energy of benzene is about 152 kJ mol^{-1}.

According to the Hückel criteria for aromaticity, a ring is aromatic if it (1) has one *p* orbital on each atom of the ring, (2) is planar, so that overlap of all *p* orbitals of the ring is continuous or nearly so, and (3) has 2, 6, 10, 14, 18, and so on (i.e. $4n + 2$), π electrons in the overlapping system of *p* orbitals. A heterocyclic aromatic compound contains one or more atoms other than carbon in an aromatic ring.

Aromatic compounds are named by the IUPAC system. The common names toluene, xylene, styrene, phenol, aniline, benzoic acid and benzaldehyde are retained. The C_6H_5— group is named phenyl, and the $C_6H_5CH_2$— group is named benzyl. To locate two substituents on a benzene ring, either number the atoms of the ring or use the locators *ortho* (*o*), *meta* (*m*) and *para* (*p*).

Polycyclic aromatic hydrocarbons contain two or more fused benzene rings. Particularly abundant are naphthalene, anthracene and phenanthrene, and their derivatives.

Reactions of Aromatic Compounds: Electrophilic Aromatic Substitution

Aromatic compounds react with many forms of positively charged electrophiles to give substituted aromatic systems.

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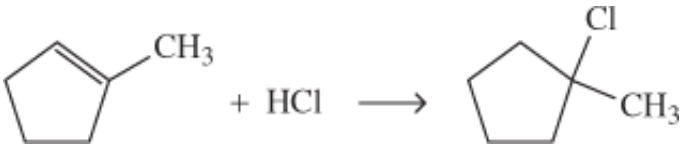
Oxidation of alkanes *(section 16.4)*

Alkanes display virtually no reactivity, except under harsh conditions where they may be completely oxidised to carbon dioxide and water. This process liberates energy and provides the basis for their use as sources of heat and power:

$$CH_3CH_2CH_3 + 5O_2 \rightarrow 3CO_2 + 4H_2O + \text{energy}$$

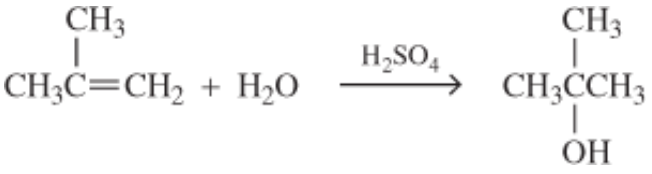
Addition of H—X to alkenes *(section 16.5)*

Addition of H—X is regioselective and follows Markovnikov's rule. Reaction occurs in two steps and involves the formation of a carbocation intermediate:



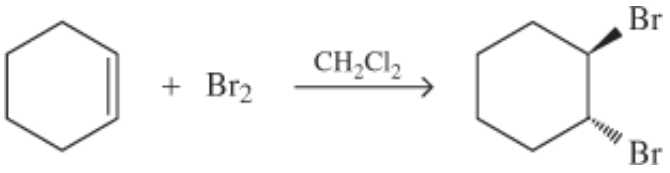
Acid-catalysed hydration of alkenes *(section 16.5)*

Hydration is regioselective and follows Markovnikov's rule. Reaction involves two steps and forms a carbocation intermediate:



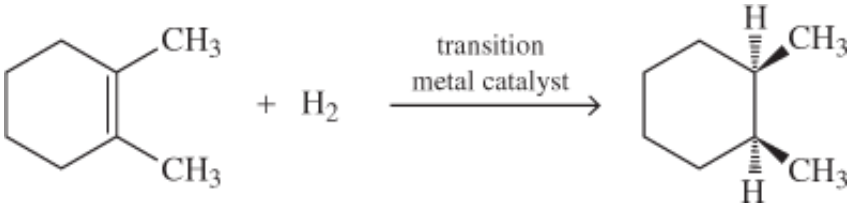
Addition of bromine and chlorine to alkenes *(section 16.5)*

Addition occurs in two steps and involves *anti* addition by way of a bridged bromonium or chloronium ion intermediate:



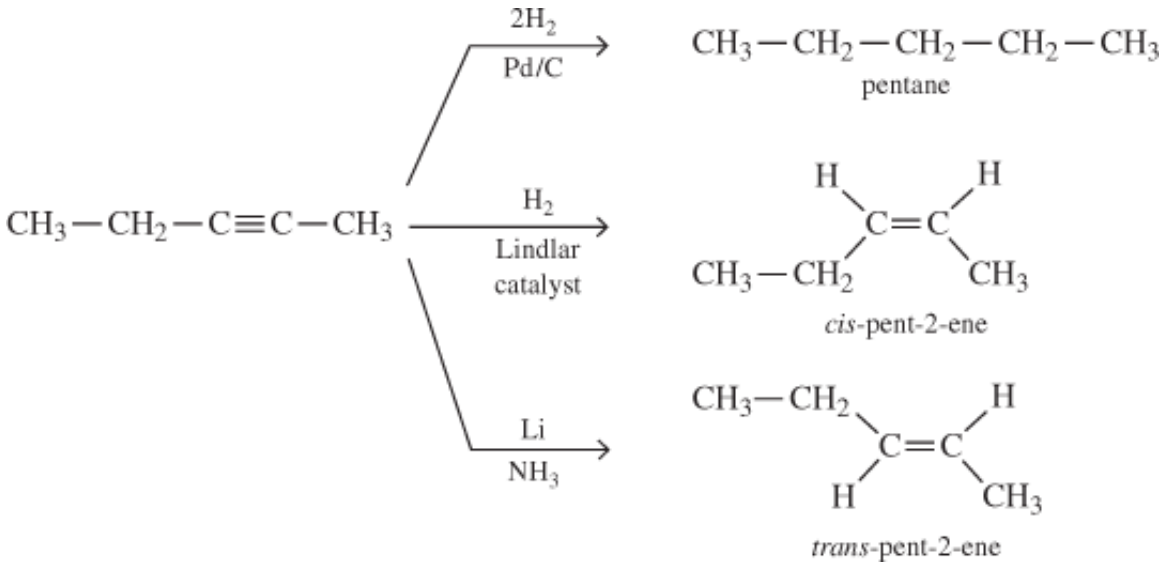
Reduction of alkenes: formation of alkanes *(section 16.5)*

Catalytic reduction involves, predominantly, the *syn* addition of hydrogen:



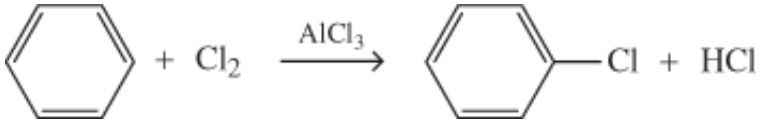
Reduction of alkynes to alkenes or alkanes *(section 16.6)*

The choice of catalyst controls the synthetic outcome of the reduction of alkynes:



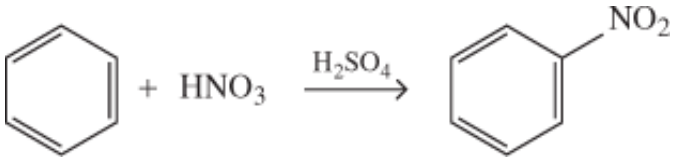
Chlorination and bromination of aromatic compounds *(section 16.8)*

The electrophile is a halonium ion, Cl^+ or Br^+, formed by treating Cl_2 or Br_2 with $AlCl_3$ or $FeCl_3$:



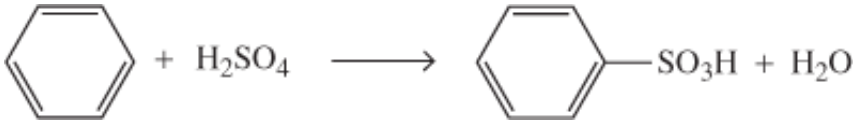
Nitration of aromatic compounds *(section 16.8)*

The electrophile is the nitronium ion, NO_2^+, formed by treating nitric acid with sulfuric acid:



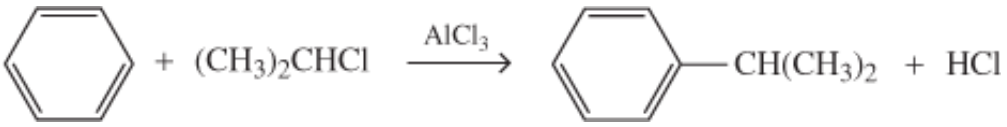
Sulfonation of aromatic compounds *(section 16.8)*

The electrophile is HSO_3^+:



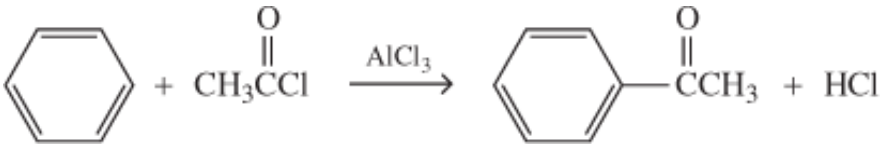
Alkylation of aromatic compounds *(section 16.8)*

The electrophile is an alkyl carbocation formed by treating an alkyl halide with a Lewis acid:



Acylation of aromatic compounds *(section 16.8)*

The electrophile is an acyl cation formed by treating an acyl halide with a Lewis acid:



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REVIEW QUESTIONS

Introduction to Hydrocarbons

16.1 Define the term ‘hydrocarbon’.

16.2 What defines each of the following?

(a) alkane

(b) alkene

(c) alkyne

(d) arene

16.3 Explain the difference between saturated and unsaturated hydrocarbons.

Alkanes

16.4 Which of these statements are true about constitutional isomers?

(a) They have the same molecular formula.

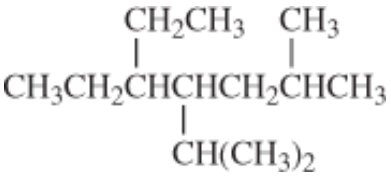
(b) They have the same molar mass.

(c) They have the same order of attachment of atoms.

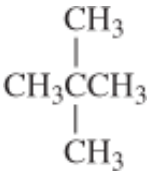
(d) They have the same physical properties.

16.5 Write a line structure for each of these condensed structural formulae.

(a)

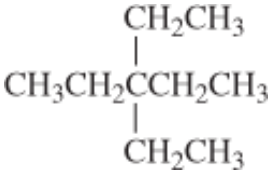


(b)



(c) $(CH_3)_2CHCH(CH_3)_2$

(d)

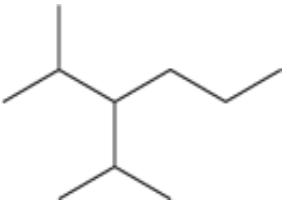


(e) $(CH_3)_3CH$

(f) $CH_3(CH_2)_3CH(CH_3)_2$

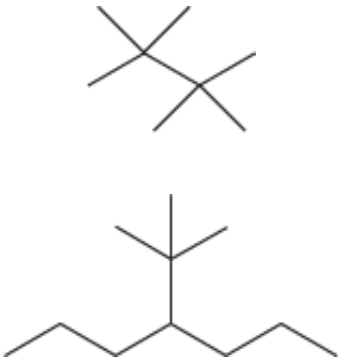
16.6 Write a condensed structural formula and the molecular formula for each of the following alkanes.

(a)



(b)

(c)

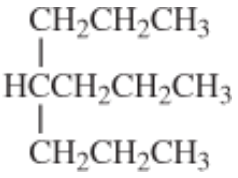


16.7 For each of the following condensed structural formulae, provide an even more abbreviated formula, using parentheses and subscripts.

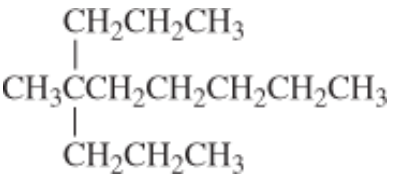
(a)



(b)



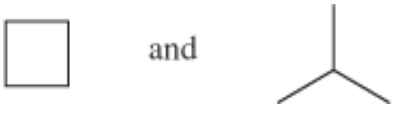
(c)



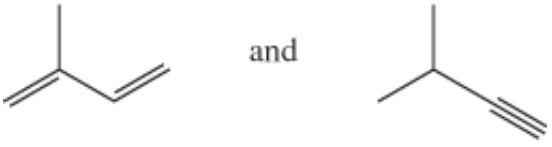
16.8 Name and draw line structures for the nine constitutional isomers with the molecular formula C_7H_{16}.

16.9 For each of the following, state whether the two structural formulae shown represent constitutional isomers.

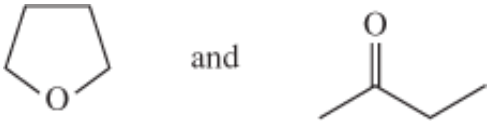
(a)



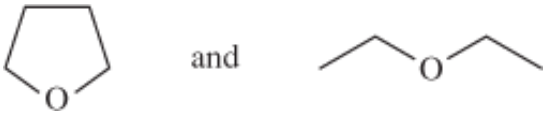
(b)



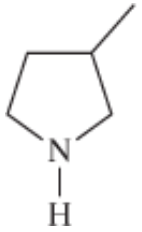
(c)



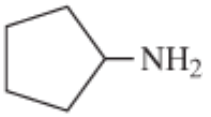
(d)



(e)



and



(f)



and



16.10 In each of the following, are the two compounds constitutional isomers?

(a) CH_3CH_2OH and CH_3OCH_3

(b) $CH_3\overset{\overset{O}{\|}}{C}CH_3$ and $CH_3CH_2\overset{\overset{O}{\|}}{C}H$

(c) $CH_3\overset{\overset{O}{\|}}{C}OCH_3$ and $CH_3CH_2\overset{\overset{O}{\|}}{C}OH$

(d) $CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_3$ and $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$

(e)



and $CH_3CH_2CH_2CH_2CH_3$

(f)



and $CH_2{=}CHCH_2CH_2CH_3$

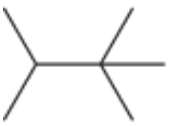
16.11 Write IUPAC names for each of the following alkanes and cycloalkanes.

(a) $CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3$

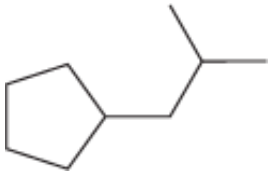
(b) $CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

(c) $CH_3(CH_2)_4\overset{\overset{CH_2CH_3}{|}}{C}HCH_2CH_3$

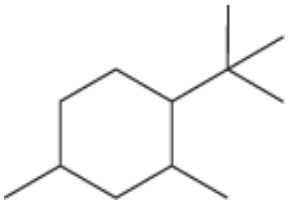
(d)



(e)



(f)



16.12 Write line structures for these alkanes.

(a) 2,2,4-trimethylhexane

(b) 2,2-dimethylpropane

(c) 3-ethyl-2,4,5-trimethyloctane

(d) 5-butyl-2,2-dimethylnonane

(e) 4-isopropyloctane

(f) 3,3-dimethylpentane

(g) *trans*-1,3-dimethylcyclopentane

(h) *cis*-1,2-diethylcyclobutane

16.13 Explain why each of the following names is an incorrect IUPAC name, and write the correct IUPAC name for the intended compound.

(a) 1,3-dimethylbutane

(b) 4-methylpentane

(c) 2,2-diethylbutane

(d) 2-ethyl-3-methylpentane

(e) 2-propylpentane

(f) 2,2-diethylheptane

(g) 2,2-dimethylcyclopropane

(h) 1-ethyl-5-methylcyclohexane

16.14 What structural feature of cycloalkanes makes it possible for them to exhibit *cis–trans* isomerism?

16.15 Is *cis–trans* isomerism possible in alkanes?

16.16 Name and draw structural formulae for the *cis* and *trans* isomers of 1,2-dimethylcyclopropane.

16.17 Name and draw structural formulae for all cycloalkanes with the molecular formula C_5H_{10}. Be certain to include *cis–trans* isomers, as well as constitutional isomers.

16.18 Using a planar pentagon representation for the cyclopentane ring, draw structural formulae for the *cis* and *trans* isomers of the following.

(a) 1,2-dimethylcyclopentane

(b) 1,3-dimethylcyclopentane

Alkenes and Alkynes

16.19 Draw a structural formula for each of these compounds.

(a) *trans*-2-methylhex-3-ene

(b) 2-methylhex-3-yne

(c) 2-methylbut-1-ene

(d) 3-ethyl-3-methylpent-1-yne

(e) 2,3-dimethylbut-2-ene

(f) *cis*-pent-2-ene

(g) (*Z*)-1-chloropropene

(h) 3-methylcyclohexene

16.20 Draw a structural formula for each of these compounds.

(a) 1-isopropyl-4-methylcyclohexene

(b) (6*E*)-2,6-dimethylocta-2,6-diene

(c) *trans*-1,2-diisopropylcyclopropane

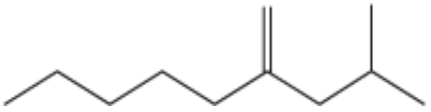
(d) 2-methylhex-3-yne

(e) 2-chloropropene

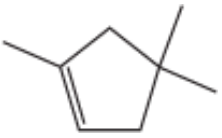
(f) tetrachloroethene

16.21 Write the IUPAC name for each of these compounds.

(a)



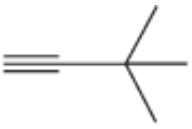
(b)



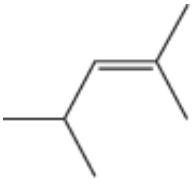
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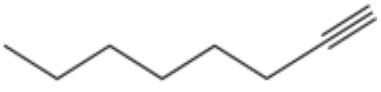
(d)



(e)



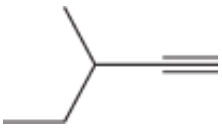
(f)



(g)



(h)



16.22 Write the structural formulae and give the IUPAC names for all possible alkynes with each of the following molecular formulae.

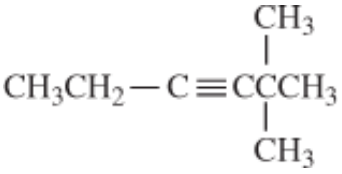
(a) C_5H_8

(b) C_6H_{10}

(c) C_8H_{12}

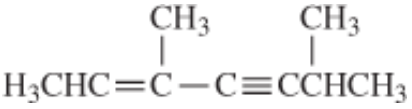
16.23 Give the IUPAC names for the following.

(a)



(b) $CH_3C{\equiv}CCH_2C{\equiv}CCH_2CH_3$

(c)



(d) $HC{\equiv}C{-}CH_2{-}HC{\equiv}CCH_2CH_3$

16.24 Explain why the following names are incorrect. Give the correct name and draw the structural formula.

(a) but-3-yne

(b) pent-3-yne-1-ene

(c) but-3-en-1-yne

16.25 Explain why these names are incorrect, and write a correct name for the intended compound.

(a) 1-methylpropene

(b) pent-3-ene

(c) 2-methylcyclohexene

(d) 3,3-dimethylpentene

(e) hex-4-yne

(f) 2-isopropylbut-2-ene

16.26 Explain why these names are incorrect, and write a correct name for the intended compound.

(a) 2-ethylprop-1-ene

(b) 5-isopropylcyclohexene

(c) 4-methylhex-4-ene

(d) 2-*sec*-butylbut-1-ene

(e) 6,6-dimethylcyclohexene

(f) 2-ethylhex-2-ene

16.27 Which of these alkenes show *cis–trans* isomerism? For each that does, draw structural formulae for both isomers.

(a) hex-1-ene

(b) hex-2-ene

(c) hex-3-ene

(d) 2-methylhex-2-ene

(e) 3-methylhex-2-ene

(f) 2,3-dimethylhex-2-ene

16.28 Which of these alkenes show *cis–trans* isomerism? For each that does, draw structural formulae for both isomers.

(a) pent-1-ene

(b) pent-2-ene

(c) 3-ethylpent-2-ene

(d) 2,3-dimethylpent-2-ene

(e) 2-methylpent-2-ene

(f) 2,4-dimethylpent-2-ene

16.29 Which of these alkenes can exist as pairs of *cis-trans* isomers? For each alkene that can, draw the *trans* isomer.

(a) $CH_2{=}CHBr$

(b) $CH_3CH{=}CHBr$

(c) $(CH_3)_2C{=}CHCH_3$

(d) $(CH_3)_2CHCH{=}CHCH_3$

16.30 Arrange the groups in each of these sets in order of increasing priority.

(a) $-CH_3$, $-Br$, $-CH_2CH_3$

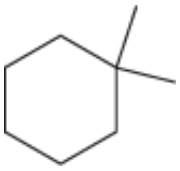
(b) $-OCH_3$, $-CH(CH_3)_2$, $-CH_2CH_2NH_2$

(c) $-CH_2OH$, $-COOH$, $-OH$

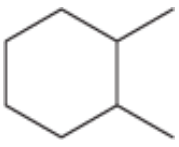
(d) $-CH{=}CH_2$, $-CH{=}O$, $-CH(CH_3)_2$

16.31 For each of these molecules that shows *cis–trans* isomerism, draw the *cis* isomer.

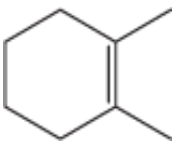
(a)



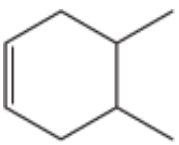
(b)



(c)



(d)



16.32 Explain why each of these names is incorrect or incomplete, and then write a correct name.

(a) (*Z*)-2-methylpent-1-ene

(b) (*E*)-3,4-diethylhex-3-ene

(c) *trans*-2,3-dimethylhex-2-ene

(d) (1*Z*,3*Z*)-2,3-dimethylbuta-1,3-diene

16.33 Draw structural formulae for all compounds with the molecular formula C_5H_{10} that are:

(a) alkenes that do not show *cis–trans* isomerism

(b) alkenes that do show *cis–trans* isomerism

(c) cycloalkanes that do not show *cis–trans* isomerism

(d) cycloalkanes that do show *cis–trans* isomerism.

Reactions of alkanes

16.34 Write balanced equations for the combustion of each of the following hydrocarbons. Assume that each is converted completely to carbon dioxide and water.

(a) hexane

(b) cyclohexane

(c) 2-methylpentane

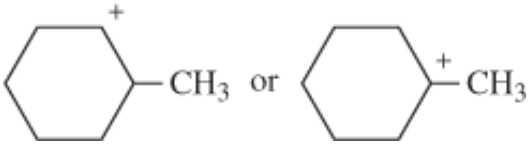
Reactions of alkenes

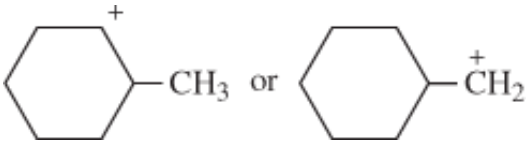
16.35 Select the more stable carbocation from each of these pairs.

(a) $CH_3CH_2\overset{+}{C}H_2$ or $CH_3\overset{+}{C}HCH_3$

(b) $CH_3CH\overset{+}{C}HCH_3$ (CH$_3$ above) or $CH_3\overset{+}{C}CH_2CH_3$ (CH$_3$ above)

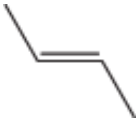
16.36 Select the more stable carbocation from each of these pairs.

(a)  or

(b)  or

16.37 Write a balanced equation for the combustion of 2-methylpropene in air to give carbon dioxide and water. The oxidising agent is O_2, which makes up approximately 20% of air.

16.38 Draw the product formed by treating each of these alkenes with H_2/Ni.

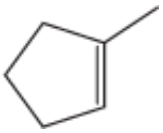
(a) 

(b) 

(c)



(d)



16.39 Show how to convert ethene into these compounds.

(a) ethane

(b) ethanol

(c) bromoethane

(d) 1,2-dibromoethane

(e) chloroethane

Reactions of Alkynes

16.40 Using any alkyne and the required catalyst, describe how you would prepare the following alkenes.

(a) *cis*-oct-2-ene

(b) *trans*-hept-2-ene

(c) 3-methylhex-1-ene

16.41 Predict the products of the reaction of hex-2-yne with the following.

(a) H_2 and Pd/C

(b) H_2 and Na/NH_3

(c) H_2 using Lindlar catalyst

(d) H_2 using Lindlar catalyst followed by the addition of Br_2

16.42 Write equations for the following reactions of alkynes.

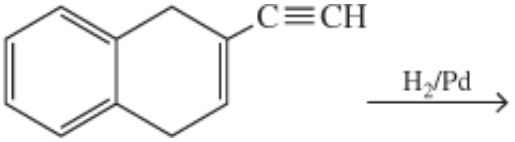
(a) pent-2-yne (1 mole) + H_2 (1 mole) + Lindlar catalyst

(b) hex-3-yne (1 mole) + Br_2 (2 moles)

(c) but-2-yne (1 mole) + Li (1 mole) in $NH_3(l)$

(d) but-1-yne (1 mole) + H_2 (2 moles) + Pd/C catalyst

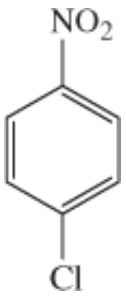
16.43 What is the product of the following reaction?



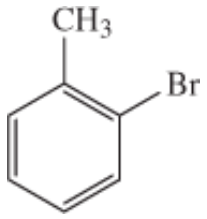
Aromatic compounds

16.44 Name these compounds.

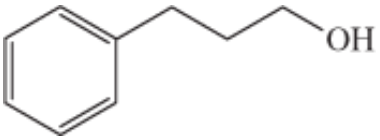
(a)



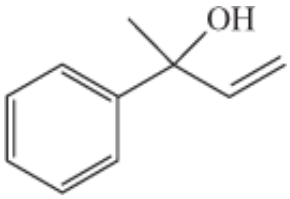
(b)



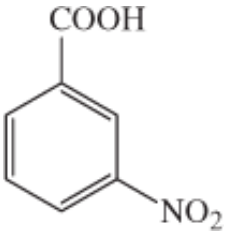
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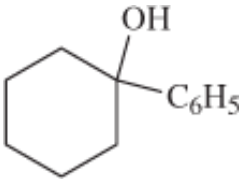
(d)



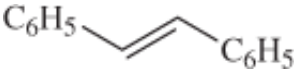
(e)



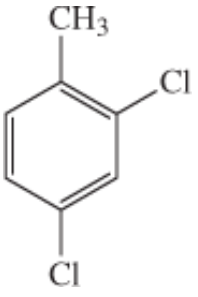
(f)



(g)



(h)



16.45 Draw structural formulae for these compounds.

(a) 1-bromo-2-chloro-4-ethylbenzene

(b) 4-iodo-1,2-dimethylbenzene

(c) 2,4,6-trinitrotoluene

(d) 4-phenylpentan-2-ol

(e) *p*-cresol (*p*-methylphenol)

(f) 2,4-dichlorophenol

(g) 1-phenylcyclopropanol

(h) styrene (phenylethene)

(i) *m*-bromophenol

(j) 2,4-dibromoaniline

(k) isobutylbenzene

(l) *m*-xylene

Reactions of Aromatic Compounds: Electrophilic Aromatic Substitution

16.46 Draw a structural formula for the compound formed by treating benzene with each of the following combinations of reagents.

(a) $CH_3CH_2Cl/AlCl_3$

(b) $CH_2{=}CH_2/H_2SO_4$

(c) CH_3CH_2OH/H_2SO_4

16.47 Show three different combinations of reagents you might use to convert benzene to isopropylbenzene.

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16.48 In question 16.8, you drew structural formulae for all constitutional isomers with molecular formula C_7H_{16}. Predict which of those isomers has the lowest boiling point and which has the highest.

16.49 What generalisations can you make about the densities of alkanes relative to that of water?

16.50 Which unbranched alkane has about the same boiling point as water (see table 16.1)? Calculate the molar mass of this alkane, and compare it with that of water.

16.51 Table 16.1 shows that each —CH_2 group added to the carbon chain of an alkane increases the boiling point of the alkane. The increase is greater going from CH_4 to C_2H_6 and from C_2H_6 to C_3H_8 than it is from C_8H_{18} to C_9H_{20} or from C_9H_{20} to $C_{10}H_{22}$. What do you think is the reason for this trend?

16.52 As stated in section 16.2, the wax found naturally in apple skins is an unbranched alkane with the molecular formula $C_{27}H_{56}$. Explain how the presence of this alkane prevents the loss of moisture from within an apple.

16.53 Predict answers to the following questions about dodecane, $C_{12}H_{26}$, an unbranched alkane.

(a) Will it dissolve in water?

(b) Will it dissolve in hexane?

(c) Will it burn when ignited?

(d) Is it a liquid, solid or gas at room temperature and atmospheric pressure?

(e) Is it more or less dense than water?

16.54 The following table shows enthalpies of combustion for methane and propane.

Hydrocarbon	Component of	$\Delta_c H^{\ominus}\left(\text{kJ mol}^{-1}\right)$
CH_4	natural gas	-886
$CH_3CH_2CH_3$	LPG	-2220

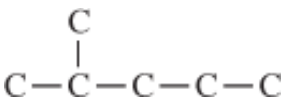
On a gram-for-gram basis, which of these hydrocarbons is the better source of heat energy?

16.55 There are three compounds with the molecular formula $C_2H_2Br_2$. Two of these compounds have a dipole moment greater than zero, and one has no dipole moment (see chapter 5, p. 183). Draw structural formulae for the three compounds, and explain why two have dipole moments but the third one does not.

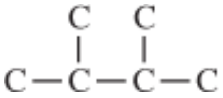
16.56 Name and draw structural formulae for all alkenes with the molecular formula C_5H_{10}. As you draw these alkenes, remember that *cis* and *trans* isomers are different compounds and must be counted separately.

16.57 Name and draw structural formulae for all alkenes with the molecular formula C_6H_{12} that have the following carbon skeletons (count *cis* and *trans* isomers separately).

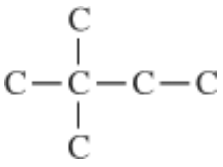
(a)



(b)



(c)



16.58 Draw the structural formula for at least one bromoalkene with the molecular formula C_5H_9Br that:

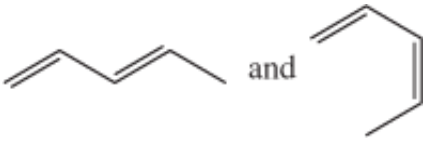
(a) shows *E*,*Z* isomerism

(b) does not show *E*,*Z* isomerism.

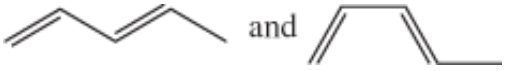
16.59 A triene found in the fragrance of cotton blossoms and several essential oils has the IUPAC name (3 *Z*)-3,7-dimethylocta-1,3,6-triene and the common name β-ocimene. Draw its structural formula.

16.60 Determine whether the structures in each of the following sets represent the same molecule, *cis–trans* isomers or constitutional isomers. If they are the same molecule, determine whether they are in the same or different conformations.

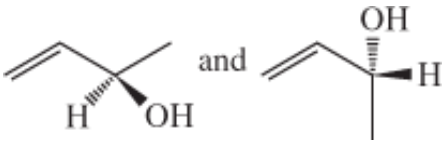
(a)



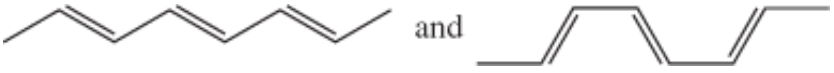
(b)



(c)



(d)



16.61 Which alkyne and which reagent could be used to give each of the following.

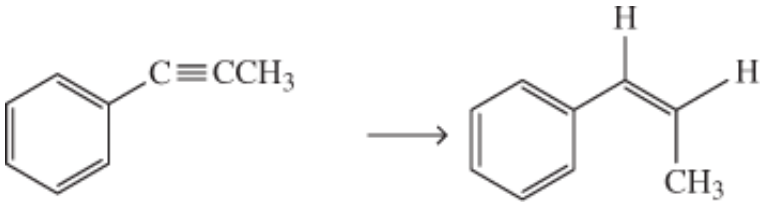
(a) 2,2-dichlorobutane

(b) butan-2-ol

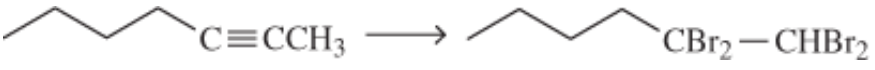
(c) 2,2,3,3-tetrabromobutane

16.62 How would you carry out the following transformations?

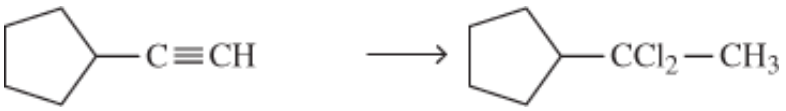
(a)



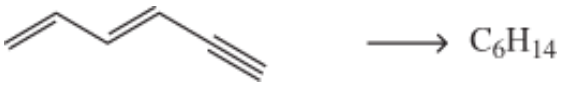
(b)



(c)

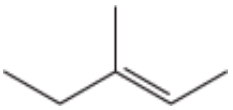


(d)



16.63 Draw structural formulae for the isomeric carbocation intermediates formed by the reaction of each of the following alkenes with HCl. Label each carbocation as primary, secondary or tertiary, and state which, if either, of the isomeric carbocations is formed more readily.

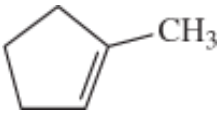
(a)



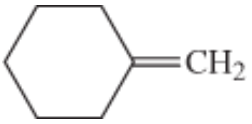
(b)



(c)

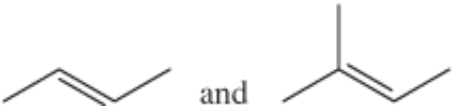


(d)

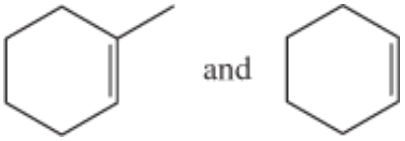


16.64 From each of these pairs of compounds, select the one that reacts more rapidly with HI, draw the structural formula of the major product formed in each case, and explain the basis for your ranking.

(a)

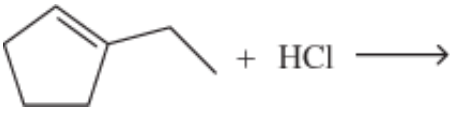


(b)

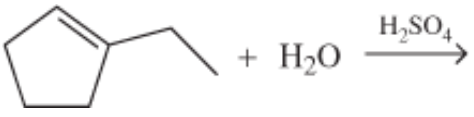


16.65 Complete these equations by predicting the major product formed in each reaction.

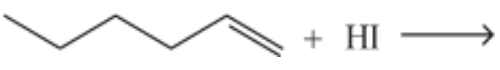
(a)



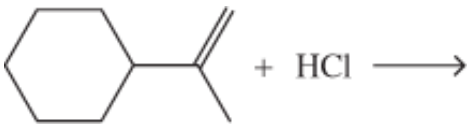
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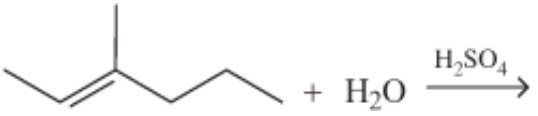
(c)



(d)



(e)



(f)



16.66 The reaction of 2-methylpent-2-ene with each of the following reagents is regioselective. Draw the structural formula for the product of each reaction, and account for the observed regioselectivity.

(a) HI

(b) H_2O in the presence of H_2SO_4

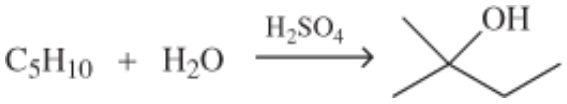
16.67 The addition of bromine and chlorine to cycloalkenes is stereospecific. Predict the stereochemistry of the product formed in each of these reactions.

(a) 1-methylcyclohexene + Br_2

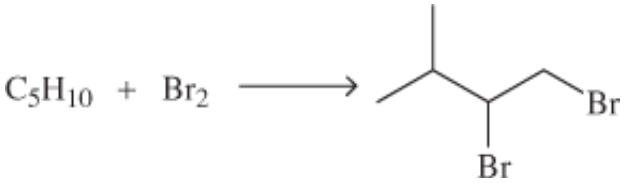
(b) 1,2-dimethylcyclopentene + Cl_2

16.68 In each of the following reactions, draw the structural formula of an alkene with the indicated molecular formula that gives the compound shown as the major product. Note that more than one alkene may give the same compound as the major product.

(a)



(b)

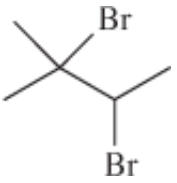


(c)



16.69 Draw the structural formula of an alkene with the molecular formula C_5H_{10} that reacts with Br_2 to give each of these products.

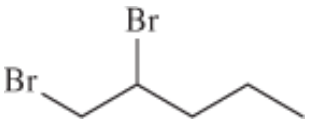
(a)



(b)

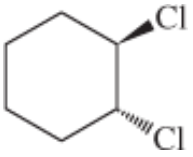


(c)

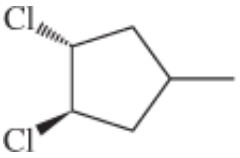


16.70 Draw the structural formula of a cycloalkene with the molecular formula C_6H_{10} that reacts with Cl_2 to give each of these compounds.

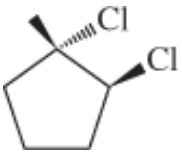
(a)



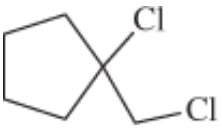
(b)



(c)

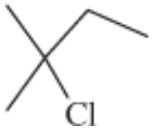


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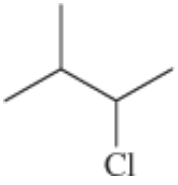


16.71 Draw the structural formula of an alkene with the molecular formula C_5H_{10} that reacts with HCl to give each of the following chloroalkanes as the major product.

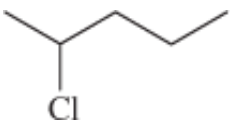
(a)



(b)



(c)



16.72 The compounds *cis*-hex-3-ene and *trans*-hex-3-ene are different and have different physical and chemical properties. Yet, when treated with H_2O/H_2SO_4, each gives the same alcohol. What is the alcohol, and how do you account for the fact that each alkene gives the same one?

16.73 Draw the structural formula of an alkene that undergoes acid-catalysed hydration to give each of the following alcohols as the major product. Note that more than one alkene may give the same compound as the major product.

(a) hexan-3-ol

(b) 1-methylcyclobutanol

(c) 2-methylbutan-2-ol

(d) propan-2-ol

16.74 Draw the structural formula of an alkene that undergoes acid-catalysed hydration to give each of the following alcohols as the major product. Note that more than one alkene may give the same compound as the major product.

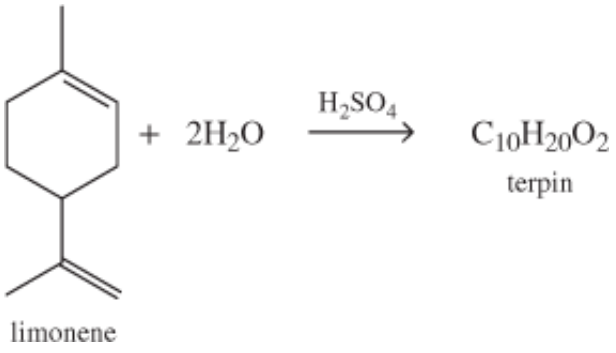
(a) cyclohexanol

(b) 1,2-dimethylcyclopentanol

(c) 1-methylcyclohexanol

(d) 1-isopropyl-4-methylcyclohexanol

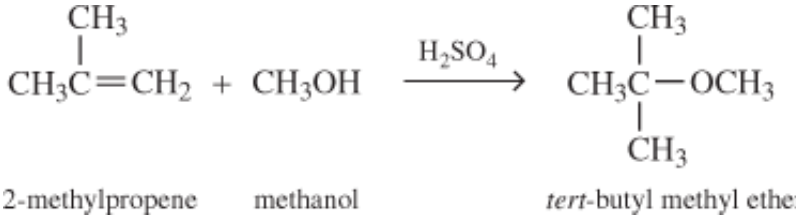
16.75 Terpin is prepared commercially by the acid-catalysed hydration of limonene:



(a) Propose a structural formula for terpin and a mechanism for its formation.

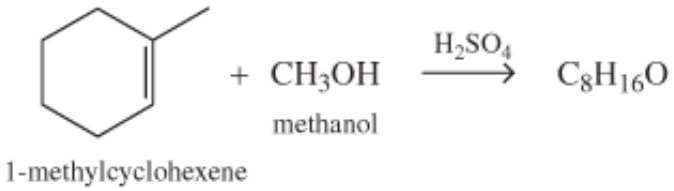
(b) How many *cis*–*trans* isomers are possible for the structural formula you proposed in (a)?

16.76 The treatment of 2-methylpropene with methanol in the presence of a sulfuric acid catalyst gives *tert*-butyl methyl ether:



Propose a thermodynamically sound mechanism for the formation of this ether.

16.77 The treatment of 1-methylcyclohexene with methanol in the presence of a sulfuric acid catalyst gives a compound with the molecular formula $C_8H_{16}O$:



Propose a structural formula for this compound and a mechanism for its formation.

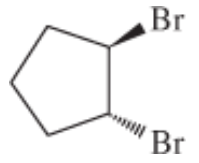
16.78 Hydrocarbon *A*, C_5H_8, reacts with 2 moles of Br_2 to give 1,2,3,4-tetrabromo-2-methylbutane. What is the structure of hydrocarbon *A*?

16.79 Alkenes *A* and *B* both have the formula C_5H_{10}. Both react with H_2/Pt and with HBr to give identical products. What are the structures of *A* and *B*?

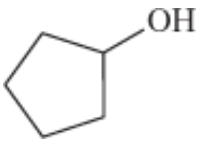
16.80 Show how to convert cyclopentene into these compounds.

(a)

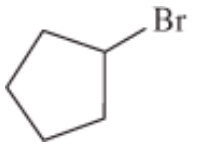
(b)



(c)



(d)





16.81 Show how to convert but-1-ene into these compounds.

(a) butane

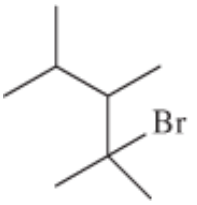
(b) 2-bromobutane

(c) butan-2-ol

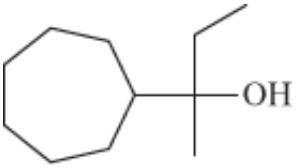
(d) 1,2-dibromobutane

16.82 Show how the following compounds can be synthesised in good yields from an alkene.

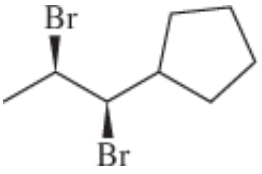
(a)



(b)



(c)



16.83 Show that pyridine can be represented as a hybrid of two equivalent contributing structures.

16.84 Show that naphthalene (pp. 727–8) can be represented as a hybrid of three contributing structures. Show also, by the use of curved arrows, how one contributing structure is related to the next.

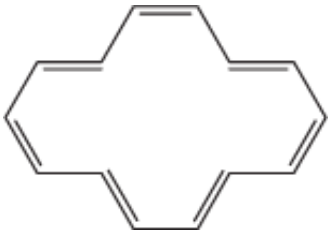
16.85 Draw four contributing structures for anthracene (p. 728).

16.86 Which of the following compounds are aromatic?

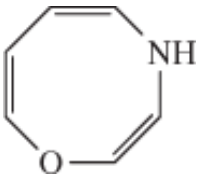
(a)



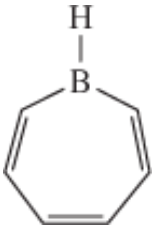
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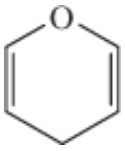
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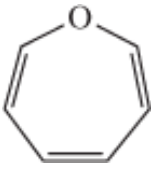
(d)



(e)



(f)



16.87 Explain why cyclopentadiene (pK_a = 16) is many orders of magnitude more acidic than cyclopentane (pK_a > 50) (*Hint:* Draw the structural formula of the anion formed by removing one of the protons on the —CH_2—group, and then apply the Hückel criteria for aromaticity.)



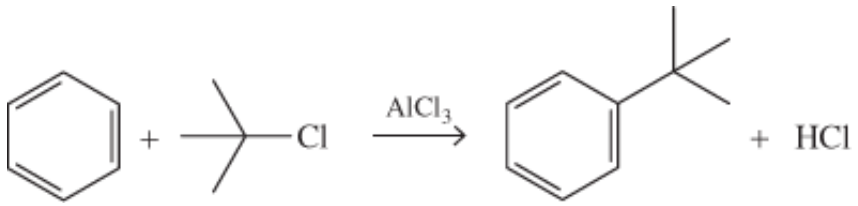
cyclopentadiene



cyclopentane

16.88 How many monochlorination products are possible when naphthalene is treated with $Cl_2/AlCl_3$?

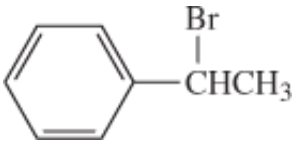
16.89 Write a stepwise mechanism for the following reaction, using curved arrows to show the flow of electrons in each step.



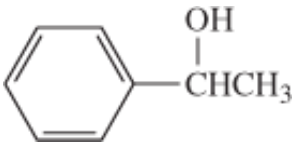
16.90 Write a stepwise mechanism for the preparation of diphenylmethane by treating benzene with dichloromethane in the presence of an aluminium chloride catalyst.

16.91 Using styrene, $C_6H_5CH{=}CH_2$, as the only aromatic starting material, show how to synthesise the following compounds. In addition to styrene, use any other necessary organic or inorganic chemicals. Any compound synthesised in one part of your answer may be used to make any other compound in the answer.

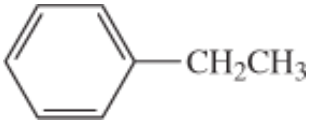
(a)



(b)



(c)



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16.92 Explain why 1,2-dimethylcyclohexane can exist as *cis–trans* isomers, while 1,2-dimethylcyclododecane cannot.

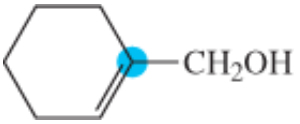
16.93 Each carbon atom in ethane and in ethene is surrounded by eight valence electrons and has four bonds to it. Explain how the valence-shell-electron-pair repulsion (VSEPR) model (section 5.4) predicts a bond angle of 109.5° around each carbon atom in ethane, but an angle of 120° around each carbon atom in ethene.

16.94 Use the valence-shell-electron-pair repulsion (VSEPR) model to predict all bond angles around each of the following highlighted carbon atoms.

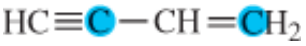
(a)



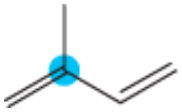
(b)



(c)



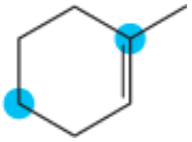
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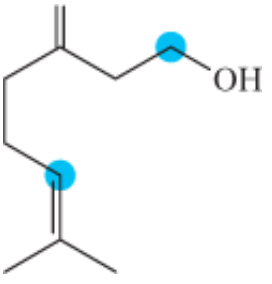
16.95 For each highlighted carbon atom in question 16.94, identify which orbitals are used to form each σ bond and which are used to form each π bond.

16.96 Predict all bond angles around each of the following highlighted carbon atoms.

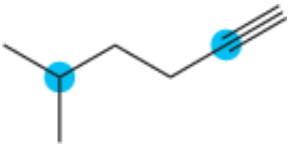
(a)



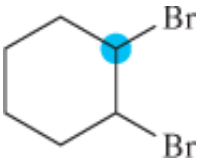
(b)



(c)

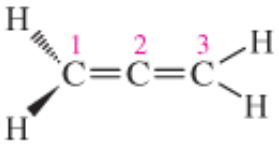


(d)

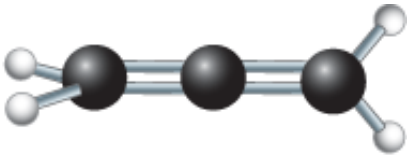


16.97 For each highlighted carbon atom in question 16.96, identify which orbitals are used to form each σ bond and which are used to form each π bond.

16.98 The structure of propa-1,2-diene (allene) is shown below. The plane created by H—C—H of C(1) is perpendicular to that created by H—C—H of C(3).



propa-1,2-diene
(allene)

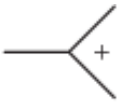


ball-and-stick model

(a) State the orbital hybridisation of each carbon atom in allene.

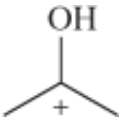
(b) Account for the molecular geometry of allene in terms of the orbital overlap model. Specifically, explain why all four hydrogen atoms are not in the same plane.

16.99 Each of the following secondary carbocations is more stable than the tertiary carbocation shown.

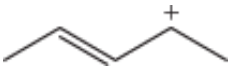


a tertiary carbocation

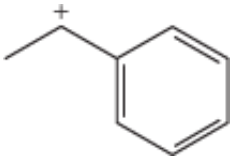
(a)



(b)



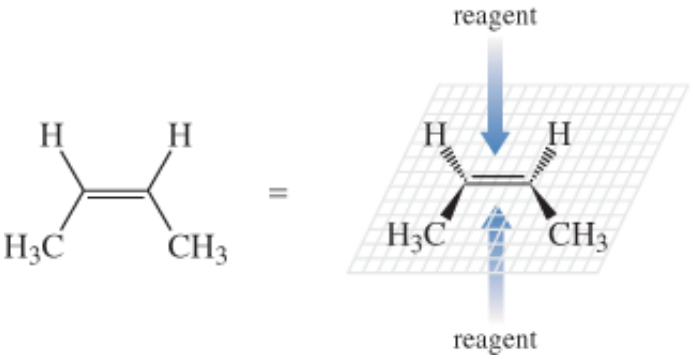
(c)



Explain why each of the carbocations might be more stable than the tertiary carbocation.

16.100 Oleic acid and elaidic acid are, respectively, the *cis* and *trans* isomers of octadec-9-enoic acid. One of these fatty acids, a colourless liquid that solidifies at 4 °C, is a major component of butterfat. The other, a white solid with a melting point of 44–45 °C, is a major component of partially hydrogenated vegetable oils. Which of these two fatty acids is the *cis* isomer and which is the *trans* isomer?

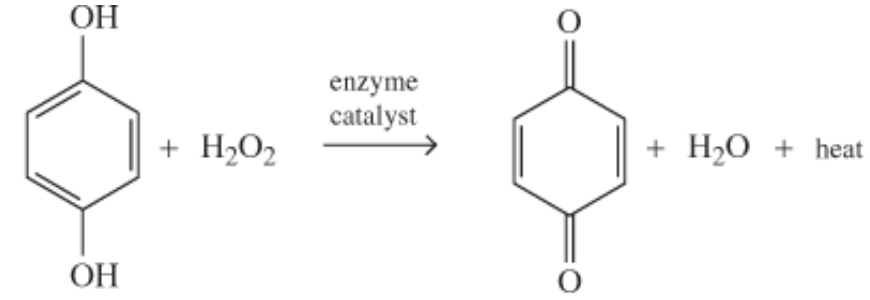
16.101 Recall that an alkene possesses a π cloud of electrons above and below the plane of the C═C bond. Any reagent can, therefore, react with either face of the double bond. Determine whether the reaction of each of the following reagents with the top face of *cis*-but-2-ene will produce the same product as the reaction of the same reagent with the bottom face. (*Hint:* Build molecular models of the products and compare them.)



(a) H_2/Pt

(b) Br_2/CH_2Cl_2

16.102 The bombardier beetle generates *p*-quinone, an irritating chemical, by the enzyme-catalysed oxidation of hydroquinone, using hydrogen peroxide as the oxidising agent. Heat generated in this oxidation produces superheated steam, which is ejected, along with *p*-quinone, with explosive force.



hydroquinone *p*-quinone

(a) Balance the equation.

(b) Is this an oxidation reaction (see chapter 12)?

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KEY TERMS

acylation
addition to the carbon–carbon double bond
aliphatic hydrocarbon
alkane
alkene
alkylation
alkyne
angle strain
aniline
anisole
anti addition
anti selectivity
arene
aromatic
aryl group
axial bonds
benzaldehyde
benzoic acid
benzyl group
boat conformation
bridged halonium ion
carbocation
catalytic hydrogenation
catalytic reduction
chair conformation
cis–trans isomers
configurational isomers
conformation
conformer
cycloalkane
cycloalkene
E,Z system
electrophile
electrophilic aromatic substitution
enthalpy of hydrogenation
equatorial bonds
Friedel–Crafts acylation
Friedel–Crafts alkylation
halonium ion
heterocyclic compound
hybridisation of atomic orbitals
hydration
hydrocarbon
inductive effect
Kekulé structure
Markovnikov's rule
meta
Newman projection
nitronium ion
ortho
oxonium ion
para
phenol
phenyl group
polycyclic aromatic hydrocarbon (PAH)
regioselective reaction
resonance energy
saturated hydrocarbon
stereospecific reaction
steric strain
styrene
syn addition
theory of resonance
toluene
torsional strain
unsaturated hydrocarbon
xylene

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CHAPTER

17 Chirality

The drug thalidomide was developed in the late 1950s to treat morning sickness suffered by some women during pregnancy. Unfortunately, thalidomide can exist in two molecular forms. One form is indeed an effective treatment for morning sickness, but the other form causes terrible birth defects in children whose mothers take the drug during the early stages of pregnancy. The Australian obstetrician Dr William McBride first alerted the world to this link through a letter to the medical journal *The Lancet* in December 1961. It took until 2010, however, before scientists from Japan were able to discover that one form of thalidomide inhibits production of a crucial protein called cereblon, which creates the key enzymes needed for limb development. Each of the two forms of thalidomide has exactly the same atom connectivity — the same atoms connected in the same sequence — but the relative positions of the atoms in space, when viewed in three dimensions, are subtly different. In the case of thalidomide, the two molecular forms are mirror images of each other. Today, pharmaceutical companies are required to prove that both forms of any such drugs are safe for their intended use. Thalidomide, now sold as Thalomid by Celgene Pty Ltd, remains in use today, but now its potent effect on cellular biochemistry is exploited as a last line of defence against some cancers and as a treatment for leprosy and certain skin diseases.

In earlier chapters, we learned about constitutional isomers and how the sequence of connections of the atoms in a molecule influences the properties of the substance. In this chapter, we will learn about molecules that contain the same atoms and the same sequence of connections (atom connectivity) but in which the atoms have different relative positions in space.

These molecules are known as stereoisomers. As we know from thalidomide, these different three-dimensional arrangements can lead to substantial differences in properties.

A sound understanding of stereoisomers is fundamental to our understanding of organic chemistry and biochemistry.



KEY TOPICS

17.1 Stereoisomers
17.2 Enantiomerism
17.3 Naming stereocentres: the *R*, *S* system
17.4 Molecules with more than one stereocentre
17.5 Optical activity: detecting chirality in the laboratory
17.6 Chirality in the biological world
17.7 Synthesising chiral drugs

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17.1 Stereoisomers

In chapter 2 we learned that **isomers** are molecules with the same molecular formula (the same numbers of each type of atom) but different structures. We described how different sequences of atom connectivity lead to molecules with different properties and we call these **constitutional isomers**. For example, butane and 2-methylpropane (isobutane) have the same numbers of carbon atoms (four) and hydrogen atoms (ten), but their carbon atoms are connected in a different sequence. Butane has a linear chain and isobutane has a branch, as shown in figure 17.1. These different sequences can give rise to differences in properties, such as boiling point.

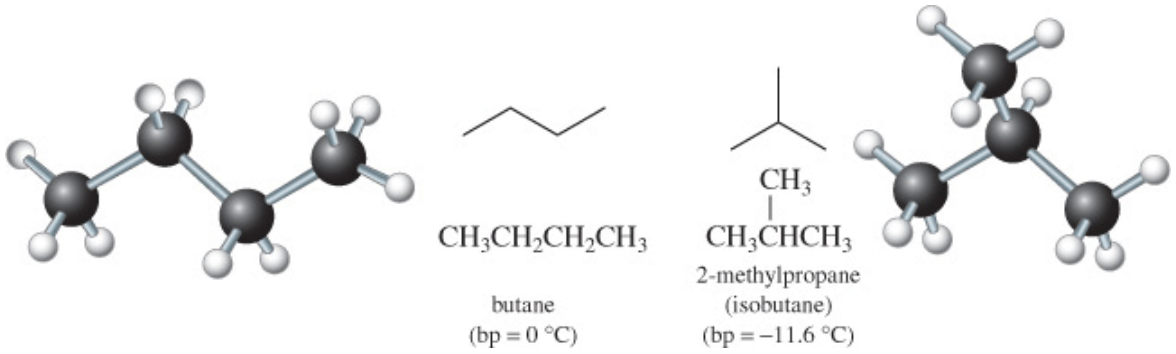


FIGURE 17.1 Butane and isobutane are constitutional isomers. Their different atom connectivity gives them different properties.

Other molecules can contain the same numbers and kinds of atoms, all bonded to each other in the same order, with the only difference between the molecules being that some bonds and, therefore, atoms are arranged differently in space. This can also give them different properties. Such isomers are called **stereoisomers**. There are two types of stereoisomers: enantiomers and diastereomers. Let's describe enantiomers first.

One of the easiest ways to grasp the concept of enantiomers is by looking at our hands. Figure 17.2 shows a left hand, its reflection in a mirror, and a right hand. Notice that the left hand's reflection looks just like the right hand. That is, our left and right hands are mirror images of each other.

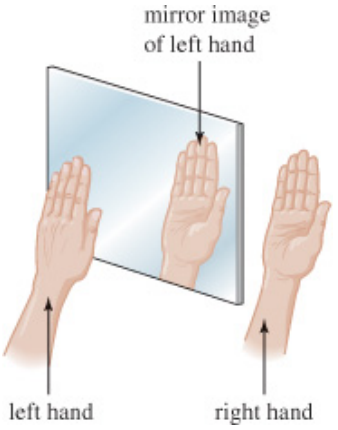


FIGURE 17.2 The left and right hands are nonsuperimposable mirror images of each other. Stereoisomers that are nonsuperimposable mirror images of each other are called enantiomers.

Now look at your own hands. The left hand has four different fingers and a thumb in a particular order, the right hand has four different fingers and a thumb in the same order, but it is quite obvious that your left and right hands are not the same. Superimposability is the ability of two objects to fit ‘one within the other’ with no mismatch of parts. No matter how you move your hands, they are not superimposable. Just try putting a left-handed glove on your right hand (see figure 17.3). Objects that are nonsuperimposable on their mirror images, such as the shells in figure 17.5, are said to be **chiral** (pronounced ki-ral to rhyme with spiral, from the Greek word *cheir* meaning ‘hand’); that is, they show handedness.



FIGURE 17.3 A left-handed glove does not fit; that is, it is not superimposable on the right hand.

Chirality is encountered in three-dimensional objects of all sorts. A spiral binding on a notebook is chiral. A clock-face is also chiral. As you examine the world around you, you will see that many objects are chiral (e.g. a ceiling fan, the thread of a screw, a computer keyboard). Chirality even underpins the workings of things that you cannot see. Modern liquid crystal displays that are found in HD televisions, smartphones (figure 17.4) and computer screens work because the structures of the materials that are present in these displays are arranged in chiral orientations. *Even individual molecules can be chiral.* Such molecules, stereoisomers that cannot be superimposed on their mirror images, are called called **enantiomers**.

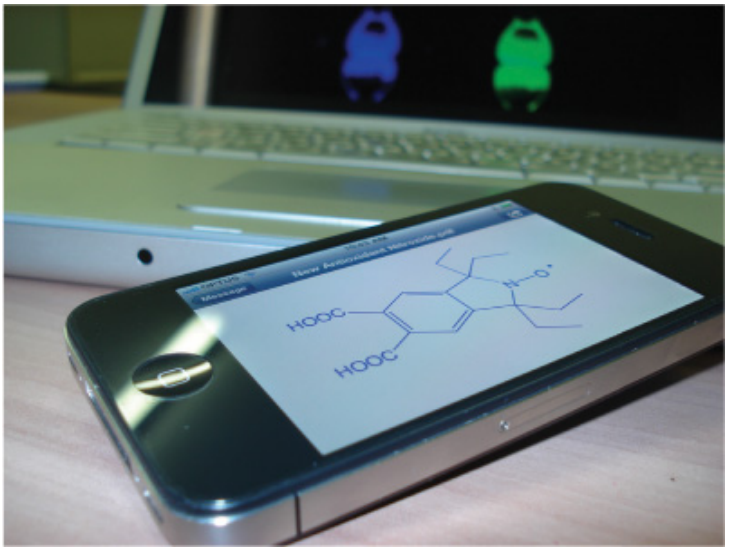


FIGURE 17.4 LCD screens rely on materials that are arranged in chiral orientations.

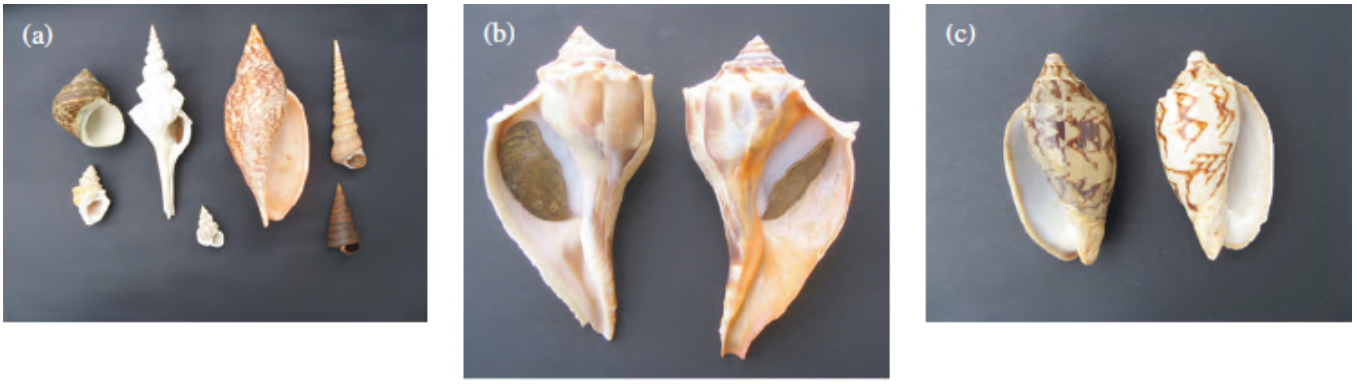


FIGURE 17.5 The next time you are at the beach, keep an eye out for a coiled shell. You will see that the coiling forms a spiral.

(a) Most coiled shells spiral in the same direction; with the shell apex pointing upwards, the shell's opening is to the right, as in these Australian and New Zealand examples. While this is the case for most coiled shells, it is not true for all species;

(b) some occur in both left-handed and right-handed forms.

(c) Interestingly, for some species in which one chiral form predominates, very infrequently examples of the opposite chirality are found; for example, 1 in 10 000 shells from the species *Cymbiola vespertilio* is left-handed.

The two types of molecules present in the drug thalidomide are enantiomers. A simpler example of enantiomers is glucose (β-D-glucopyranose) and its mirror image, as can be seen in figure 17.6.

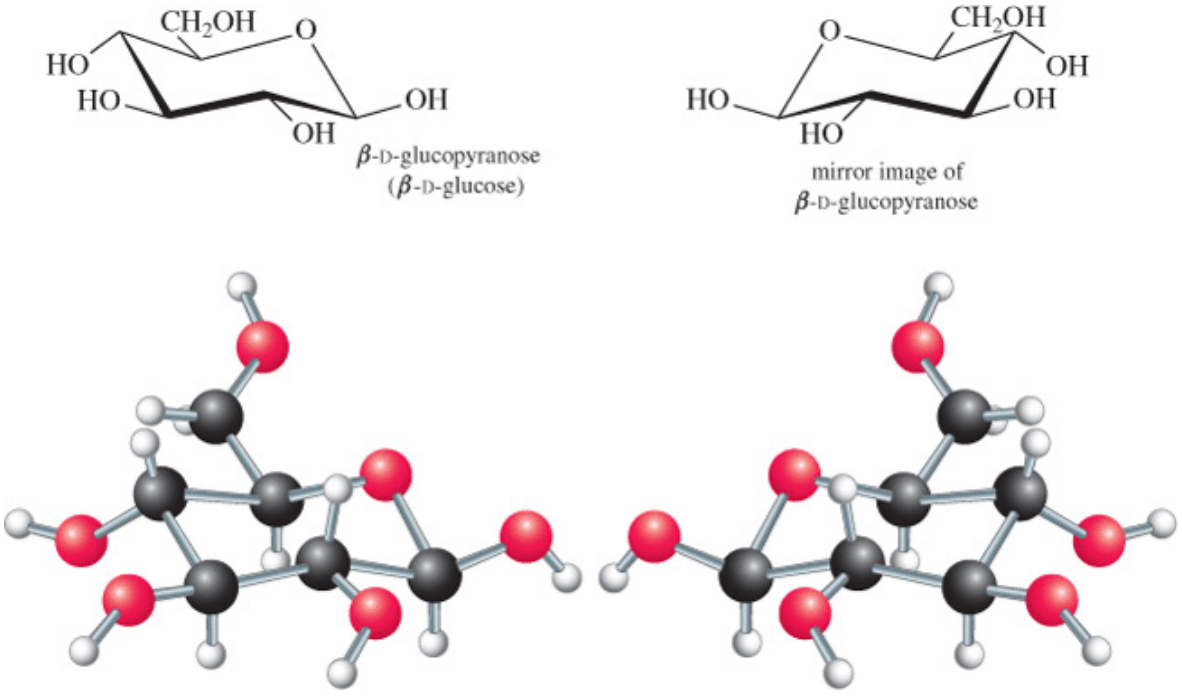


FIGURE 17.6 A pair of enantiomers: β-D-glucopyranose and its nonsuperimposable mirror image.

If our hands were superimposable, we would have two left hands or two right hands. If the mirror images of molecules were superimposable, they would be the same molecule. Objects that have superimposable mirror images are said to be **achiral**. That is, they do not exhibit handedness.

Imagine for a moment that you can make the little finger of your right hand stand at 90° to the other fingers on your right hand (perhaps you can). Hold it next to your left hand. There are still four fingers and a thumb on each hand, connected in the same sequence, but, as shown in figure 17.7, the hands no longer look like mirror images. That is, if you held your left hand to a mirror, its reflection would not look like the right hand in this position.

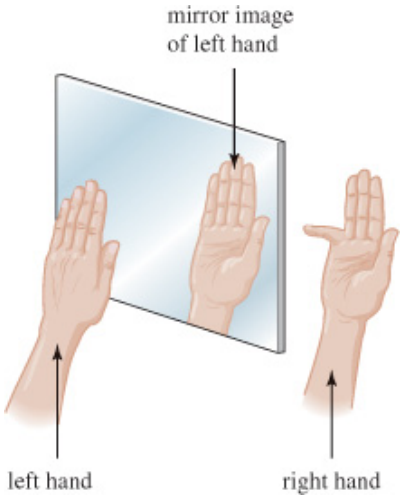


FIGURE 17.7 Provided that you don't move the little finger on your right hand from this position, the left and right hands are no longer mirror images of each other. Stereoisomers that are not mirror images of each other are called diastereomers.

Stereoisomers that are not mirror images of each other are called **diastereomers**. An example of diastereomers that we have already encountered (p. 695) is shown in figure 17.8: *cis–trans* isomers in cycloalkanes. (Remember that the solid wedge represents a bond pointing above the plane of the page and a hashed wedge represents a bond pointing below the plane of the page.) In *cis*-1,2-dimethylcyclopentane, both —CH_3 groups are above the plane of the page. In *trans*-1,2-dimethylcyclopentane, one —CH_3 group is below the plane of the page and one is above the plane of the page.

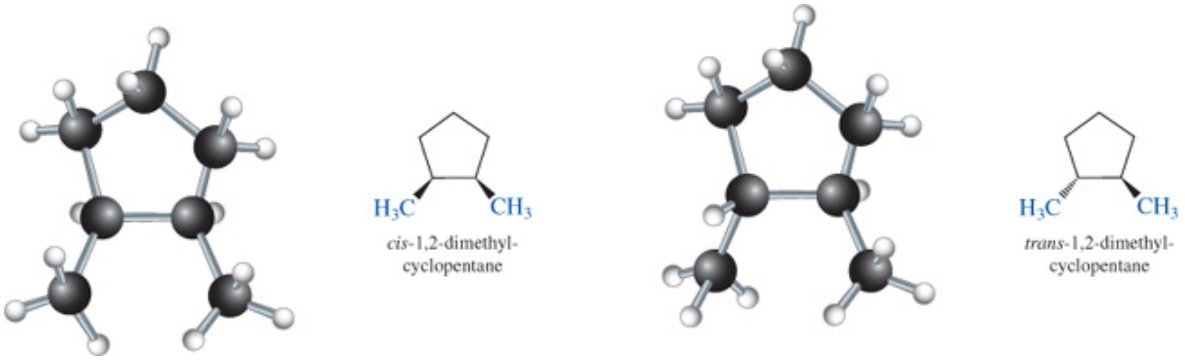


FIGURE 17.8 The *cis–trans* isomers of 1,2-dimethylcyclopentane are a pair of diastereomers. They are stereoisomers, but they are not mirror images and so they are not enantiomers.

The different types of isomers are summarised in figure 17.9. This chapter will focus on enantiomers and, to a lesser extent, on diastereomers. The significance of diastereomers will become clear when carbohydrates are discussed in chapter 22.

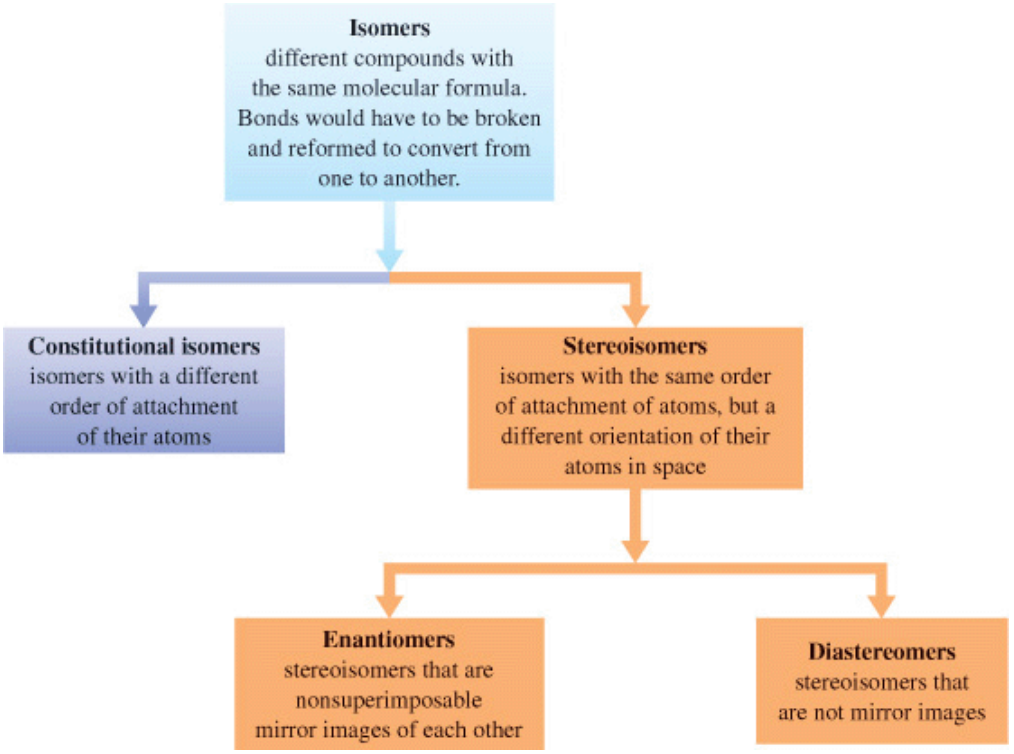


FIGURE 17.9 Relationships among isomers. (*Note:* This description excludes conformers (see p. 688), which can interconvert without breaking bonds.)

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17.2 Enantiomerism

As we have learned above, enantiomers are stereoisomers that are nonsuperimposable mirror images of each other. Except for inorganic compounds and a few simple organic compounds, the vast majority of molecules in the biological world show enantiomerism, including carbohydrates (chapter 22), lipids (chapter 23), amino acids and proteins (chapter 24), and nucleic acids (chapter 25). Further, approximately half of all pharmaceuticals show enantiomerism.

To understand the significance of enantiomerism, recall that enantiomers have some different properties. While they have the same boiling points, melting points and solubilities, each of a pair of enantiomers reacts differently towards other chiral molecules. This is especially important in biology. For example, one form of thalidomide acts in the body to produce a sedative/hypnotic effect that controls the symptoms of morning sickness, whereas the other form acts to produce birth defects.

As the structure of thalidomide is complicated, we will start by looking at a simpler example. In figure 17.10, different atoms are presented as different shapes and colours to help us visualise and mentally manipulate the molecules in three dimensions. In figure 17.10, (a) is an atom with four different groups attached to it. We can use a mirror to produce (b), its mirror image. Imagine that we can lift (b) out of the mirror. No matter how we try to move (b), we cannot superimpose the two molecules. Because they are mirror images and nonsuperimposable, they are enantiomers.

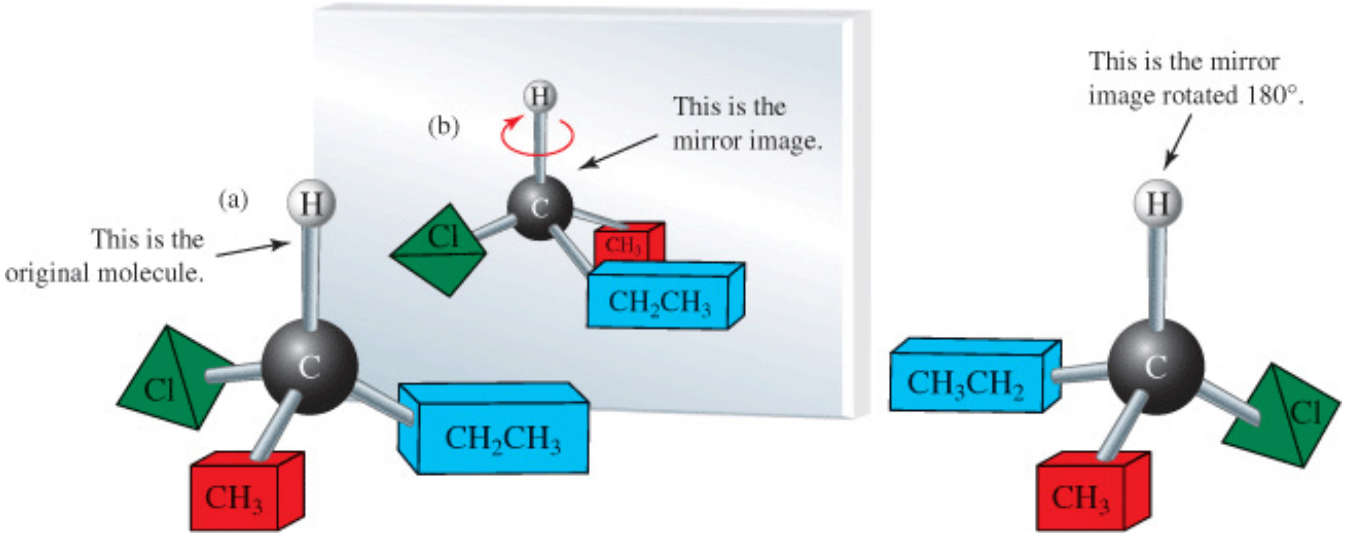
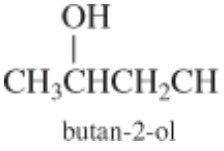


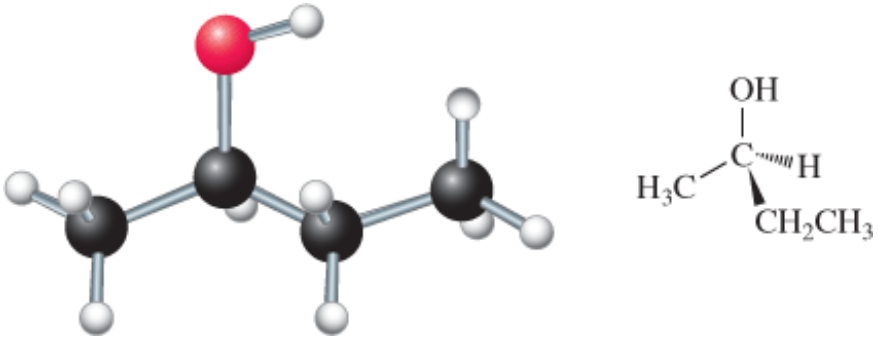
FIGURE 17.10 Enantiomers are mirror images of each other that cannot be superimposed, no matter how we rotate the original molecule and its mirror image.

Now let's look at a real example. The molecule butan-2-ol, a natural by-product of fermentation used as a flavouring agent and as a solvent for paints, has four different groups bonded to a central carbon atom.



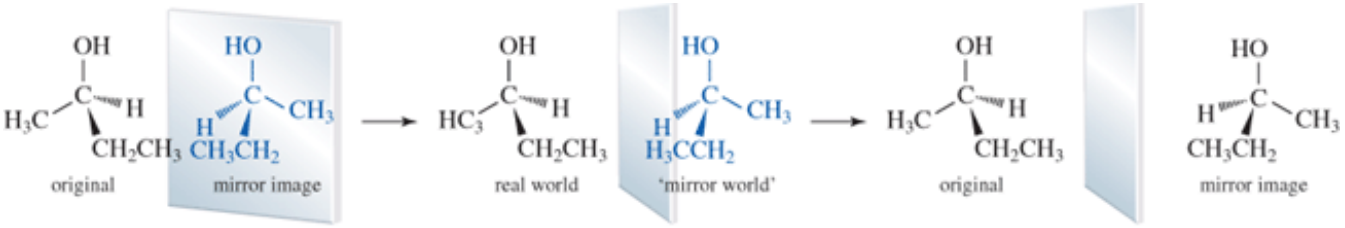
butan-2-ol

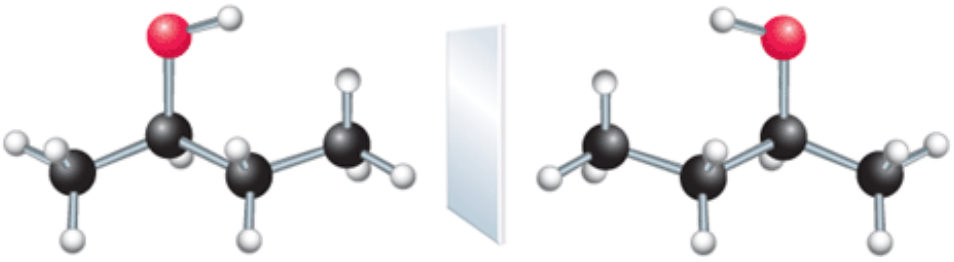
The structural formula above does not show the shape of butan-2-ol or the orientation of its atoms in space. Let's look at the molecule in three dimensions:



On the left is a ball-and-stick model and on the right is how we draw the three-dimensional line structure.

Now let's look at the mirror image of this structure. Imagine if you could somehow look into both the 'mirror world' and the real world. Then you could see both the original molecule and its mirror image as three-dimensional molecules:

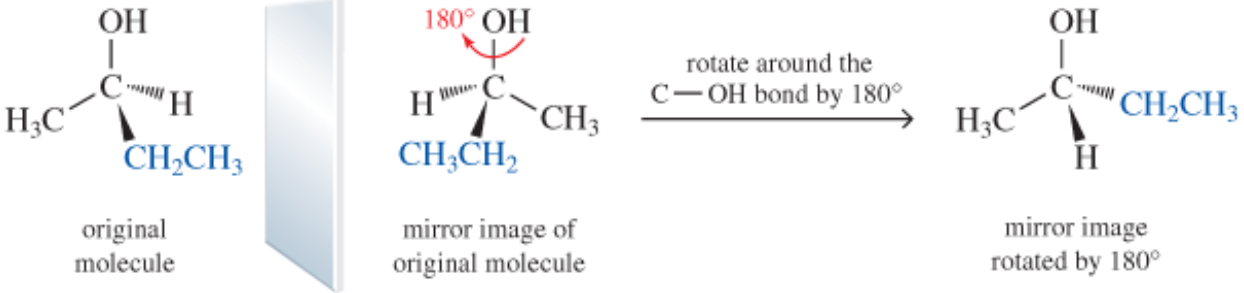




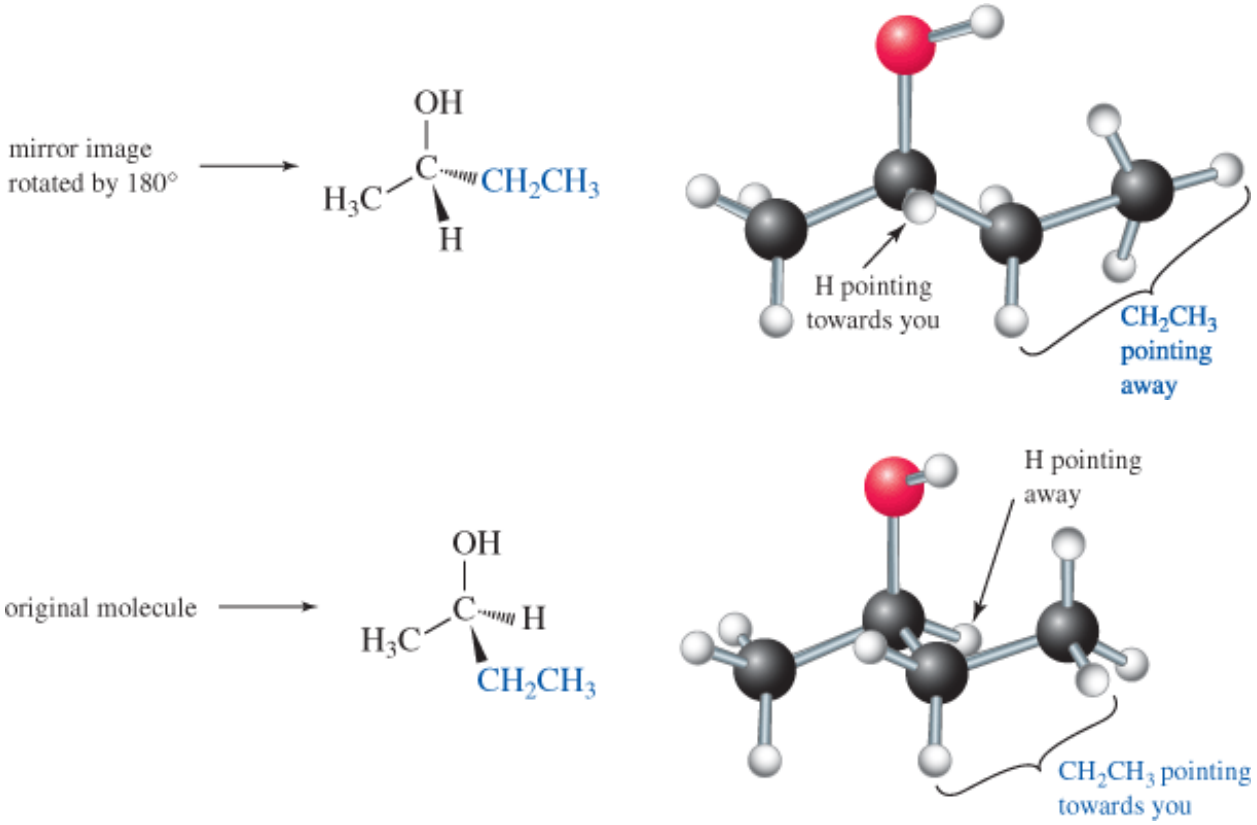
On the left at the bottom of the previous page is what we will call the original molecule. On the right is the mirror image. At first glance, they may look the same: The —OH and —CH_3 groups on C(2) are in the plane of the paper, the —H is behind the plane and the —CH_2CH_3 group is in front of it.

The question is: Are they the same?

Imagine that you can pick up the mirror image and move it in space in any way you wish. If you hold the mirror image by the C—OH bond and rotate the bottom part of the molecule by 180° around this bond as shown below, the —OH group retains its position in space, but the —CH_3 group, the —CH_2CH_3 group and the H atom are now in different orientations.



No matter how you move the mirror image in space, you cannot fit (superimpose) it on the original so that all bonds and atoms match.



No matter which way you orient the molecule, as long as no bonds are broken or rearranged, only two of the four groups bonded to the central carbon atom of the mirror image can be made to coincide with those on the original. The molecules are mirror images *and* nonsuperimposable. Recall that we describe such objects as *chiral* and such molecules as *enantiomers*. Like gloves, each enantiomer always has a partner; enantiomers occur in pairs with one being the reflection of the other.

Not all mirror images of molecules are different. If we can move the mirror image in space and find that it fits over the original so that every bond, atom and detail of the mirror image exactly matches the bonds, atoms and details of the original, then the two are *superimposable*. This is shown in figure 17.11: (a) is an atom with four groups attached to it, and we can use a mirror to produce (b), its mirror image. Imagine that we can lift (b) out of the mirror. We can see that we can indeed superimpose the two molecules. In this case, the mirror image and the original represent the same molecule.

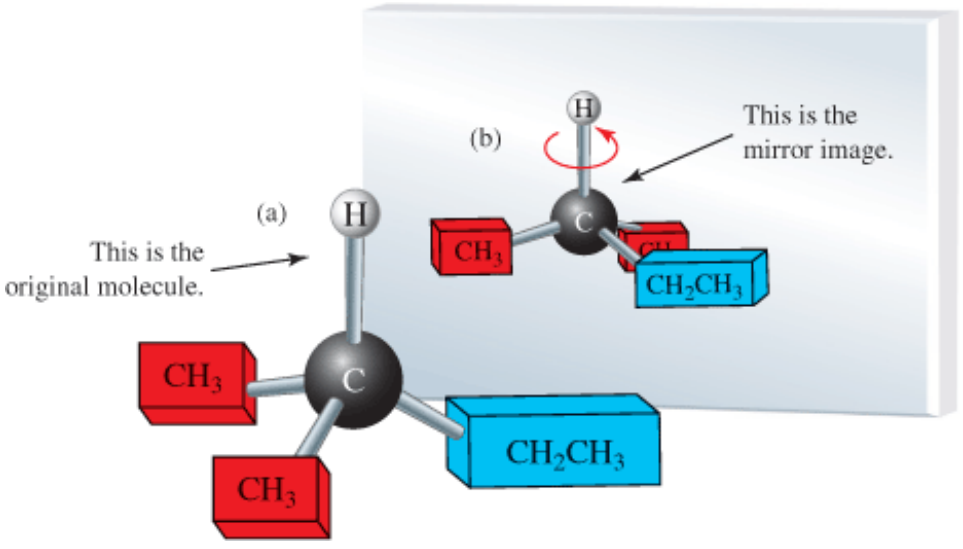
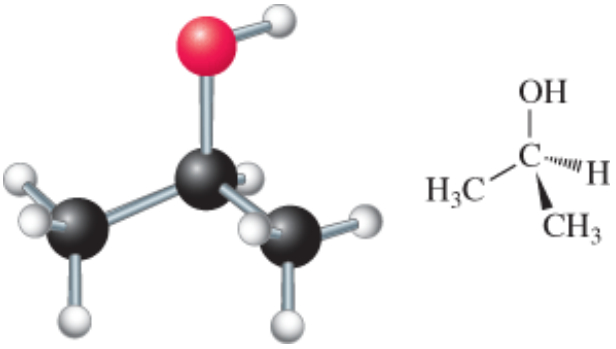
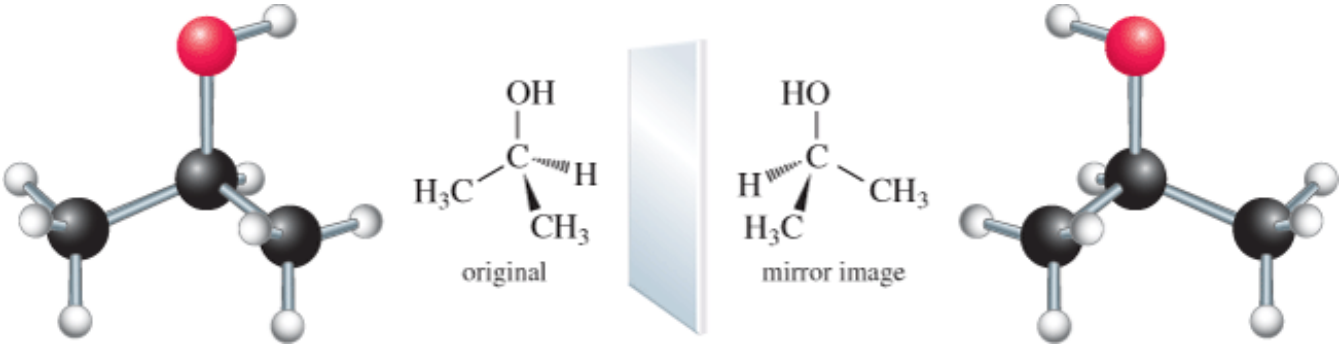


FIGURE 17.11 Superimposable mirror images are exactly the same molecule.

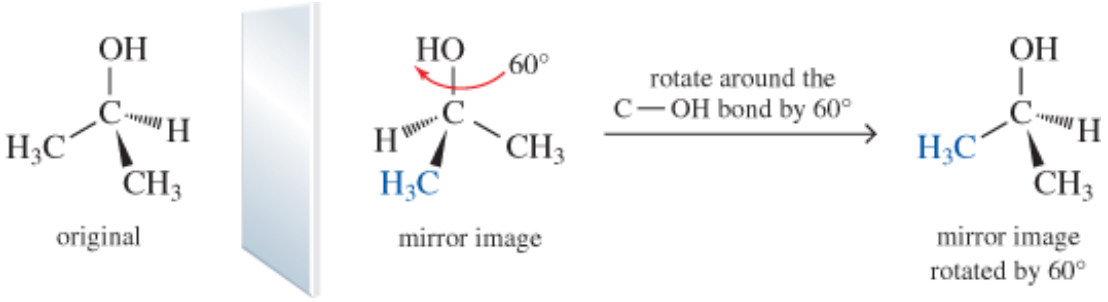
Let's consider a molecule such as propan-2-ol, which has a central carbon atom bonded to four groups, two of which are the same, a —CH_3 group:



The following diagram shows a three-dimensional representation of propan-2-ol on the left and its mirror image on the right:



As we can see below, the mirror image of this molecule is superimposable on the original.



If a molecule and its mirror image are superimposable, then the molecule and its mirror image are identical, and there is no possibility of enantiomerism. Recall that we describe such a molecule as *achiral* (without chirality). It does not have left-hand and right-hand versions.

Any achiral object generally has at least one **plane of symmetry**. A plane of symmetry (also called a *mirror plane*) is an imaginary plane passing through an object and dividing it so that one half of the object is the

reflection of the other half. The beaker shown in figure 17.12 has a single plane of symmetry, whereas a cube (figure 17.12b) has several planes of symmetry. An example of a molecule with a single plane of symmetry is propan-2-ol (figure 17.12c).

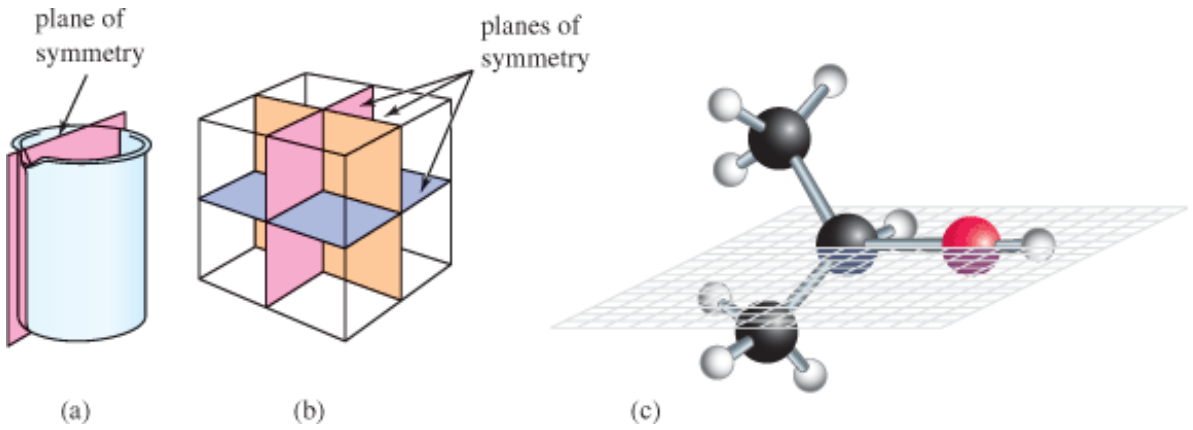
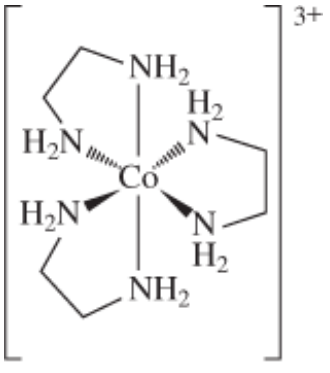


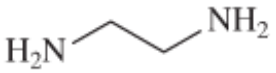
FIGURE 17.12 Planes of symmetry in
(a) a beaker,
(b) a cube and
(c) propan-2-ol. The beaker and propan-2-ol each has one plane of symmetry; the cube has several planes of symmetry, only three of which are shown in the figure (the diagonals form the other planes of symmetry).

Stereocentres

The most common basis for enantiomerism in organic molecules is the presence of a carbon atom bonded to four different groups. Such a carbon atom is an example of a **stereocentre**. A stereocentre is the part of a molecule that can be assembled in two different ways to form stereoisomers.

Inorganic molecules can also exhibit enantiomerism. Whereas the majority of examples of enantiomers in organic chemistry are based on a carbon atom bonded to four different groups, a metal atom is often the stereocentre in inorganic enantiomers. Inorganic enantiomers exhibit a wide variety of geometries. A classic example of a coordination complex (see chapter 13) that can exist as enantiomers is the golden-yellow $[Co(en)_3]^{3+}$ ion (figure 17.13).





ethylenediamine

FIGURE 17.13 The structures of $[Co(en)_3]^{3+}$ and ethylenediamine, or ethane-1,2-diamine (en).

$[Co(en)_3]^{3+}$ comprises a central 6-coordinate Co^{3+} ion bound to three bidentate ethylenediamine ligands. Ethylenediamine, which is also known more correctly as ethane-1,2-diamine, is given the abbreviation 'en'. Here the stereocentre is the central cobalt atom, with the enantiomers arising from the two different ways in which the three ligands are arranged around it (figure 17.14). (Notice that the bidentate ethylene diamine ligand itself is achiral.)

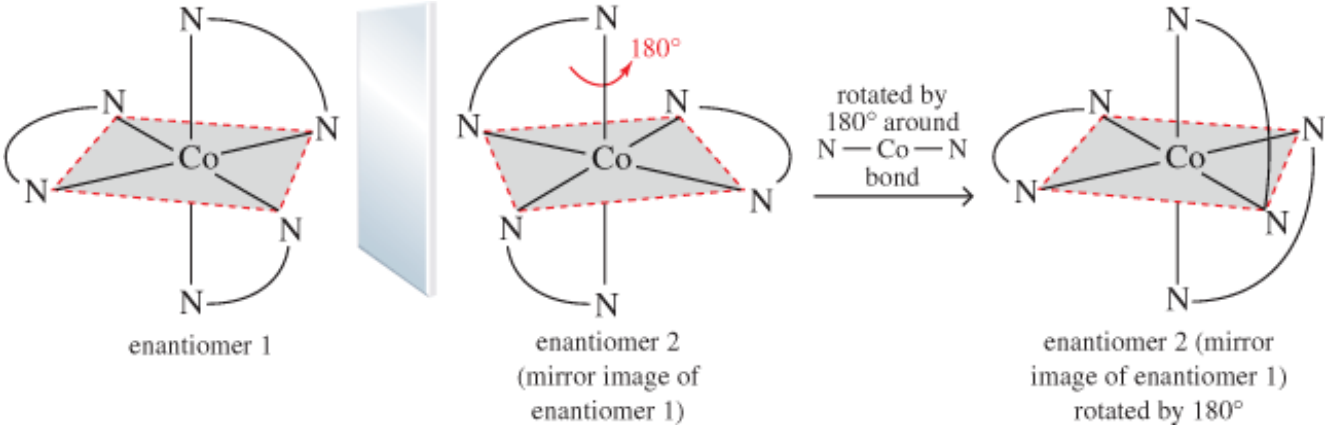


FIGURE 17.14 The two enantiomers of $[Co(en)_3]^{3+}$. Enantiomer 2 is constructed as the mirror image of enantiomer 1. No matter how enantiomer 2 is turned, it is not superimposable on enantiomer 1.

Similarly, enantiomers can exist for complexes that contain only two en ligands, such as *cis*-$[Co(en)_2Cl_2]^+$ (figure 17.15).

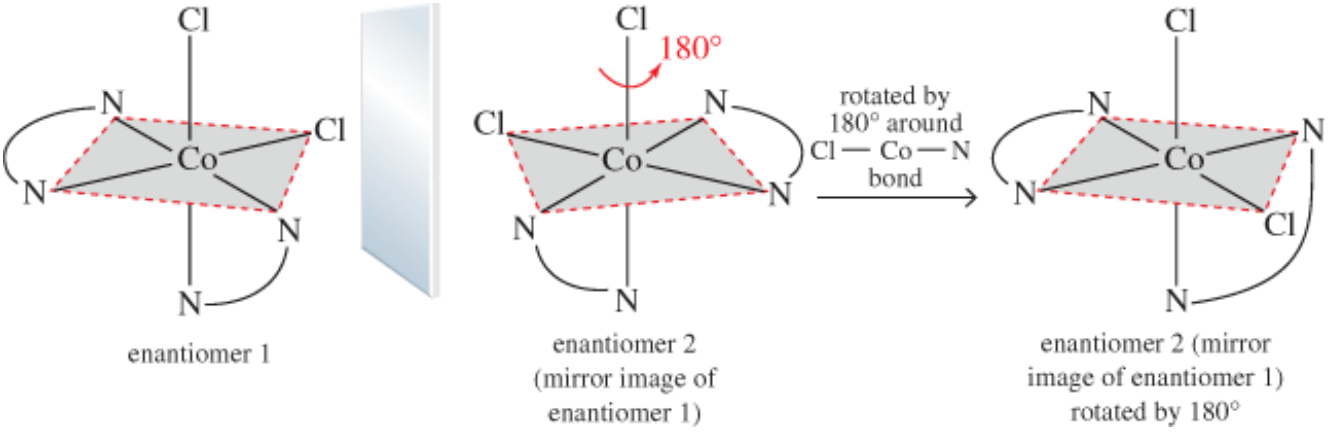


FIGURE 17.15 Isomers of the $[Co(en)Cl_2]^+$ ion. The mirror image of the *trans* isomer (not shown) can be superimposed exactly on the original, so the *trans* isomer is not chiral. However, the *cis* isomer (enantiomer 1) is chiral because its mirror image (enantiomer 2) cannot be superimposed on the original.

Enantiomers can also exist for complexes containing one en ligand; an example of this is *cis*-$[Co(en)(NH_3)_2Cl_2]^+$.

Representing Enantiomers of Complicated Organic Molecules

It is important that we can clearly represent the three-dimensional structures of enantiomers on a two-dimensional page. This is relatively straightforward for simple molecules such as those we have already encountered in this chapter, but it becomes more challenging for complicated molecules.

In our initial discussions of butan-2-ol, we used the representation in figure 17.16a to show the tetrahedral geometry of the central carbon atom (the stereocentre); in it, two groups (—CH_3 and —OH) are in the plane of the paper, one (—CH_2CH_3) is coming out of the plane towards us, and one (—H) is behind the plane, away from us.

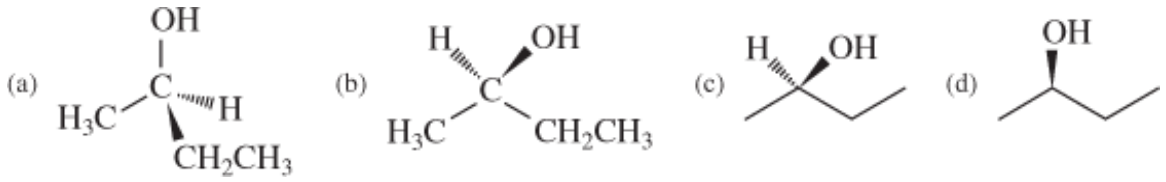
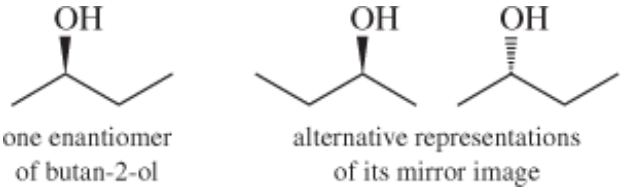


FIGURE 17.16 Four representations of one enantiomer of butan-2-ol.

In figure 17.16, we can turn (a) slightly in space and tip it a bit to place the carbon frame-work in the plane of the paper. Doing so gives us representation (b), in which we still have two groups in the plane of the paper (—CH_3 and —CH_2CH_3), one coming towards us (—OH) and one going away from us (—H). For an even more abbreviated representation of this enantiomer of butan-2-ol, we can turn (b) into the line structure (c). Although we don't normally show hydrogen atoms in a line structure, we do in (c) just to remind ourselves that the fourth group on this stereocentre is really there and that it is —H. Finally, we can carry the abbreviation a step further and write butan-2-ol as (d). Here, we omit the —H on the stereocentre, but we know that it must be there (carbon needs four bonds), and we know that it must be behind the plane of the paper. Clearly, the abbreviated representations (c) and (d) are the easiest to draw, especially for very complicated structures, and we will tend to rely on these abbreviated representations throughout the remainder of the text.

When you have to write three-dimensional representations of stereocentres, try to keep the carbon framework in the plane of the paper and the other two atoms or groups of atoms on the stereocentre towards and away from you, respectively. Using representation (d) as a model, we get the following two different representations of its enantiomer:



Notice that the right-hand structure is the middle structure rotated horizontally by 180°.

When drawing the enantiomeric pairs of more complicated structures, you may find it useful to ‘map’ a molecule's image across an imaginary mirror, which we can represent by a vertical line. If the mirror ‘reflection’ is not superimposable, it is a different molecule (an enantiomer). Figure 17.17 shows this technique for 4-methylcyclopent-2-enone.

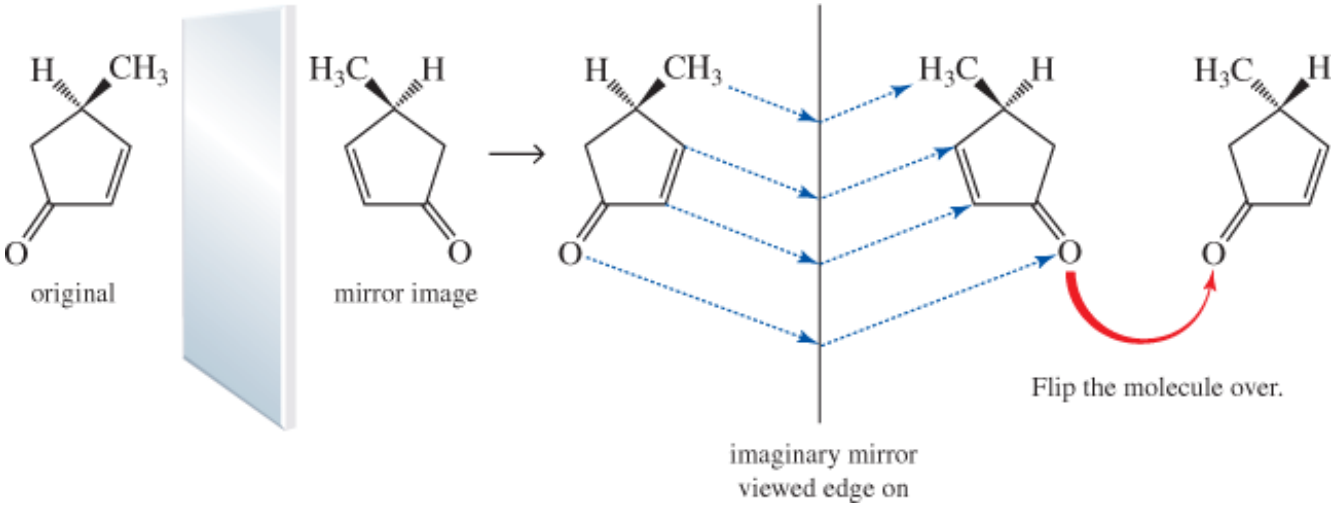


FIGURE 17.17 An imaginary mirror can be used to map a molecule's mirror image: in this case, 4-methylcyclopent-2-enone.

Rotating the mirror image by 180° brings the double bond in the ring into alignment with the molecule on the left. However, notice that, in the molecule on the left of the mirror, the methyl group sits above the plane of the page whereas it lies beneath in the rotated molecule on the right of the mirror. Similarly, the hydrogen atom, which is below the plane of the page in the molecule on the left of the mirror is above the plane in the rotated mirror image.

The reason we need a simplified way of drawing three-dimensional structures becomes apparent when we have to represent very complicated organic molecules such as Taxol® (figure 17.18).

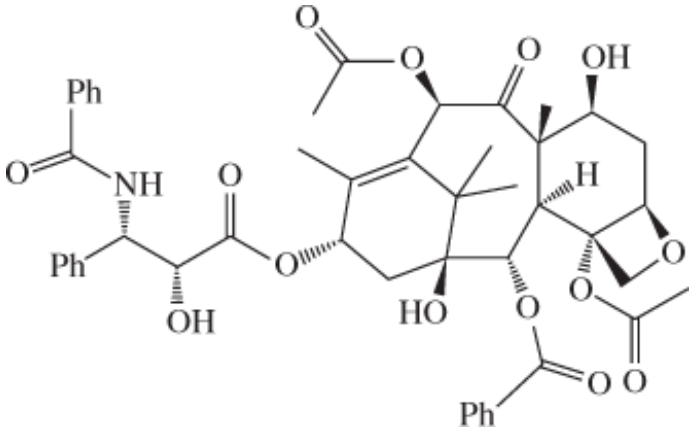


FIGURE 17.18 Structure of the important anticancer drug Taxol® showing the many stereocentres present in this complicated molecule.

WORKED EXAMPLE 17.1

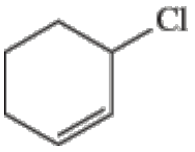
Drawing Stereoisomers

Each of the following molecules has one stereocentre.

(a)



(b)

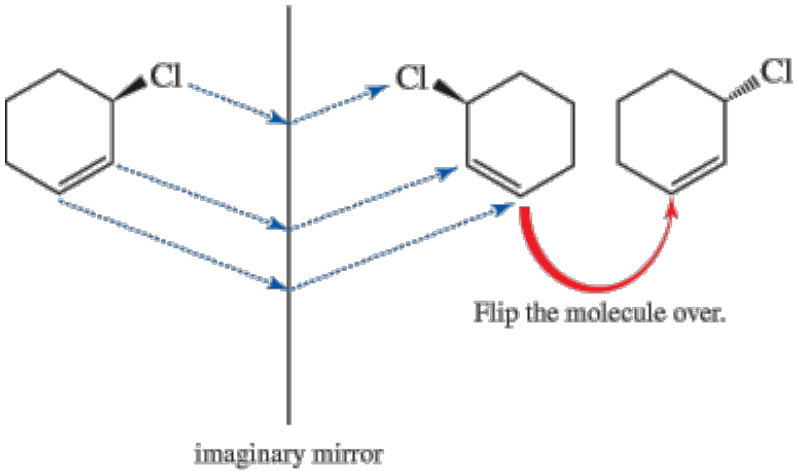


Draw three-dimensional representations of the enantiomers of each of these molecules.

Analysis

You will find it helpful to study the models of each pair of enantiomers and to view them from different perspectives. As you work with these models, notice that each enantiomer has a carbon atom bonded to four different groups, which makes the molecule chiral.

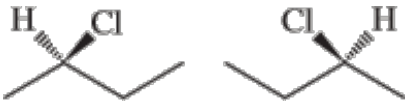
You may find it helpful to use the mapping process to represent the enantiomers involved. For (b), this process gives:



Solution

The hydrogen atom at the stereocentre is shown in (a), but not in (b).

(a)



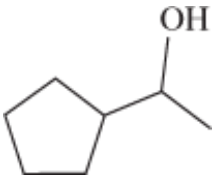
(b)



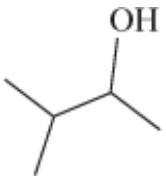
PRACTICE EXERCISE 17.1

Each of the following molecules has one stereocentre.

(a)



(b)

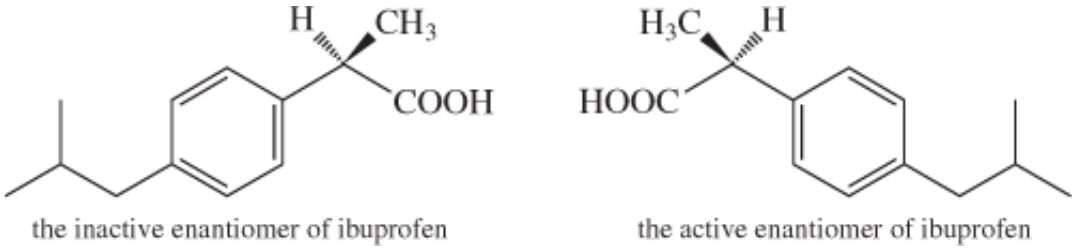


Draw three-dimensional representations of the enantiomers of each of these molecules.

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17.3 Naming Stereocentres: The *R,S* System

Because enantiomers are different compounds, each must have a different name. The over-the-counter drug ibuprofen (an analgesic sold under various names including Nurofen®, figure 17.19), for example, shows enantiomerism and can exist as the following pair of enantiomers:



the inactive enantiomer of ibuprofen

the active enantiomer of ibuprofen



FIGURE 17.19 Ibuprofen is a commonly used analgesic.

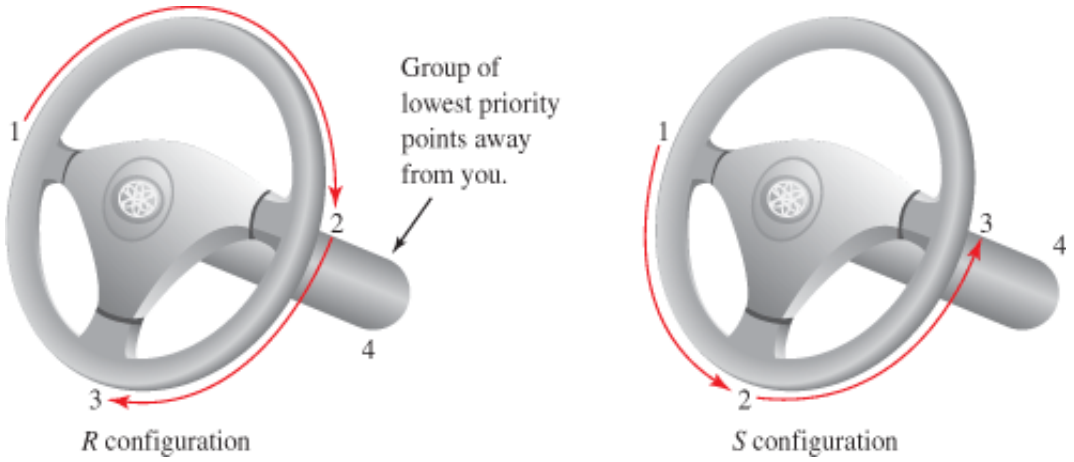
Only one enantiomer of ibuprofen has a therapeutic effect. This enantiomer reaches effective concentrations in the human body in approximately 12 minutes. However, in this case, the inactive enantiomer is not wasted. The body slowly converts it to the active enantiomer.

We need to be able to assign a unique name to each enantiomer of ibuprofen (or any other pair of enantiomers, for that matter). To do this, chemists have developed the *R,S* system for organic molecules. The **R, S system** is a set of rules for specifying the configuration around a stereocentre. This can be an *R* configuration or an *S* configuration. The first step in assigning an *R* or *S* configuration is to arrange the groups bonded to the stereocentre in *order of priority*. For this, we use the same set of priority rules we used in section 16.3 to assign an *E,Z* configuration to an alkene.

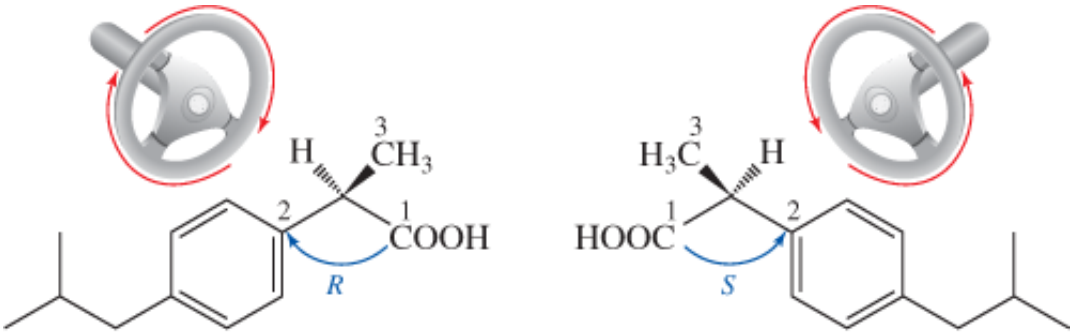
To assign an *R* or *S* configuration:

1. Locate the stereocentre, identify its four substituents, and assign a priority from 1 (highest) to 4 (lowest) to each substituent (as described in section 16.3).
2. Orient the molecule in space so that the group of lowest priority (4) is directed away from you, as the steering column of a car would be. The three groups of higher priority (1–3) then project towards you, as the spokes of a steering wheel would.
3. Read the three groups projecting towards you in order, from highest priority (1) to lowest priority (3).

4. If reading the groups proceeds in a clockwise direction, the configuration is designated **R** (from the Latin word *rectus* meaning 'straight' or 'correct'); if reading proceeds in an anticlockwise direction, the configuration is **S** (from the Latin word *sinister* meaning 'left'). You can also visualise this situation as follows: Turning the steering wheel to the right equals *R*, and turning it to the left equals *S*.



Now let us assign *R* and *S* configurations to our three-dimensional drawings of the enantiomers of ibuprofen. In order of decreasing priority, the groups bonded to the stereocentre are —COOH > —C_6H_4 > —CH_3 > —H. In the enantiomer below on the left, the sequence of groups on the stereocentre in order of priority occurs clockwise. Therefore, this enantiomer is (*R*)-ibuprofen, and its mirror image is (*S*)-ibuprofen:



(*R*)-ibuprofen
(the inactive enantiomer)

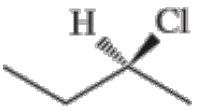
(*S*)-ibuprofen
(the active enantiomer)

WORKED EXAMPLE 17.2

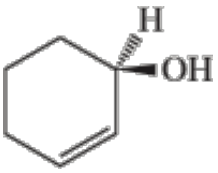
Using the *R,S* System

Assign an *R* or *S* configuration to the stereocentres in the following molecules.

(a)



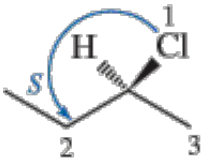
(b)

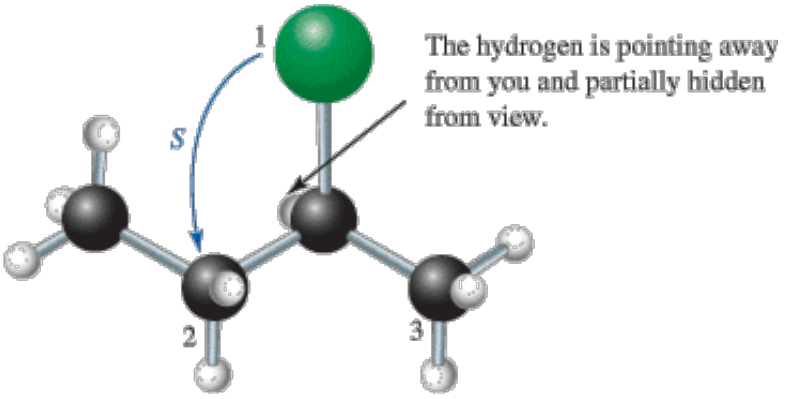


Analysis and solution

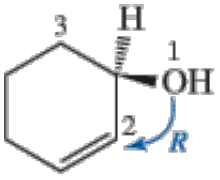
View each molecule through the stereocentre and along the bond from the stereocentre towards the group of lowest priority.

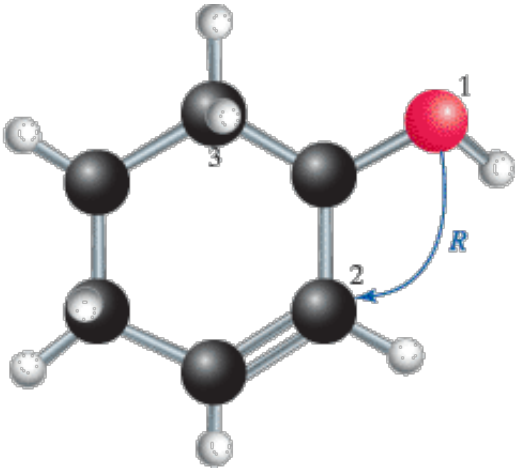
(a) The order of priority is —Cl > —CH_2CH_3 > —CH_3 > —H. The group of lowest priority, H, points away from you. Reading the groups in the order 1, 2, 3 occurs in an anticlockwise direction, so the configuration is *S*.





(b) The order of priority is —OH > —CH═CH > —CH_2—CH_2 > —H. With hydrogen, the group of lowest priority, pointing away from you, reading the groups in the order 1, 2, 3 occurs in a clockwise direction, so the configuration is *R*.

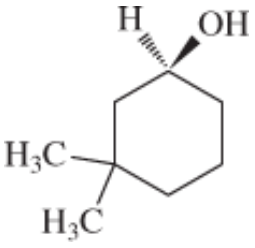




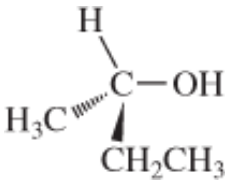
PRACTICE EXERCISE 17.2

Assign an *R* or *S* configuration to each of the following stereocentres.

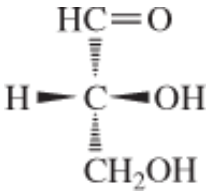
(a)



(b)



(c)



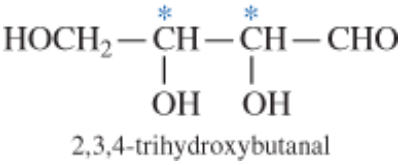
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17.4 Molecules with More Than One Stereocentre

We have now seen several examples of molecules with one stereocentre and verified that, for each, two stereoisomers (one pair of enantiomers) are possible. Now let us consider molecules with multiple stereo centres. To generalise, for a molecule with *n* stereocentres, the maximum possible number of stereoisomers is 2^n. We know that, for a molecule with one stereocentre, $2^1 = 2$ stereoisomers are possible. For a molecule with two stereocentres, $2^2 = 4$ stereoisomers are possible; for a molecule with three stereocentres, $2^3 = 8$ stereoisomers are possible, and so on. However, it should be noted that sometimes the maximum number of stereoisomers is not possible, as we will see on p. 758 for *meso* compounds.

Acyclic Molecules with Two Stereocentres

We begin our study of acyclic molecules with two stereocentres by considering 2,3,4-trihydroxybutanal. This aldehyde comprises a linear sequence of four carbon atoms and has two stereo-centres: that is, two carbon atoms with four different groups attached. The two stereocentres, at C(2) and C(3), are marked with asterisks:



2,3,4-trihydroxybutanal

The maximum number of stereoisomers possible for this molecule is $2^n = 2^2 = 4$, each of which is drawn in figure 17.20. Each of these molecules has a unique name, and we use the *R*,*S* system to assign a configuration around each of the stereocentres, C(2) and C(3). We use a special notation to describe these configurations. For example, 2*R* (see figure 17.20).

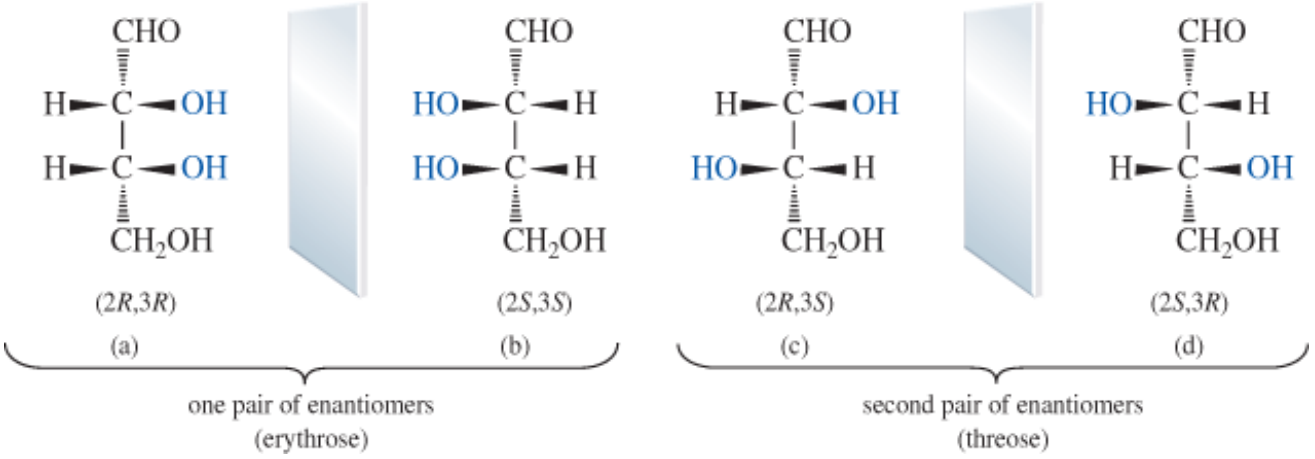


FIGURE 17.20 The four stereoisomers of 2,3,4-trihydroxybutanal, a compound with two stereocentres.

Stereoisomers (a) and (b) are nonsuperimposable mirror images and are, therefore, a pair of enantiomers. Stereoisomers (c) and (d) are also nonsuperimposable mirror images and represent a second pair of enantiomers. We describe the four stereoisomers of 2,3,4-trihydroxybutanal by saying that they consist of two pairs of enantiomers. Enantiomers (a) and (b) are named erythrose, which is synthesised in erythrocytes (red blood cells) — hence the name. Enantiomers (c) and (d) are named threose. Erythrose and threose belong to the class of compounds called carbohydrates.

We also need to define the relationship between (a) and (c). They are stereoisomers but are not mirror images of each other. As you will recall from p. 747, we call stereoisomers of this type diastereomers. Similarly, (a) and (d), (b) and (c), and (b) and (d) are pairs of diastereomers. *Diastereomers are stereoisomers that are not enantiomers; that is, they are stereoisomers that are not mirror images of each*

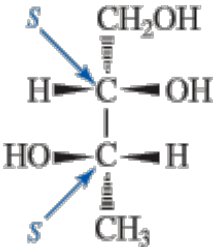
other. Like enantiomers, diastereomers have the same sequence of connection. However, while enantiomers have mostly the same physical properties (melting point, boiling point, density etc.), diastereomers can have completely different properties. This is very evident with carbohydrates, which we will talk about in chapter 22.

WORKED EXAMPLE 17.3

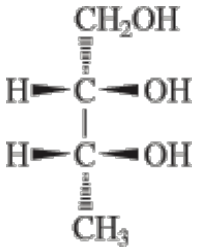
Enantiomers and Diastereomers

The following are stereorepresentations of the four stereoisomers of butane-1,2,3-triol.

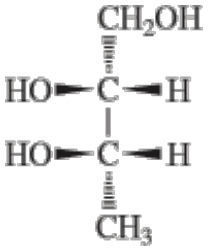
i.



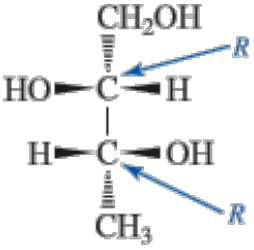
ii.



iii.



iv.



Configurations are given for the stereocentres in (i) and (iv).

(a) Which pairs of compounds are enantiomers?

(b) Which pairs of compounds are diastereomers?

Analysis and solution

(a) Enantiomers are stereoisomers that are nonsuperimposable mirror images. Compounds (i) and (iv) are one pair of enantiomers, and compounds (ii) and (iii) are a second pair of enantiomers. Note that the configurations of the stereocentres in (i) are the opposite of

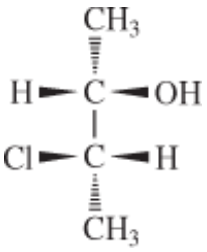
those in (iv), its enantiomer.

(b) Diastereomers are stereoisomers that are not mirror images. Compounds (i) and (ii), (i) and (iii), (ii) and (iv), and (iii) and (iv) are diastereomers.

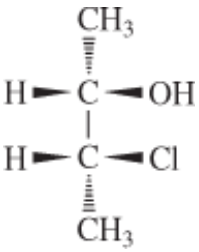
PRACTICE EXERCISE 17.3

The following are stereorepresentations of the four stereoisomers of 3-chlorobutan-2-ol.

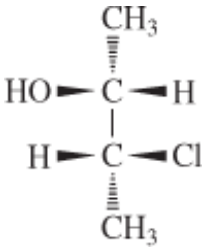
i.



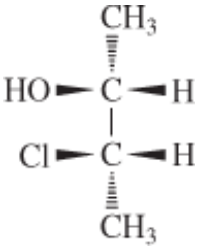
ii.



iii.



iv.



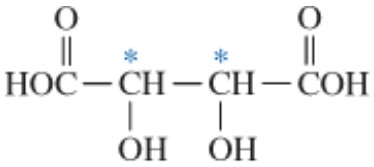
(a) Which pairs of compounds are enantiomers?

(b) Which pairs of compounds are diastereomers?

Meso Compounds

Certain molecules with two or more stereocentres do not have as many stereoisomers as you might expect

from the 2^n rule. One such molecule is 2,3-dihydroxybutanedioic acid, more commonly named tartaric acid. Tartaric acid is a colourless, crystalline compound occurring largely in plants, especially in grapes. The structure of tartaric acid is:



2,3-dihydroxybutanedioic acid
(tartaric acid)

C(2) and C(3) of tartaric acid are stereocentres, and, from the 2^n rule, the maximum number of stereoisomers you might expect is $2^2 = 4$. Figure 17.21 shows the two pairs of mirror images of this compound. Structures (a) and (b) are nonsuperimposable mirror images and, therefore, they are a pair of enantiomers. Structures (c) and (d) are also mirror images, but they are super-imposable if they are rotated to the appropriate orientation. Therefore, (c) and (d) are *not* different molecules; they are the same molecule, just oriented differently. Because (c) and its mirror image (d) are superimposable, they are the same molecule and achiral. This means that they are optically inactive and do not interact with plane-polarised light (see section 17.5 for more details).

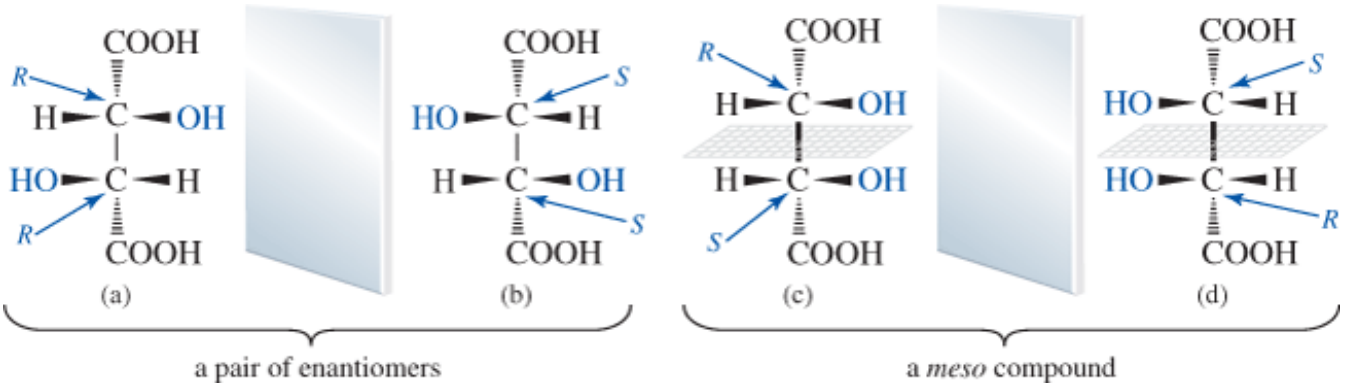


FIGURE 17.21 Stereoisomers of tartaric acid, one pair of enantiomers and one *meso* compound. The presence of an internal plane of symmetry indicates that the molecule is achiral.

Recall from p. 751 that any molecule with an internal plane of symmetry such that one half is the reflection of the other half is achiral and does not have enantiomers. Thus, even though (c) has two stereocentres, it is achiral. Its plane of symmetry is shown in figure 17.21. The stereo-isomer of tartaric acid represented by (c) or (d) is called a **meso compound**, defined as an achiral compound with two or more stereocentres.

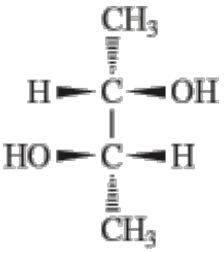
We can now return to the original question: How many stereoisomers are there of tartaric acid? The answer is three: one *meso* compound and one pair of enantiomers. Note that the *meso* compound is a diastereomer of each of the other stereoisomers.

WORKED EXAMPLE 17.4

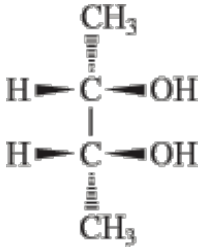
Enantiomers and *meso* Compounds

The following are stereorepresentations of the three stereoisomers of butane-2,3-diol.

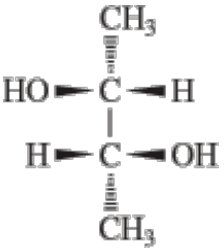
i.



ii.



iii.



(a) Which pair of molecules are enantiomers?

(b) Which is the *meso* compound?

Solution

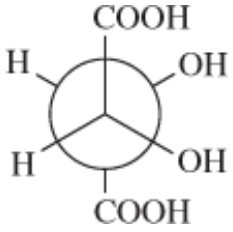
(a) Compounds (i) and (iii) are enantiomers.

(b) Compound (ii) is a *meso* compound.

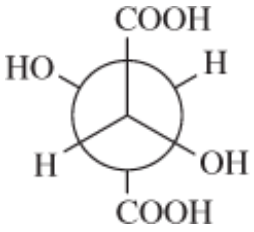
PRACTICE EXERCISE 17.4

The following are four Newman projection formulae (see section 16.2) of tartaric acid.

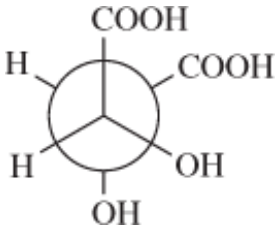
i.



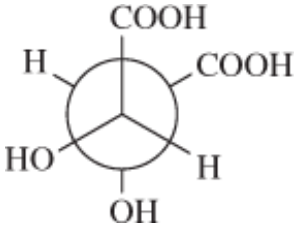
ii.



iii.



iv.



(a) Which formulae represent the same compound?

(b) Which formulae represent enantiomers?

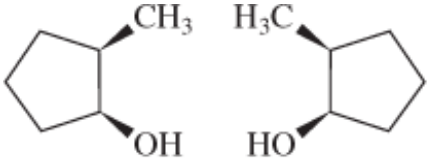
(c) Which formula(e) represent(s) *meso*-tartaric acid?

Cyclic Molecules with Two Stereocentres

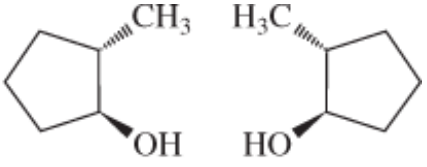
In this section, we concentrate on derivatives of cyclopentane and cyclohexane containing two stereo centres. We can analyse chirality in these cyclic compounds in the same way we did for acyclic compounds.

Disubstituted Derivatives of Cyclopentane

Let us start with 2-methylcyclopentanol, a compound with two stereocentres. Using the 2^n rule, we predict a maximum of $2^2 = 4$ stereoisomers. Both the *cis* isomer and the *trans* isomer (section 16.2) are chiral, with the *cis* isomer existing as one pair of enantiomers and the *trans* isomer existing as a second pair:

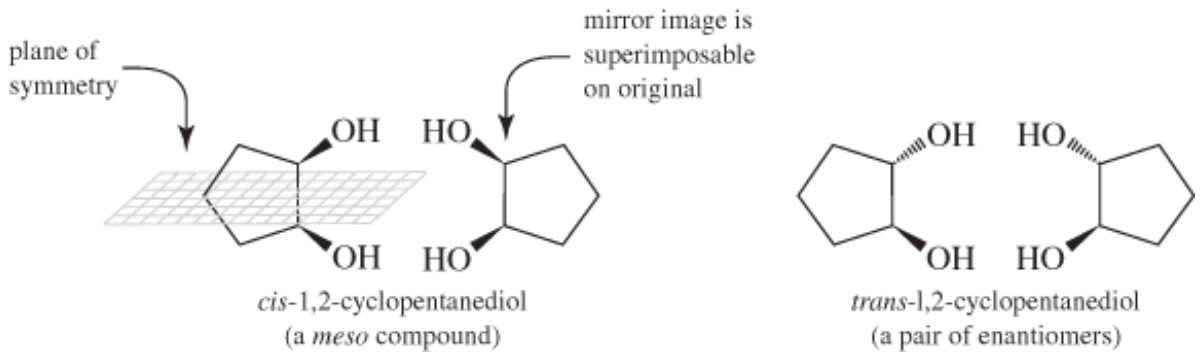


cis-2-methylcyclopentanol
(a pair of enantiomers)



trans-2-methylcyclopentanol
(a pair of enantiomers)

Because 1,2-cyclopentanediol also has two stereocentres, the 2^n rule predicts a maximum of $2^2 = 4$ stereoisomers. However, as seen in the following diagram, only three stereoisomers exist for this compound:



The *cis* isomer is achiral (*meso*) because it is superimposable on its mirror image. To put it another way, the *cis* isomer is achiral because it possesses a plane of symmetry that bisects the molecule into two mirror-image halves. The *trans* isomer is chiral and exists as a pair of enantiomers.

WORKED EXAMPLE 17.5

Stereoisomers for 3-methylcyclopentanol

How many stereoisomers are possible for 3-methylcyclopentanol?

Analysis and solution

There are four stereoisomers of 3-methylcyclopentanol, with the *cis* isomer existing as one pair of enantiomers and the *trans* isomer as a second pair:



cis-1,3-methylcyclopentanol
(a pair of enantiomers)



trans-3-methylcyclopentanol
(a pair of enantiomers)

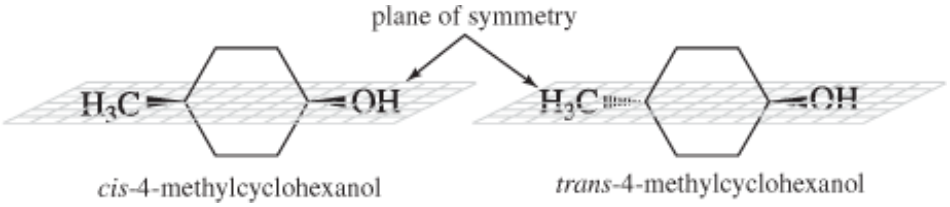
PRACTICE EXERCISE 17.5

How many stereoisomers are possible for 1,3-cyclopentanediol?

Disubstituted Derivatives of Cyclohexane

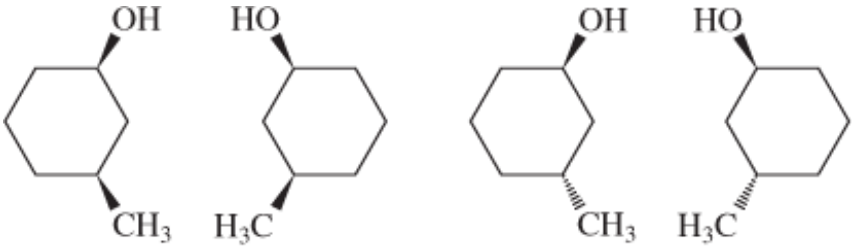
As an example of a disubstituted cyclohexane, let us consider the methylcyclohexanols. Firstly, 4-methylcyclohexanol can exist as two stereoisomers — a pair of *cis–trans* isomers. Both the *cis* and *trans*

isomers are *meso* compounds and are achiral. In each, a plane of symmetry runs through the —CH_3 and —OH groups and the two attached carbon atoms.



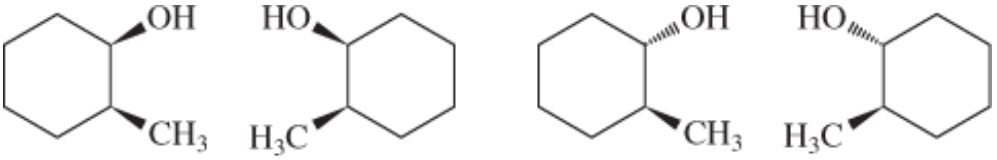
cis-4-methylcyclohexanol *trans*-4-methylcyclohexanol

Similarly, 3-methylcyclohexanol contains two stereocentres and exists as $2^2 = 4$ stereoisomers, with the *cis* isomer as one pair of enantiomers and the *trans* isomer as a second pair:



cis-3-methylcyclohexanol (a pair of enantiomers) *trans*-3-methylcyclohexanol (a pair of enantiomers)

Again, 2-methylcyclohexanol has two stereocentres and exists as $2^2 = 4$ stereoisomers, with the *cis* isomer as one pair of enantiomers and the *trans* isomer as a second pair:



cis-2-methylcyclohexanol (a pair of enantiomers) *trans*-2-methylcyclohexanol (a pair of enantiomers)

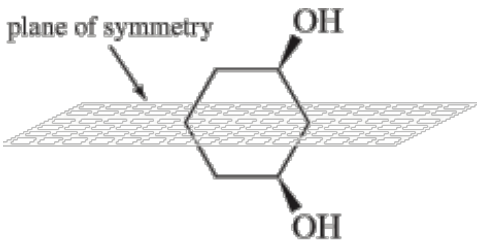
WORKED EXAMPLE 17.6

Stereoisomers for Cyclohexane-1,3-diol

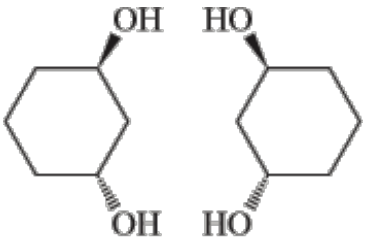
How many stereoisomers exist for cyclohexane-1,3-diol?

Analysis and solution

According to the 2^n rule, cyclohexane-1,3-diol has two stereocentres, so it has a maximum of $2^2 = 4$ stereoisomers. The *trans* isomer of this compound exists as a pair of enantiomers. The *cis* isomer has a plane of symmetry so is a *meso* compound.



cis-cyclohexane-1,3-diol
(a *meso* compound)



trans-cyclohexane-1,3-diol
(a pair of enantiomers)

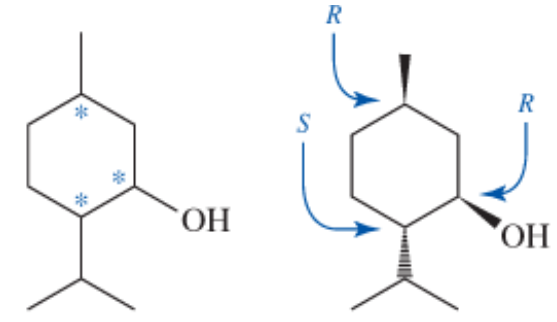
Therefore, although the 2^n rule predicts a maximum of four stereoisomers for cyclohexane-1,3-diol, only three exist — one pair of enantiomers and one *meso* compound.

PRACTICE EXERCISE 17.6

How many stereoisomers exist for cyclohexane-1,4-diol?

Molecules with Three or More Stereocentres

The 2^n rule applies equally to molecules with three or more stereocentres. Here is a disubstituted cyclohexanol with three stereocentres, each marked with an asterisk:

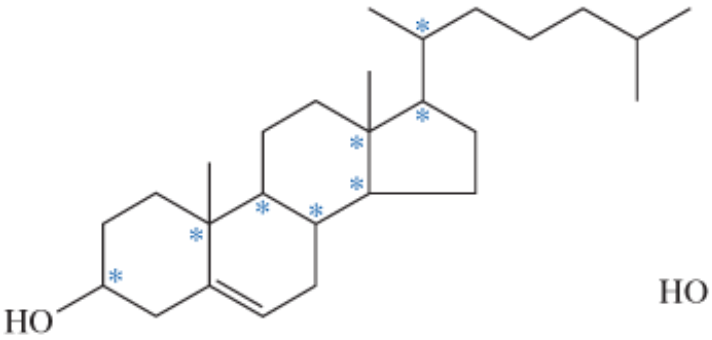


2-isopropyl-5-methyl-cyclohexanol

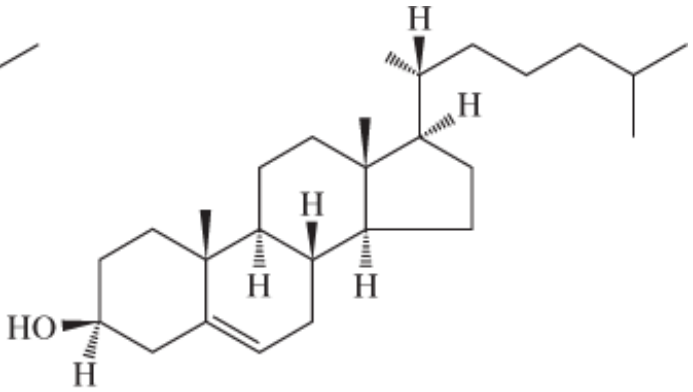
(−)-menthol
(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-cyclohexanol

There is a maximum of $2^3 = 8$ stereoisomers possible for this molecule. Menthol, one of the eight, has the configuration shown above on the right. The configuration at each stereocentre is indicated. Menthol is the major component present in peppermint and other mint oils that gives these their characteristic taste.

Cholesterol, a more complicated molecule, has eight stereocentres:



Cholesterol has eight stereocentres; 256 stereoisomers are possible.



This is the stereoisomer found in human metabolism.

To identify the stereocentres, remember to add an appropriate number of hydrogen atoms to complete the tetravalence of each carbon atom you think might be a stereocentre.

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17.5 Optical Activity: Detecting Chirality in the Laboratory

We indicated in the previous section that one diastereomer (menthol) of 2-isopropyl-5-methylcyclohexanol is primarily responsible for the flavour of peppermint. Diastereomers have markedly different properties. Enantiomers also have different properties, but the differences are more subtle. In general, enantiomers have identical physical and chemical properties. For instance, they have the same melting point, the same boiling point and the same solubilities in water and other common solvents. They do differ, however, in their **optical activity** (the ability to rotate a plane of polarised light). This property is particularly useful to chemists as it allows us to detect enantiomers in the laboratory.

Each member of a pair of enantiomers rotates a plane of polarised light in the opposite direction. To understand how optical activity is detected in the laboratory, we must first understand plane-polarised light and a polarimeter, the instrument used to detect optical activity.

Plane-polarised Light

Ordinary light consists of waves oscillating in all planes perpendicular to its direction of propagation (shown on the left side of figure 17.22). Certain materials, such as calcite and Polaroid™ sheet (a plastic film with oriented crystals of an organic substance embedded in it), selectively transmit light waves vibrating in parallel planes (shown on the right side of figure 17.22). Electro magnetic radiation vibrating only in parallel planes is said to be **plane polarised**.

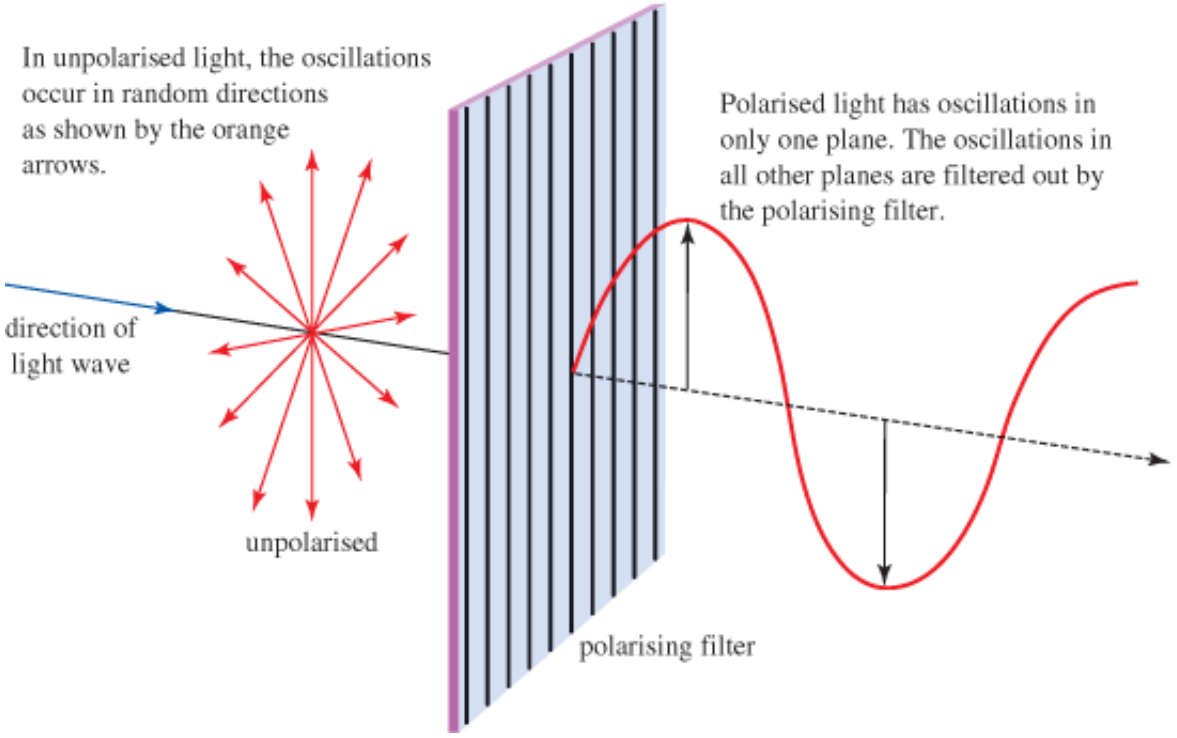


FIGURE 17.22 The effect of a polarising filter on light.

Polarimeters

A **polarimeter** consists of a light source, a polarising filter and an analysing filter (each made of calcite or Polaroid film), and a sample tube (figures 17.23 and 17.24). If the sample tube is empty, the intensity of light reaching the detector (in this case, your eye) is at its maximum when the polarising axes of the two filters are parallel. If the analysing filter is turned either clockwise or anticlockwise, less light is transmitted. When the axis of the analysing filter is at right angles to the axis of the polarising filter, the field of view is dark. This position of the analysing filter is taken to be 0° on the optical scale.



FIGURE 17.23 A light polarimeter.

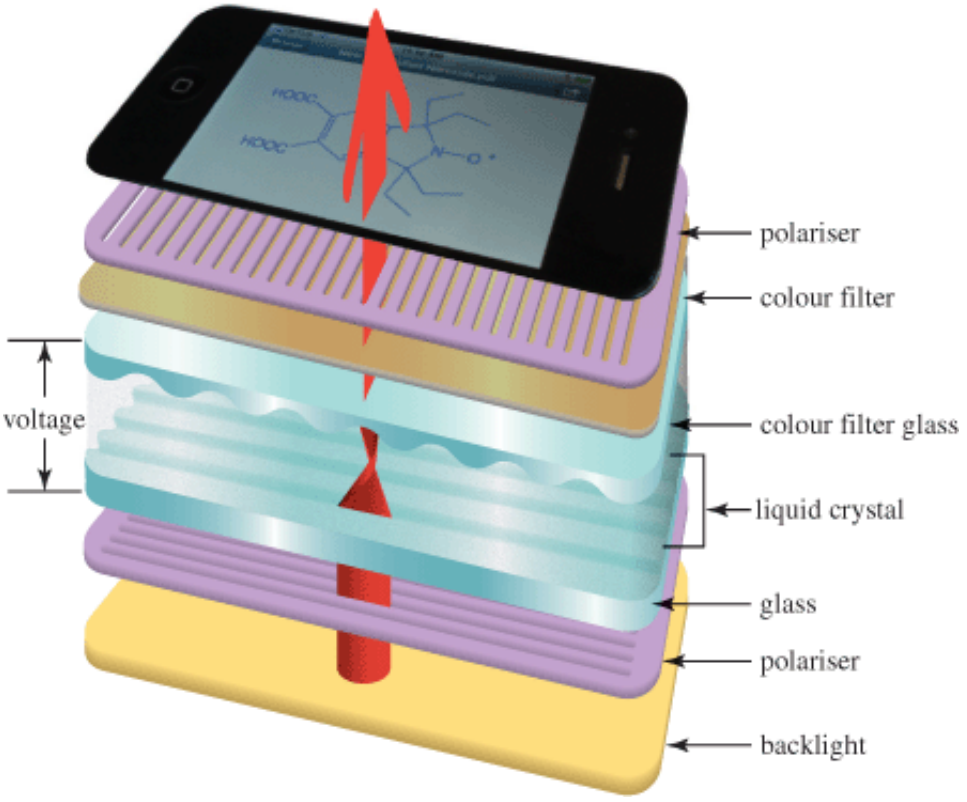


FIGURE 17.24 Polarising filters are used in liquid crystal displays (LCD).

This same principle forms the basis for how images are produced on the LCD screens of smart-phones and laptops (see figure 17.24).

Measuring the Rotation of Plane-polarised Light

The ability of molecules to rotate a plane of polarised light can be observed with the use of a polarimeter in the following way (see figure 17.25). First, a sample tube filled with solvent is placed in the polarimeter, and the analysing filter is adjusted so that no light passes through to the observer; that is, the filter is set to 0°. Then we place a solution of an optically active compound in the sample tube. When we do so, we find that a certain amount of light now passes through the analysing filter. We also

find that the plane of polarised light from the polarising filter has been rotated so that it is no longer at an angle of 90° to the analysing filter. We then rotate the analysing filter to restore darkness in the field of view. The number of degrees, α, through which we must rotate the analysing filter to restore darkness to the field of view is called the **observed rotation**. If we must turn the analysing filter to the right (clockwise) to restore the dark field, we say that the compound is **dextrorotatory** (from the Latin word *dexter* meaning 'on the right side'); if we must turn it to the left (anticlockwise), we say that the compound is **levorotatory** (from the Latin word *laevus* meaning 'on the left side').

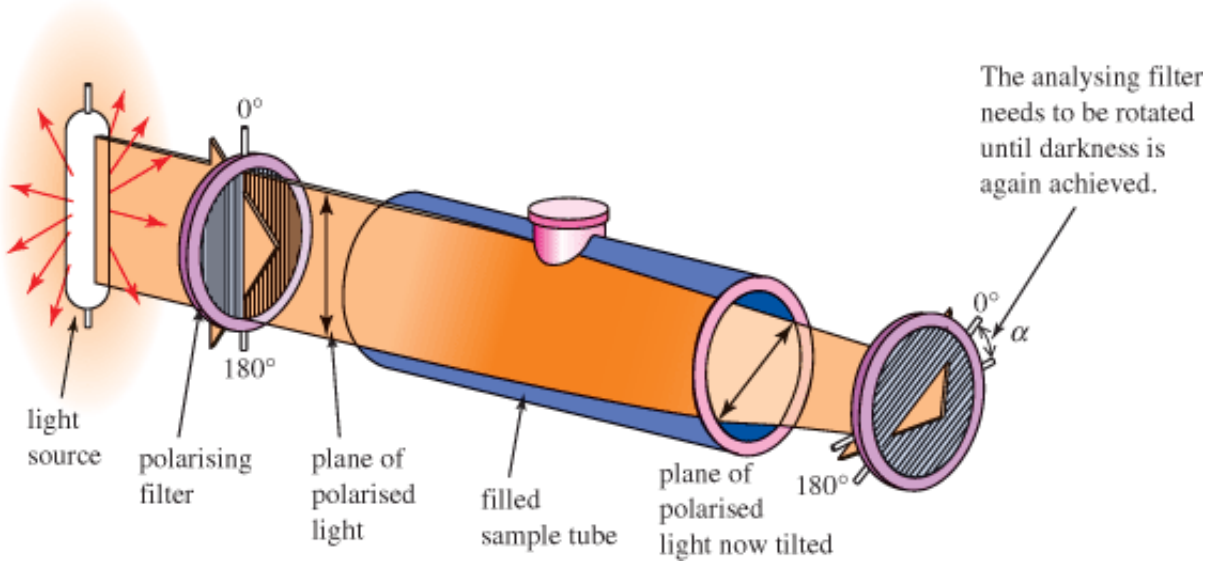


FIGURE 17.25 Schematic diagram of a polarimeter with its sample tube containing a solution of an optically active compound. The analysing filter would need to be turned clockwise by α degrees to restore the dark field.

The magnitude of the observed rotation for a particular compound depends on its concentration, the length of the sample tube, the temperature, the solvent and the wavelength of the light used. The **specific rotation ([α])** is defined as the observed rotation at a specific cell length and sample concentration:

$$\text{specific rotation} = [\alpha]_{\lambda}^{T} = \frac{\text{observed rotation (degrees)}}{\text{length (dm)} \times \text{concentration (g/mL)}}$$

The standard cell length is 1 decimetre (1 dm = 0.1 m, see figure 17.26), although cells of different lengths can be used. The concentration of a sample dissolved in a solvent is expressed as grams per millilitre of solution. The temperature (*T*, in degrees Celsius) and wavelength (λ, in nanometres) of light are designated, respectively, as superscript and subscript. The light source most commonly used in polarimetry is the so-called 'sodium D line' (λ = 589 nm), first named by German physicist Joseph von Fraunhofer when he observed the dark bands in the optical spectrum of the Sun. The same line is responsible for the yellow colour of sodium-vapour lamps seen in many street lights (see worked example 4.3 on pp. 116 -17).

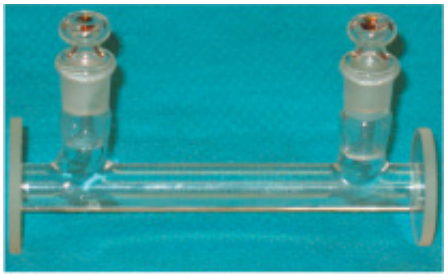
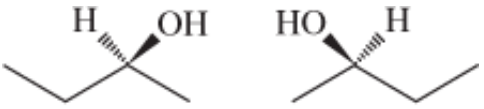


FIGURE 17.26 A 1 dm polarimeter cell.

In reporting either observed or specific rotation, it is common to indicate a dextrorotatory compound with a plus sign in parentheses, (+), and a levorotatory compound with a minus sign in parentheses, (-). For any pair of enantiomers, one enantiomer is dextrorotatory and the other is levorotatory. For each pair, the values of the specific rotation are exactly the same, but the signs are opposite. The following are the specific rotations of the enantiomers of butan-2-ol at 25 °C, observed with the D line of sodium:



(*S*)-(+)-butan-2-ol $[\alpha]_D^{25} = +13.52°$ (*R*)-(−)-butan-2-ol $[\alpha]_D^{25} = -13.52°$

You will notice in the specific rotations for butan-2-ol that *S* is the dextrorotatory enantiomer and *R* is the levorotatory enantiomer. The *R* and *S* designation is not related to the optical activity; that is, *S* enantiomers may be either levorotatory or dextrorotatory, and vice versa.

WORKED EXAMPLE 17.7

Calculating Specific Rotation

A solution is prepared by dissolving 4.00 g of testosterone, a male sex hormone, in 100 mL of ethanol and placing it in a sample tube 1.00 dm in length. The observed rotation of this sample at 25 °C, using the D line of sodium, is +4.36°. Calculate the specific rotation of testosterone.

Analysis and solution

The concentration of testosterone is 4.00 g/100 mL = 0.0400 g/mL. The length of the sample tube is 1.00 dm. Inserting these values into the equation for calculating specific rotation gives:

$$\text{specific rotation} = \frac{\text{observed rotation}}{\text{length} \times \text{concentration}} = \frac{+4.36°}{1.00 \times 0.0400} = 109°$$

PRACTICE EXERCISE 17.7

The specific rotation of progesterone, a female sex hormone, is +172°, measured at 20 °C. Calculate the observed rotation for a solution prepared by dissolving 4.00 g of progesterone in 100 mL of dioxane and placing it in a sample tube 1.00 dm long.

Racemic Mixtures

An equimolar mixture of two enantiomers is called a **racemic mixture**, a term derived from the name ‘racemic acid’ (from the Latin word *racemus* meaning ‘cluster of grapes’), originally given to an equimolar mixture of the enantiomers of tartaric acid. Because a racemic mixture contains equal numbers of the dextrorotatory and the levorotatory molecules, its specific rotation is 0. Alternatively, we say that a racemic mixture is optically inactive. A racemic mixture is indicated by adding the prefix (±) to the name of the compound.

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17.6 Chirality in the Biological World

Almost all the molecules in living systems, both plant and animal, are chiral. Although these chiral molecules can exist as a number of stereoisomers, almost invariably only one stereoisomer is found in nature. Of course, instances do occur in which more than one stereoisomer is found, but these rarely exist together in the same biological system.

Perhaps the most conspicuous examples of chirality among biological molecules are the enzymes, all of which have many stereocentres. An example is chymotrypsin, an enzyme found in the intestines of animals that catalyses the digestion of proteins. Chymotrypsin has 251 stereo-centres. The maximum possible number of stereoisomers is thus staggeringly large, almost beyond comprehension. Fortunately, nature does not squander its precious energy and resources unnecessarily; only one of these stereoisomers is produced and used by any given organism. Because enzymes are chiral substances, most produce or react only with substances that match their stereochemical requirements.

How an Enzyme Distinguishes Between Enantiomers

For an enzyme to catalyse a biological reaction, the molecule involved must first attach to a chiral binding site on the enzyme's surface. An enzyme with binding sites specific for three of the four groups on a stereocentre can distinguish between a molecule and its enantiomer or one of its diastereomers. Let's look at figure 17.27, which is a representation of an enzyme that catalyses a reaction of glyceraldehyde. The enzyme has three sites arranged on its surface: a binding site specific for —H, a second specific site for —OH and a third specific site for —CHO. The enzyme can distinguish (*R*)-(+)-glyceraldehyde (the natural, or biologically active, form) from its enantiomer because the natural enantiomer can be bound, with three groups interacting with their appropriate binding sites; for the *S* enantiomer, only two groups at most can interact with these binding sites.

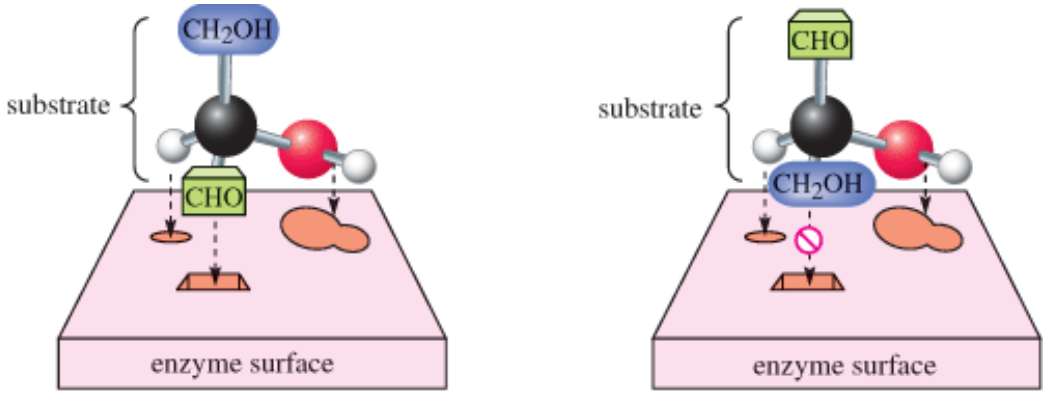
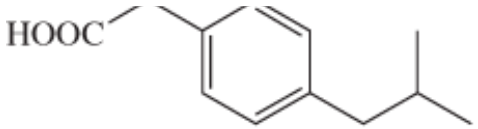


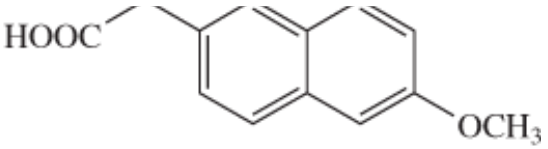
FIGURE 17.27 A schematic diagram of an enzyme surface capable of interacting with (*R*)-(+)-glyceraldehyde at three binding sites, but with (*S*)-(-)-glyceraldehyde at only two of these sites.

Because interactions between molecules in living systems take place in a chiral environment, we should expect that a molecule and its enantiomer or one of its diastereomers elicit different physiological responses. As we have already seen, (*S*)-ibuprofen is active as a pain and fever reliever, whereas its *R* enantiomer is inactive. The *S* enantiomer of the closely related analgesic naproxen is also the active pain-relieving form of this compound, but its *R* enantiomer is a liver toxin!





(*S*)-ibuprofen



(*S*)-naproxen

Chemical Connections

Chemistry and Forensics

Some of the most popular shows on TV today involve scientists solving crimes using chemistry skills. Crime stories have always been popular; however, today's forensic scientists have access to tools and techniques that allow modern scriptwriters to develop complex and wide-ranging story-lines for these shows, even if they are often viewed as unrealistic by actual forensic scientists. However, even 80 years ago, crime writers were using their knowledge of chemistry to produce original stories. One such example is the 1930 crime story *The Documents in the Case* co-written by Dorothy L Sayers and Robert Euston.

In possibly the first example of the involvement of realistic forensic science to solve a whodunit, a murderer was brought to justice through an understanding of chirality in organic chemistry. The 1930 story by Sayers and Euston concerned George Harrison, found dead in the kitchen of his small cottage in the woods called *The Shack*. Beside Harrison's body were some wild mushrooms, which it was known he was fond of collecting from the woods. In the subsequent inquest, the Home Analyst, Sir James Lubbock, testified that the cause of death was poisoning by muscarine, the active principle from the mushroom *Amanita muscaria* (figure 17.28), a large amount of which was found in the stomach and vomitus of the victim. Sir James had no hesitation in declaring to the coroner that the death arose through accidental ingestion of the poison during the preparation of a meal involving the mushrooms. The jury agreed and brought in a verdict of ‘Accidental Death due to poisoning by *Amanita muscaria*’.



FIGURE 17.28 *Amanita muscaria*.

And there the matter would have ended except for the efforts of John Bunting, a friend of the

deceased, who could not believe that Harrison would have mistaken the mushroom for an edible variety. Bunting's initial investigations were all fruitless until he talked to an organic chemist. In doing so, he discovered that ‘life has a kind of bias — a lopsidedness so to speak’, and it is sometimes possible to distinguish between synthetic substances and those derived from living organisms. Synthesis generally produces the racemate, the combined chiral forms of a mol ecule, whereas the natural products are usually of one form only, single enantiomers. The organic chemist told Bunting that a simple polarimeter measurement would confirm that the poison came from the mushroom and, after some effort, Bunting was able to convince the Home Analyst to undertake the analysis. When Lubbock's measurement showed no optical activity, it was clear that the muscarine (figure 17.29) was a racemic mixture and therefore of synthetic origin. Harrison's death must have been due to foul play. Subsequently, the source of the racemic mixture of muscarine was traced to Mrs Harrison's lover who paid the full penalty under the law — death by hanging.

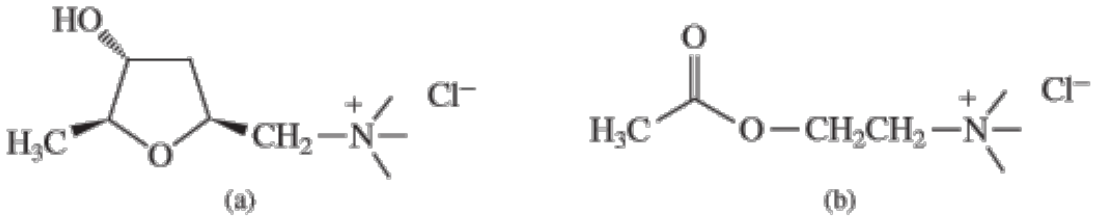


FIGURE 17.29

(a) Muscarine activates the nervous system by mimicking acetylcholine.

(b) Acetylcholine — the messenger molecule involved in nerve impulse transmission.

Chirality is much more involved with saving lives than ending them, as many modern medicines are sold as a single enantiomer. The chiral drug industry now represents close to one-third of all drug sales worldwide. Single enantiomer drugs and intermediates represent more than 150 billion dollars in sales each year. AstraZeneca for instance sold over 5.7 billion dollars worth of one drug alone (esomeprazole, used to treat ulcers) in one year, making it the third biggest selling pharmaceutical drug that year. The industry's growth is rooted, in part, in the chemistry by which molecules interact with biological systems. Biological messenger molecules and cell surface receptors that medicinal chemists try to affect or mimic are chiral, so drug molecules must match this asymmetry. The chiral drugs synthesised by the pharmaceutical industry today are generated by synthetic reactions that lead predominantly to one enantiomer, or by special separation techniques used to isolate the enantiomers.

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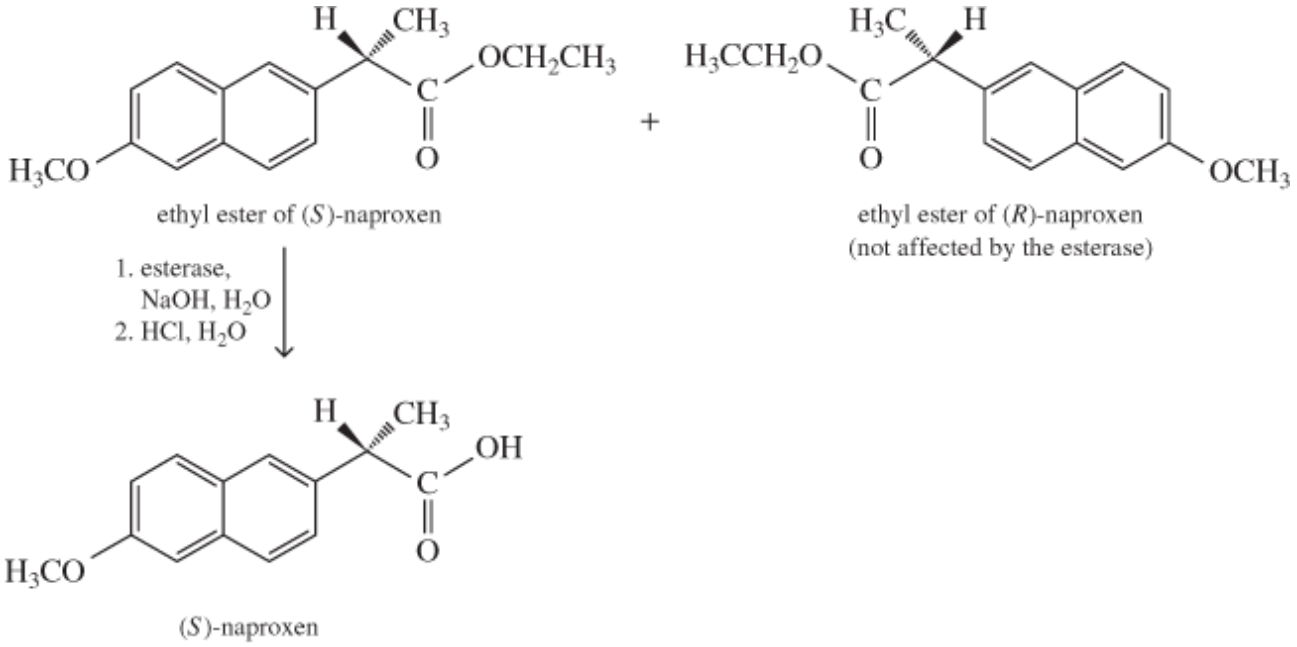
17.7 Synthesising Chiral Drugs

Many of today's medicines involve chiral compounds. Some of these, such as ibuprofen (see p. 754), are sold as a mixture of both enantiomers. Others, however, must be enantiomerically pure because only one enantiomer has the desired therapeutic effect. Pharmaceutical companies approach the production of enantiomerically pure medicines in two ways; they can synthesise a racemic mixture of the drug and then separate the two enantiomers (resolution) or they can control the synthetic conditions so that only one enantiomer is formed (asymmetric synthesis).

Resolution

Resolution is the separation of a mixture into its individual components. Resolution of enantiomers is, in general, difficult, but several laboratory methods can be used. In this section, we illustrate just one: the use of enzymes as chiral catalysts. The principle involved in this method is that a particular enzyme will catalyse a reaction of a chiral molecule, but not of its enantiomer (see figure 17.27 on p. 764).

The esterases have received particular attention in this regard. This class of enzyme catalyses the hydrolysis of esters to give an alcohol and a carboxylic acid. Figure 17.30 illustrates the resolution of (*R*,*S*)-naproxen. The ethyl esters of both (*R*)- and (*S*)-naproxen are solids with very low solubilities in water. Chemists use an esterase in alkaline solution to selectively hydrolyse the (*S*)-ester, which goes into aqueous solution as the sodium salt of the (*S*)-carboxylic acid. The (*R*)-ester is unaffected by these conditions. Filtering the alkaline solution recovers the crystals of the (*R*)-ester. After the crystals are removed, the alkaline solution is acidified to precipitate pure (*S*)-naproxen. The recovered (*R*)-ester can be racemised (converted to an *R*,*S*-mixture) and treated again with the esterase. By recycling the (*R*)-ester, the racemic ester is converted to (*S*)-naproxen.



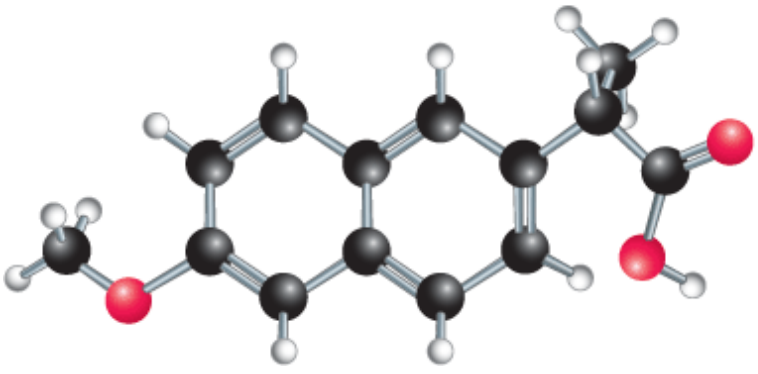


FIGURE 17.30 The resolution of (*R*,*S*)-naproxen.

The sodium salt of (*S*)-naproxen is the active ingredient in many over-the-counter nonsteroidal anti-inflammatory drugs (NSAIDs). The (*S*)-enantiomer is much more effective than the (*R*)-enantiomer, and more importantly the (*R*)-enantiomer has significant liver toxicity so must not be present in the drug.

Removing the (*R*)-enantiomer of naproxen to provide enantiomerically pure (*S*)-naproxen makes this a useful and effective drug, but this is not the case for all single enantiomers. For example, resolution of the enantiomers of thalidomide would still result in a drug with unwanted side effects because the body is able to convert one enantiomer to the other.

Asymmetric Synthesis

Inorganic stereoisomers are essential for the industrial synthesis of some important chiral drugs. In 2001 the Nobel Prize in chemistry was awarded to chemists William Knowles, Ryoji Noyori and Barry Sharpless who developed chiral inorganic catalysts that, for the first time, enabled the practical synthesis of chirally pure compounds used to make medicines, such as L-DOPA, for treatment of Parkinson's disease, and naproxen, the structures of which are shown below.

Asymmetric synthesis is the name chemists give to procedures that give rise to predominantly one enantiomer. Efficient asymmetric synthesis is crucial, particularly for companies that make pharmaceuticals. The first commercialised catalytic asymmetric synthesis using a chiral transition-metal complex as the catalyst was the production of L-DOPA from a nonchiral aromatic alkene. This reaction has been in commercial use since 1974 and is now known as the *Monsanto process* (figure 17.31) after the name of the company that developed it. The commercial success of the synthesis of L-DOPA stimulated the subsequent development and application of other catalytic asymmetric reactions.

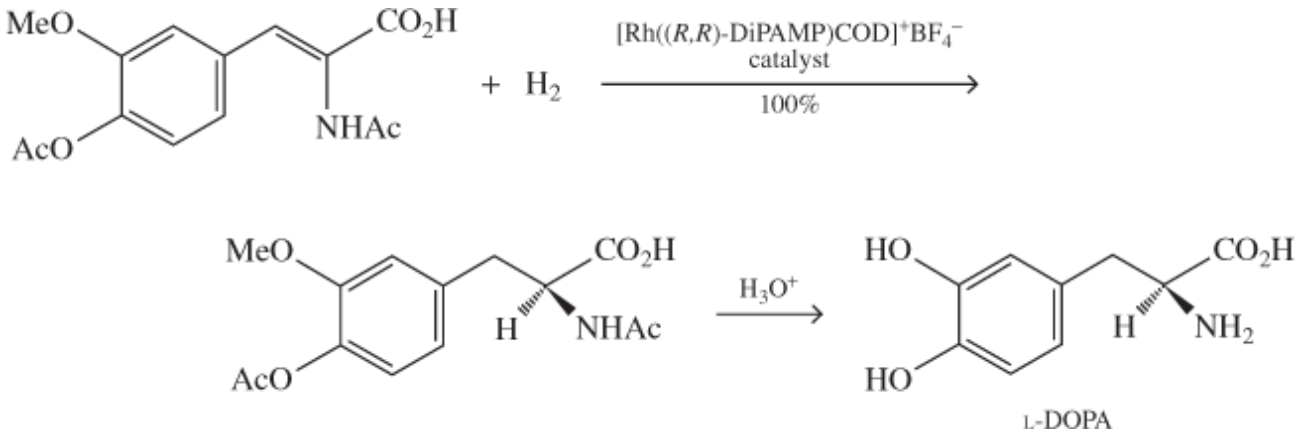


FIGURE 17.31 The Monsanto process for the production of L-DOPA, which is used to treat Parkinson's disease.

As well as being produced by resolution as discussed previously, (*S*)-naproxen can also be synthesised industrially using special catalysts with chiral ligands. This asymmetric synthesis (figure 17.32) uses the chiral BINAP complex. This clean, simple and economical approach may be applied on any scale from <100 mg to >100 kg. BINAP-catalysed asymmetric syntheses are applied to the industrial production of medicinal compounds in quantities of well over 100 tonnes a year. This approach has been used to develop a range of pharmaceuticals, agrochemicals, flavours and fragrances.

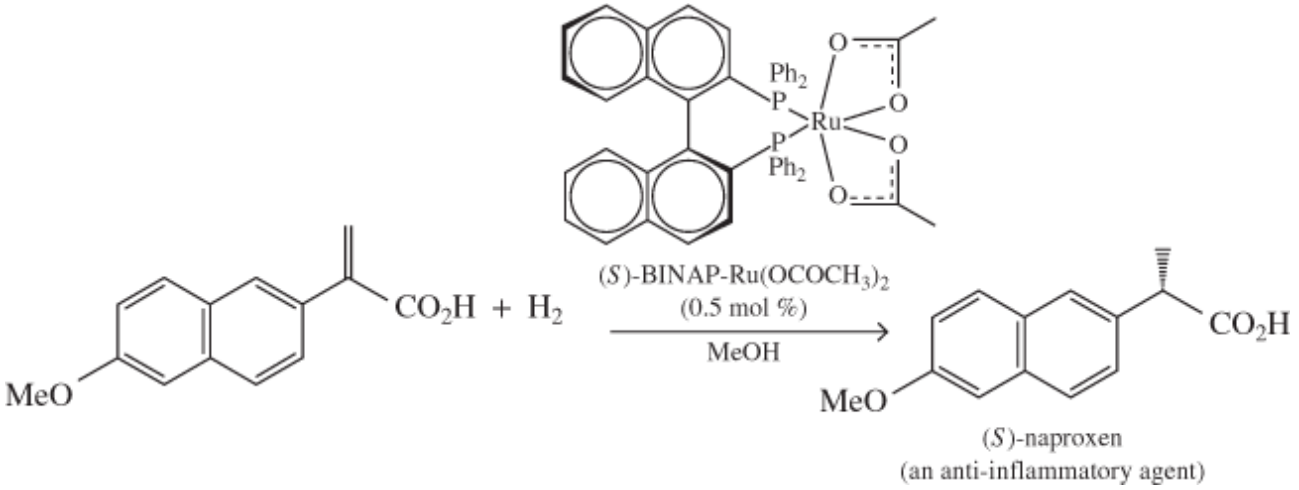


FIGURE 17.32 The commercial asymmetric synthesis of the anti-inflammatory drug naproxen (sold as Naprogesic™ in Australia and New Zealand).

Because asymmetric synthesis is difficult, even for relatively small molecules, the complete synthesis of complex organic molecules such as the important cancer-fighting drug Taxol (see p. 753) provides a tremendous challenge. Chemists produce Taxol by starting with a simpler compound found in nature and then making a few, less demanding, asymmetric transformations to achieve the desired material.

Asymmetric synthesis allows us to create new medicines and compounds with specific biological effects. Achieving stereochemical control over synthetic reactions, however, is one of the greatest challenges facing chemists today. To master such challenging methodology, we must first learn about the key functional groups, their properties and how they react; this will be covered in the following chapters.

Chemistry Research

Where did Chirality Come From?

The Big Bang is the currently accepted scientific explanation for the formation of the universe. The best estimates put the age of the universe at between 13 and 14 billion years, while the Earth is thought to be about 4.5 billion years old. The simple molecules present on Earth in its infancy have gradually evolved over this time to give extraordinarily complex molecules, such as DNA, which are the basis of life as we

know it.

One intriguing unanswered question is ‘Why do many molecules in biological systems exist as only one of two possible enantiomers?’ For example, as we will see in chapter 24, the 19 chiral amino acids, the building blocks of proteins, exist nearly exclusively as a single enantiomer in biological systems. This must mean that, somewhere over the past 4.5 billion years, nature developed a preference for one of the two enantiomers. One of the many hypotheses for this bio-molecular homochirality is that there might be a tiny energy difference between them. This runs somewhat counter to our everyday experience with chiral molecules, as, when two enantiomers of the same molecule are placed in an achiral environment, they appear to behave chemically and physically identically. Therefore, if any such energy difference does exist, it must be absolutely tiny.

Professor Peter Schwerdtfeger of Massey University (New Zealand) is currently searching for chiral molecules that exhibit energy differences between their enantiomers (figure 17.33), and he is using high-level computational chemistry as his primary technique. Calculations have shown that very heavy molecules are much more likely to exhibit such behaviour. Therefore, his research concentrates on calculating the energies of the two enantiomers of chiral molecules containing very heavy atoms such as third-row transition metals and actinide elements. This introduces significant difficulties into the calculations, as the time required is proportional to at least n^3, where n is the number of electrons in the system, and therefore supercomputers are required to complete these in a reasonable time.

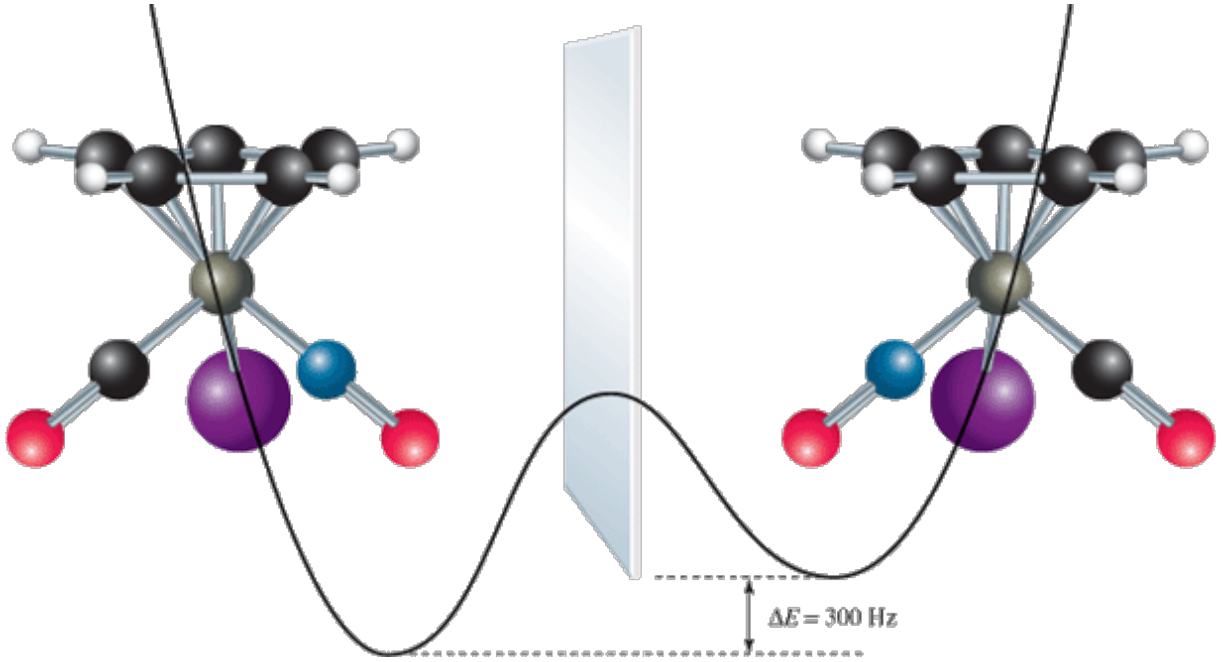


FIGURE 17.33 Sophisticated calculations on the chiral molecule [$(C_5H_5)Re(CO)(NO)I$] suggest that there may be a small energy difference of 300 Hz (=10^{-10} kJ mol^{-1}) between the two enantiomers. Such a difference should be detectable with the correct instruments.

Once the calculations are complete, the candidate molecules must be prepared and techniques found to determine the small energy differences expected. Professor Schwerdtfeger is collaborating with a group in France to use vibrational spectroscopy as a possible energy probe, while other groups around the world are proposing to use NMR spectroscopy. Regardless of the technique used, the observation of an energy difference between enantiomers will be a massive scientific achievement and will force us to change the way we think about chirality. The calculations do suggest that such an energy difference exists, so the race is on!

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SUMMARY

Stereoisomers

Isomers are molecules with the same molecular formula but different structures. Constitutional isomers are isomers with different sequences of atom connectivity. Stereoisomers have the same order of attachment of atoms, but a different three-dimensional orientation of their atoms in space. A chiral object is one that is not superimposable on its mirror image. Enantiomers are stereoisomers that are chiral. An achiral object is the same as its mirror image. Diastereomers are stereoisomers that are not superimposable and are not mirror images.

Enantiomerism

Most biological molecules are enantiomeric. Enantiomers have the same physical and chemical properties but each of a pair reacts differently with other chiral molecules. A plane of symmetry is an imaginary plane passing through an object, dividing it such that one half is the reflection of the other half. Objects with planes of symmetry are achiral. A stereocentre is the part of a molecule that can be assembled in two different ways to generate stereoisomers. The most common type of stereocentre among organic compounds is a tetrahedral carbon atom with four different groups bonded to it. Inorganic molecules can also have stereocentres and, therefore, enantiomers and diastereomers.

Naming stereocentres: The *R*,*S* System

The configuration at a stereocentre can be specified by the *R*,*S* system. To apply this naming system, (1) each atom or group of atoms bonded to the stereocentre is assigned a priority and is numbered from highest priority to lowest priority, (2) the molecule is oriented in space so that the group of lowest priority is directed away from the observer, (3) the remaining three groups are read in order, from highest priority to lowest priority, and (4) if the sequence of the groups is clockwise, the configuration is *R*, if anticlockwise, the configuration is *S*.

Molecules with More Than One Stereocentre

For a molecule with n stereocentres, the maximum possible number of stereoisomers is 2^n. A plane of symmetry in a molecule reduces the number of stereoisomers to fewer than that predicted by the 2^n rule. A *meso* compound contains two or more stereocentres assembled so that its molecules are achiral.

Optical Activity: Detecting Chirality in the Laboratory

Enantiomers differ in their optical activity — that is, their ability to rotate a plane of polarised light. Plane-polarised light oscillates only in parallel planes. A polarimeter is an instrument used to detect and measure the magnitude of optical activity. Observed rotation is the number of degrees a plane of polarised light is rotated. Specific rotation is the observed rotation measured with a cell 1 dm long. Levorotatory compounds rotate a plane of polarised light anticlockwise. Dextrorotatory compounds rotate a plane of polarised light clockwise. A racemic mixture is a mixture of equal amounts of two enantiomers and has a specific rotation of 0.

Chirality in the Biological World

Chirality is very important in biology. Almost all the molecules in living systems, both plant and animal, are chiral. Enzymes catalyse biological reactions for one specific enantiomer. Each enantiomer of a drug can have different biological activity.

Synthesising Chiral Drugs

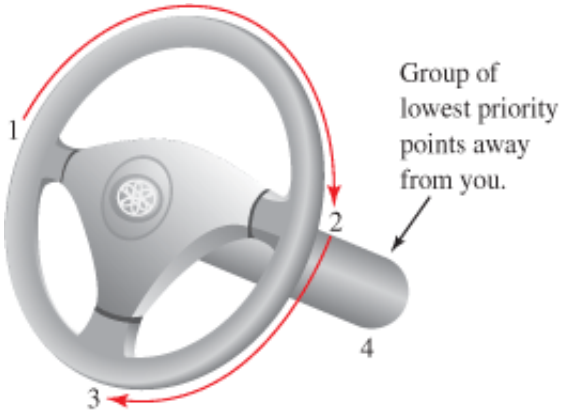
Enantiomerically pure drugs can be produced via two approaches: a racemic mixture of the drug can be separated in a process called resolution, or the synthetic conditions can be controlled so that only one

enantiomer is formed. One means of resolution is to treat the racemic mixture with an enzyme that catalyses a specific reaction of one enantiomer but not the other. Chiral inorganic catalysts can be useful tools in asymmetric synthesis to control reactions so that only one enantiomer is formed.

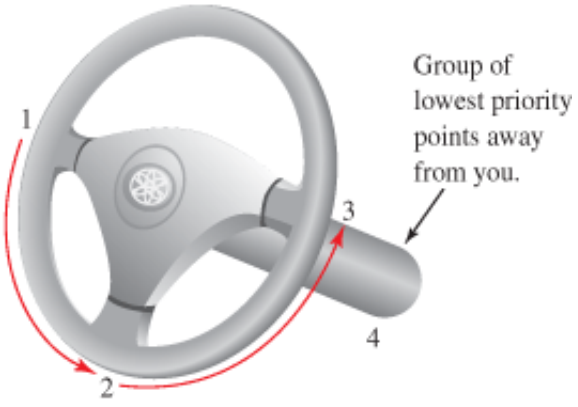
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The *R*,*S* system *(section 17.3)*

Orienting molecules with the lowest priority bond away from the point of view and prioritising the three remaining groups gives a clockwise (*R*) or an anticlockwise (*S*) sequence.



R configuration



S configuration

The 2^n rule *(section 17.4)*

For a molecule with n stereocentres, there will be at most $2n$ stereoisomers.

Specific rotation formula for enantiomers *(section 17.5)*

$$\text{specific rotation} = [\alpha]_{\lambda}^{T} = \frac{\text{observed rotation(degrees)}}{\text{length(dm)} \times \text{concentration(g/mL)}}$$

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REVIEW QUESTIONS

Stereoisomers

17.1 Define the term ‘stereoisomer’.

17.2 How are constitutional isomers different from stereoisomers? How are they the same?

17.3 Which of these objects are chiral? (Assume that there is no label or other identifying mark.)

(a) pair of scissors



(b) tennis ball



(c) paperclip



(d) bulldog clip



(e) beaker



(f) screw



17.4 Consider the helical coil of a telephone cord or the spiral binding on a notebook. If you view the spiral from one end and find that it has a left-handed (anticlockwise) twist, does the spiral have a right-handed (clockwise) or a left-handed twist when viewed from the other end?

17.5 Next time you have the opportunity to view a collection of coneshells or other seashells with a helical twist, study the chirality of their twists. Do you find an equal number of left-handed and right-handed shells or, for example, do they all have the same handedness?



Median cross-section through the shell of a chambered nautilus found in the deep waters of the Pacific Ocean. The shell shows handedness; this cross-section is a right-handed spiral.

17.6 When you next have an opportunity to examine any of the seemingly endless varieties of spiral pasta, look how they are twisted to form a spiral. Do pieces of any one kind of pasta all twist in the same direction? (That is, do they all have a right-handed twist or a left-handed twist, or are they a mixture, possibly even a racemic mixture?)

Enantiomerism

17.7 State whether each of the following statements is true.

(a) All enantiomers are chiral.

(b) A diastereomer of a chiral molecule must also be chiral.

(c) A molecule with an internal plane of symmetry can never be chiral.

(d) All achiral molecules have enantiomers.

(e) All achiral molecules have diastereomers.

(f) All chiral molecules have enantiomers.

(g) All chiral molecules have diastereomers.

17.8 Which of the following compounds contain stereocentres?

(a) 2-chloropentane

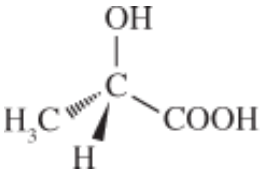
(b) 3-chloropentane

(c) 3-chloropent-1-ene

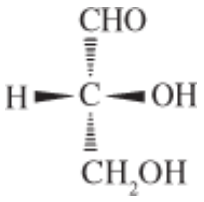
(d) 1,2-dichloropropane

17.9 Draw the enantiomer of each of the following molecules.

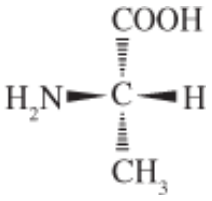
(a)



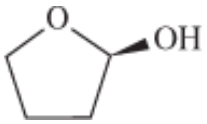
(b)


CHO
H
C
OH
CH2OH

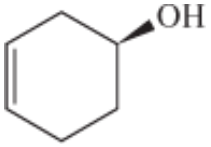
(c)


COOH
H2N
C
H
CH3

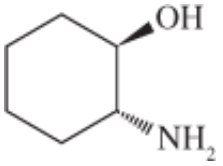
(d)


O
OH

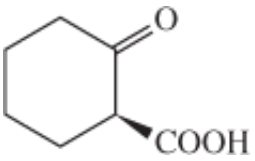
(e)


OH

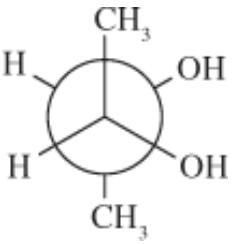
(f)


OH
NH2

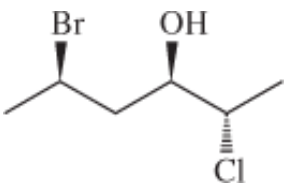
(g)


O
COOH

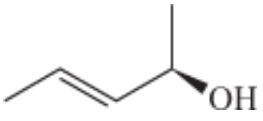
(h)


CH3
H
OH
H
OH
CH3

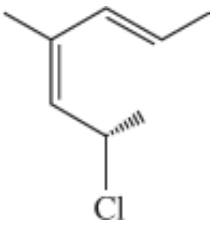
(i)


Br
OH
Cl

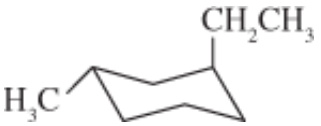
(j)


OH

(k)

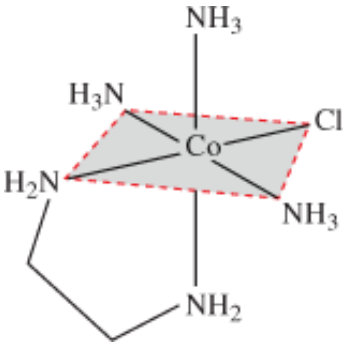


(l)

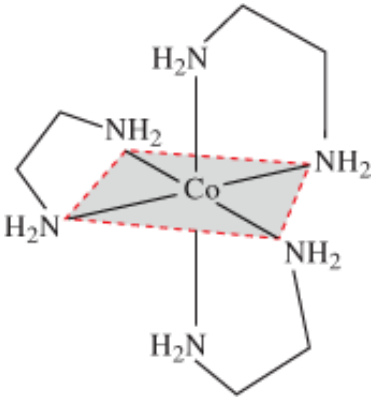


17.10 Closely examine the following four metal complexes. Which of these complexes are chiral — that is, has an enantiomer? Draw these enantiomers.

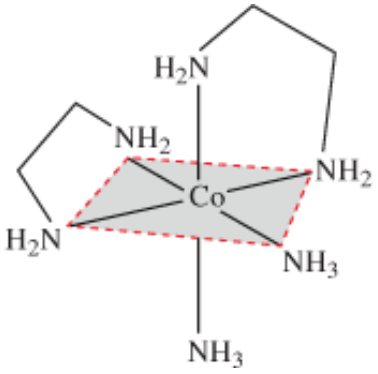
(a)



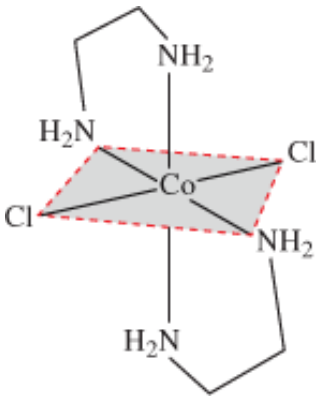
(b)



(c)



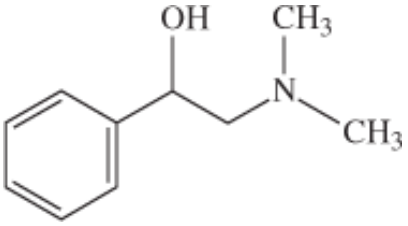
(d)



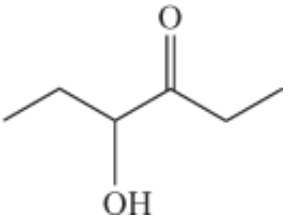
17.11 Draw the two enantiomers of the complex $[Co(C_2O_4)_3]^{3-}$, which has three bidentate oxalate ligands (see chapter 13, p. 547).

17.12 Mark each stereocentre in the following molecules with an asterisk. (*Note:* Not all contain stereocentres.)

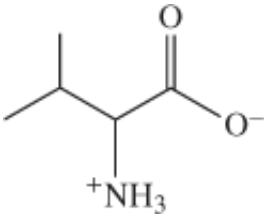
(a)



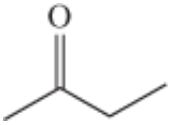
(b)



(c)

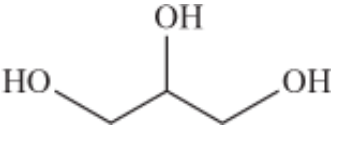


(d)

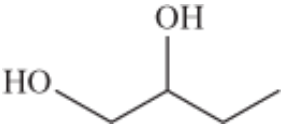


17.13 Mark each stereocentre in the following molecules with an asterisk. (*Note:* Not all contain stereocentres.)

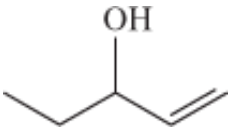
(a)



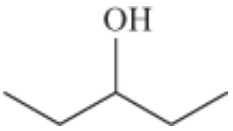
(b)



(c)



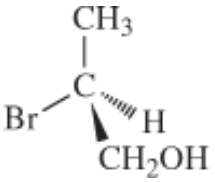
(d)



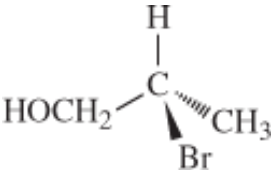
Naming Stereocentres: the *R*,*S* System

17.14 Which of the following molecules have an *R* configuration?

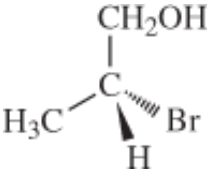
(a)



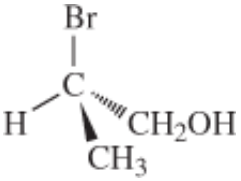
(b)



(c)



(d)



17.15 Assign priorities to the groups in each of the following sets.

(a) —H, —CH_3, —OH, —CH_2OH

(b) — $CH_2CH{=}CH_2$, —$CH{=}CH_2$— CH_3, —CH_2COOH

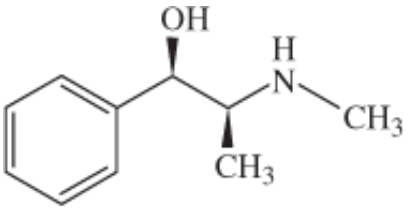
(c) — CH_3, —H, —COO^-, —$^+NH_3$

(d) — CH_3, —CH_2SH, —$^+NH_3$, —COO^-

Molecules with More Than One Stereocentre

17.16 Write the structural formula of an alcohol with a molecular formula $C_6H_{14}O$ that contains two stereocentres.

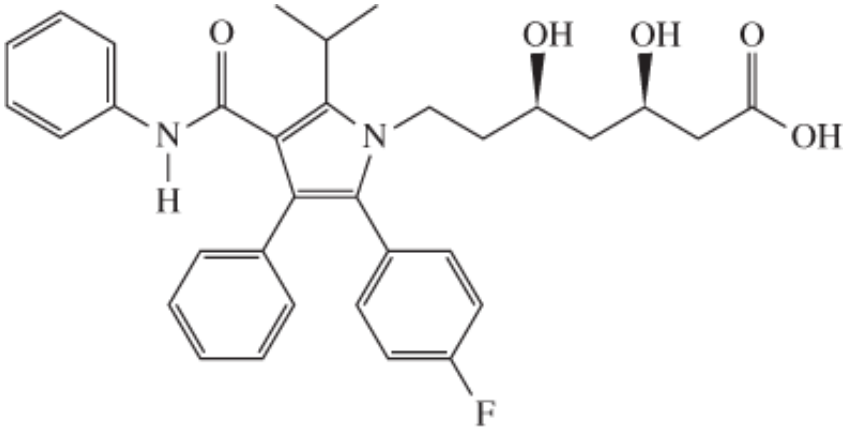
17.17 For centuries, Chinese herbal medicine has used extracts of *Ephedra sinica* to treat asthma. Investigation of this plant resulted in the isolation of ephedrine, a potent dilator of the air passages of the lungs. The naturally occurring stereoisomer is levorotatory and has the following structure:



ephedrine

Assign an *R* or *S* configuration to each stereocentre.

17.18 Atorvastatin is sold under the trade name Lipitor and is used for lowering cholesterol. Annual global sales of this compound exceed $13 billion. Assign a configuration to each chirality centre in atorvastatin.



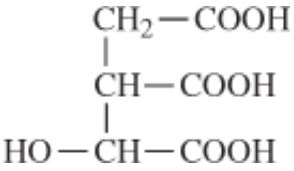
atorvastatin

17.19 Label each stereocentre in the following molecules with an asterisk.

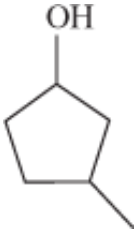
(a)



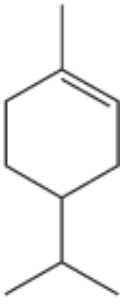
(b)



(c)

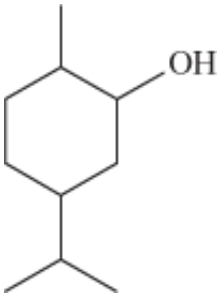


(d)

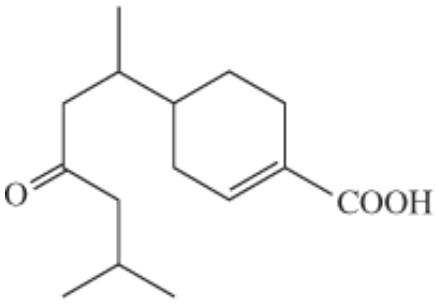


(e)

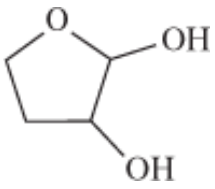
(f)

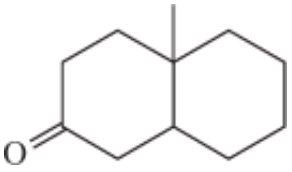


(g)



(h)

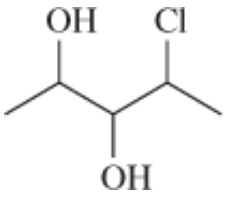




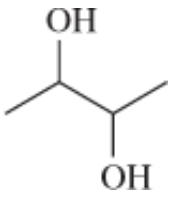
How many stereoisomers are possible for each molecule?

17.20 Identify the number of stereoisomers expected for each of the following.

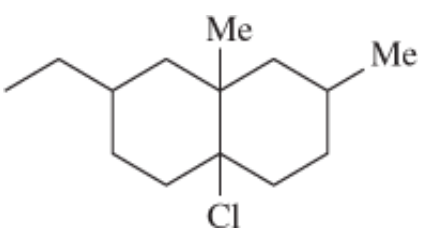
(a)



(b)

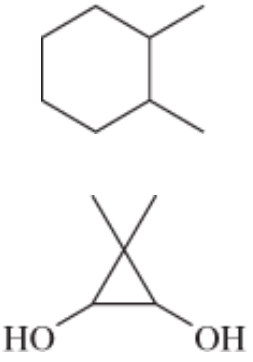


(c)

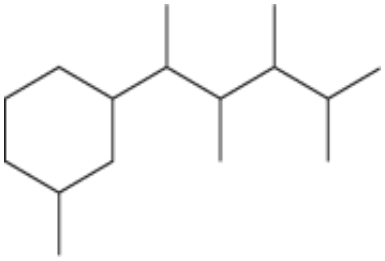


(d)

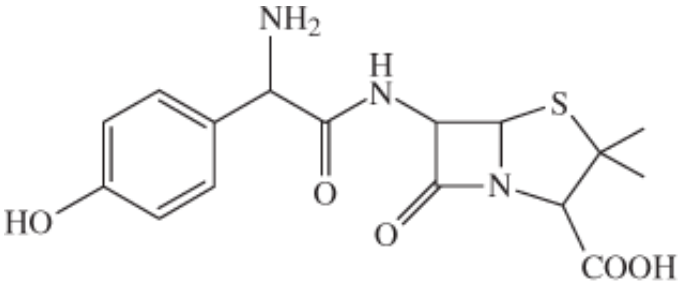
(e)



(f)

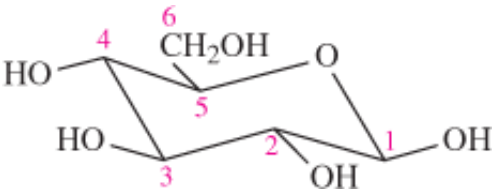


17.21 Label with asterisks the four stereocentres in amoxicillin, which belongs to the family of semisynthetic penicillins.



amoxicillin

17.22 In the more stable chair conformation of glucose, all groups on the 6-membered ring are equatorial:



(a) Identify all stereocentres in this molecule.

(b) How many stereoisomers are possible?

(c) How many pairs of enantiomers are possible?

(d) What is the configuration (*R* or *S*) at C(1) and C(5) in the stereoisomer shown?

Optical Activity: Detecting Chirality in the Laboratory

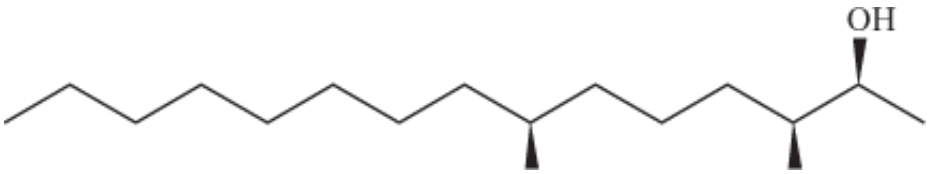
17.23 What is a racemic mixture? Is a racemic mixture optically active (i.e. will it rotate a plane of polarised light)?

17.24 The specific rotation of naturally occurring ephedrine, shown in question 17.17, is - 41°. What is the specific rotation of its enantiomer?

Chirality in the Biological World

17.25 Insects use particular organic molecules called pheromones as signals to attract mates. As an example, the pine sawfly species *Neodiprion* and *Diprion* use an ester derivative of 3,7-

dimethylpentadecan-2-ol as a sex pheromone:



(a) How many different stereoisomers exist for this molecule?

(b) The stereoisomer shown produces much of the pheromone activity of this molecule. Using the *R*,*S* naming system, give the correct name for this molecule.

(c) (c) Interestingly, the stereoisomer shown must be mixed with precisely 0.1% of the (2*S*,3*R*, 7*S*) diastereomer for maximum activity. Draw the structure of this key (2*S*,3*R*, 7*S*) isomer.

Synthesising Chiral Drugs

17.26 What are the two approaches to achieving enantiomerically pure compounds?

17.27 Why is it necessary for some drugs to be resolved into their separate enantiomers?

17.28 Ibuprofen is sold as a (±) racemic mixture. Why is it not necessary to resolve this mixture into the pure enantiomers?

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REVIEW PROBLEMS

17.29 One reason we can be sure that sp^3 hybridised carbon atoms are tetrahedral is the number of stereoisomers that can exist for different organic compounds.

(a) How many stereoisomers are possible for $CHCl_3$, CH_2Cl_2 and CHBrClF if the four atoms bonded to the carbon atom have a tetrahedral arrangement?

(b) How many stereoisomers are possible for each of the compounds if the four atoms bonded to the carbon atom have a square planar arrangement?

17.30 Using only C, H and O, write structural formulae for the lowest molar mass chiral molecule of each of the following classes of compounds.

(a) alkane

(b) alcohol

(c) aldehyde

(d) ketone

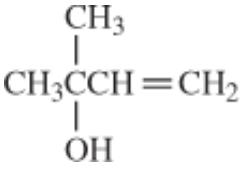
(e) carboxylic acid

17.31 Which alcohols with the molecular formula $C_5H_{12}O$ are chiral?

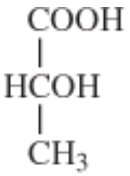
17.32 Which carboxylic acids with the molecular formula $C_6H_{12}O_2$ are chiral?

17.33 Mark each stereocentre in the following molecules with an asterisk. (*Note:* Not all contain stereocentres.)

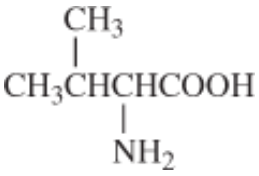
(a)



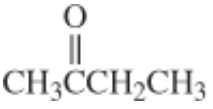
(b)



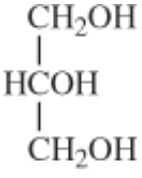
(c)



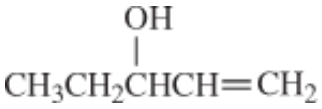
(d)



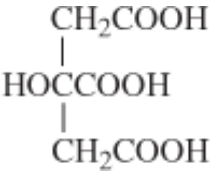
(e)



(f)

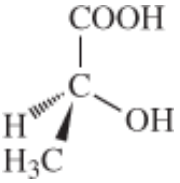


(g)

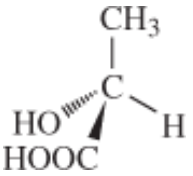


17.34 The following are eight stereorepresentations of lactic acid.

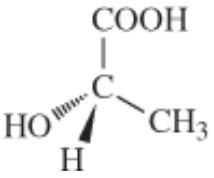
(a)



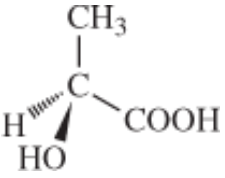
(b)



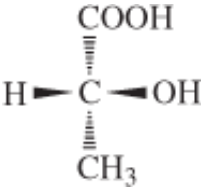
(c)



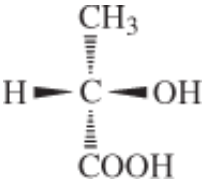
(d)



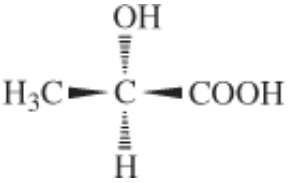
(e)



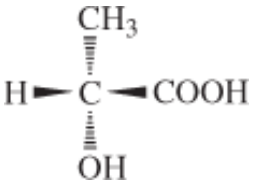
(f)



(g)

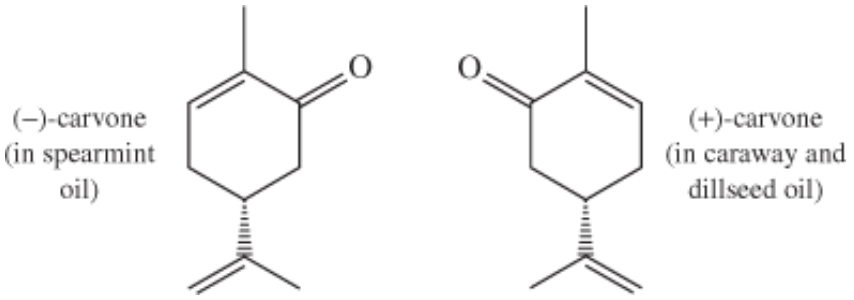


(h)



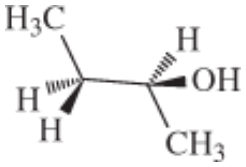
Take (a) as the reference structure. Which stereorepresentations are identical to (a) and which are mirror images of (a)?

17.35 The following are structural formulae for the enantiomers of carvone.



Each enantiomer has a distinctive odour characteristic of its source. Assign an *R* or *S* configuration to the stereocentre in each. How can they have such different properties when they are so similar in structure?

17.36 The following is a staggered conformation of one of the stereoisomers of butan-2-ol.



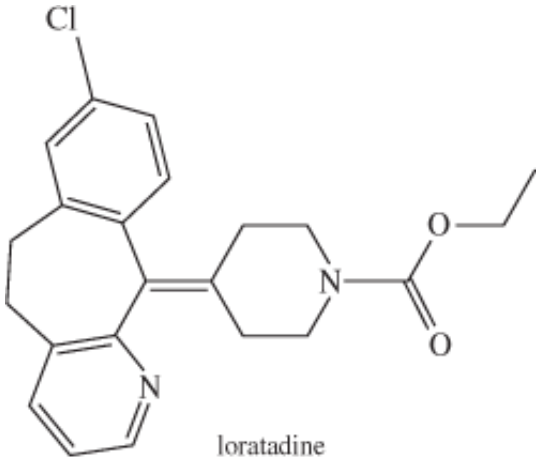
(a) Is this (*R*)-butan-2-ol or (*S*)-butan-2-ol?

(b) Draw a Newman projection for this staggered conformation, viewed along the bond between C(2) and C(3).

(c) Draw a Newman projection for one more staggered conformation of this molecule. Which of your conformations is the more stable? Assume that the —OH and —CH_3 groups are comparable in size.

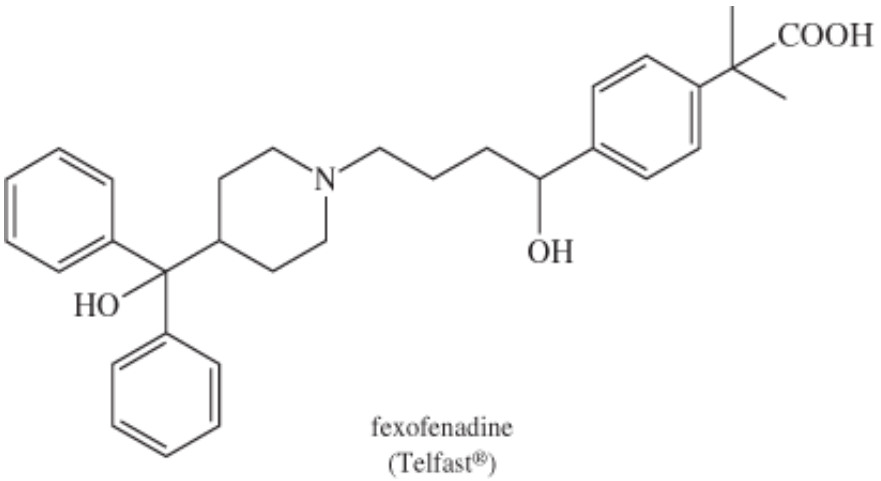
17.37 Label all stereocentres in loratadine (Claritin® in New Zealand or Claratyne® in Australia) and fexofenadine (Telfast®), now the top-selling antihistamines in Australia and New Zealand.

(a)



loratadine
(Claritin® or Claratyne®)

(b)

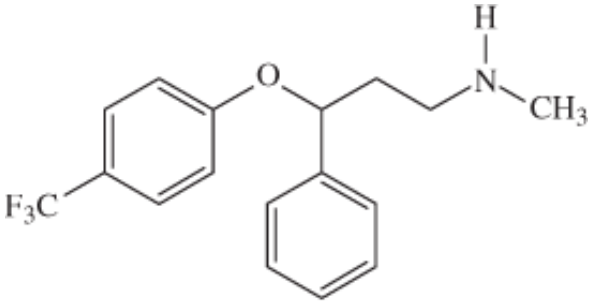


fexofenadine
(Telfast®)

How many stereoisomers are possible for each compound?

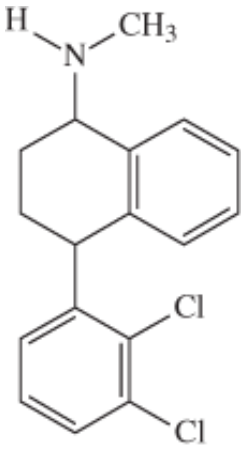
17.38 The following are structural formulae for three of the most widely prescribed drugs used to treat depression.

(a)



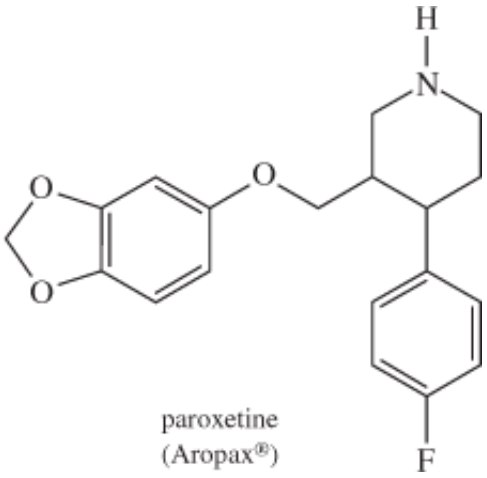
fluoxetine
(Prozac®)

(b)



Sertraline
(Zoloft®)

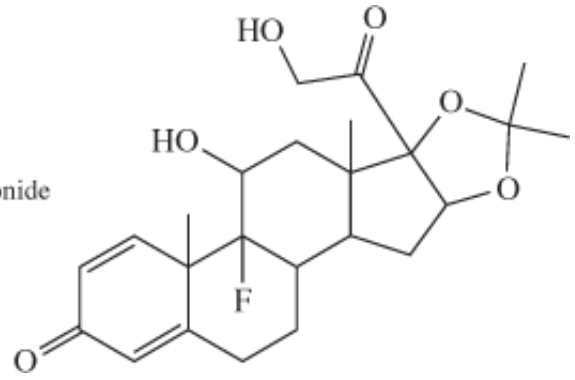
(c)



paroxetine
(Aropax®)

Label all stereocentres in each compound, and state the number of stereoisomers possible for each.

17.39 Triamcinolone acetonide, the active ingredient in Azmacort® inhalers, is a steroid used to treat bronchial asthma.



triamcinolone acetonide

(a) Label the eight stereocentres in this molecule.

(b) How many stereoisomers are possible for the molecule? (Only one stereoisomer is the active ingredient in Azmacort.)

17.40 How many stereoisomers are possible for 1,2-cyclobutanediol?

17.41 How many stereoisomers are possible for 1,3-cyclobutanediol?

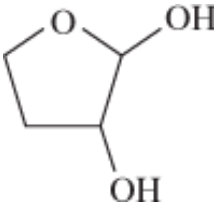
17.42 How many stereoisomers are possible for 1,2-cyclopentanediol?

17.43 How many stereoisomers are possible for 1-ethyl-2-methylcyclobutane?

17.44 How many stereoisomers are possible for 1-ethyl-3-methylcyclobutane?

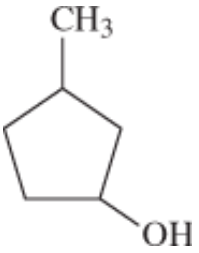
17.45 How many stereoisomers are possible for each of the following compounds?

(a)

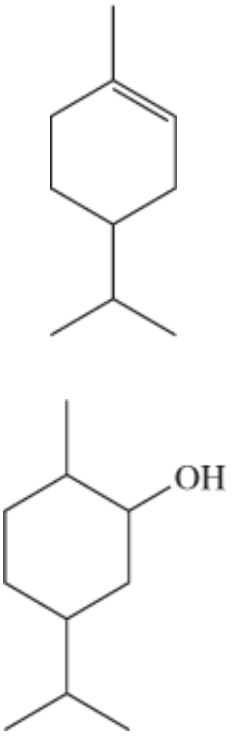


(b)

(c)

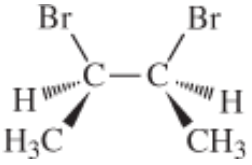


(d)

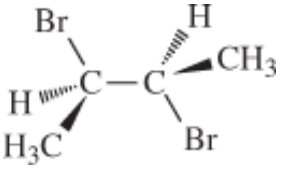


17.46 Which of the following structural formulae represent *meso* compounds?

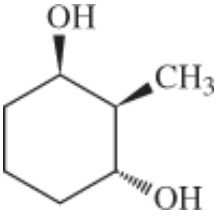
(a)



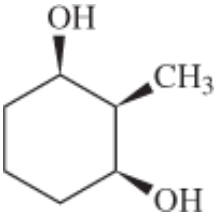
(b)



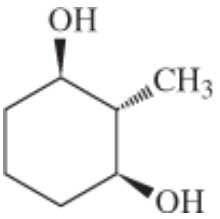
(c)



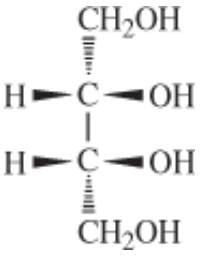
(d)



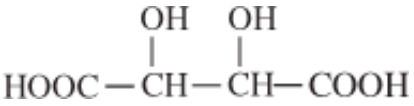
(e)



(f)

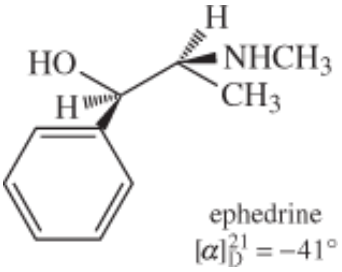


17.47 Draw a Newman projection, viewed along the bond between C(2) and C(3), for both the most stable and the least stable conformations of *meso*-tartaric acid:



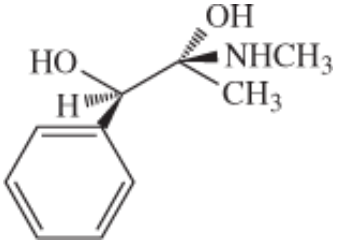
17.48 How many stereoisomers are possible for 1,3-dimethylcyclopentane? Which are pairs of enantiomers? Which are *meso* compounds?

17.49 As described in question 17.24, ephedrine is optically active and rotates a plane of polarised light 41° anticlockwise. Which of the following compounds would rotate plane-polarised light 41° in a clockwise direction?

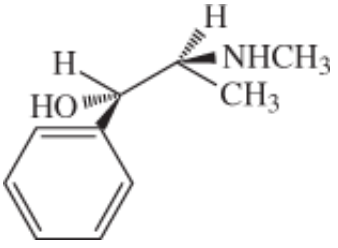


ephedrine
$[\alpha]_D^{21} = -41°$

(a)

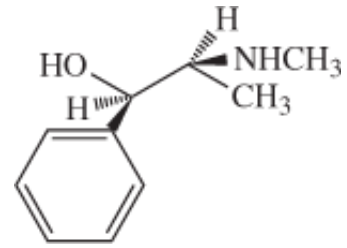


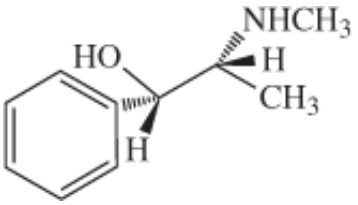
(b)



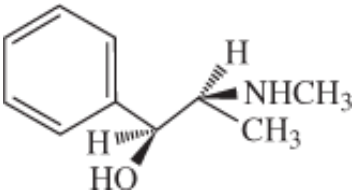
(c)

(d)





(e)

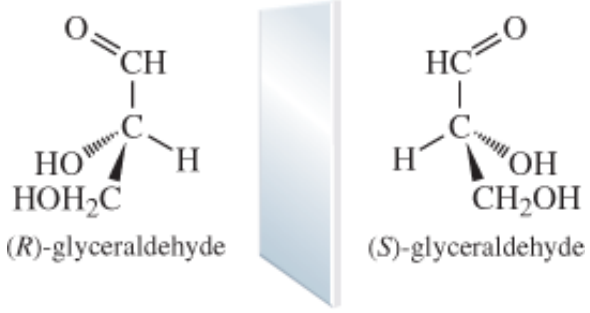


17.50 The natural product (*R*)-glyceraldehyde shown below has a specific rotation, $[\alpha]_D$ at 25 °C, of +13.5° when measured in aqueous solution. When a sample from the laboratory was measured, the observed rotation was +9.4°.

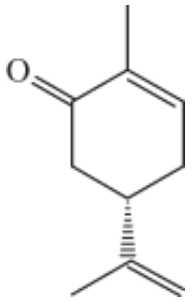
(a) Use the formula for calculating the optical activity of enantiomers to determine the concentration of (*R*)-glyceraldehyde used in this measurement.

(b) What would be the observed optical activity of this compound if the concentration used in the measurement was halved?

(c) What would be the value measured if the mixture contained half the original concentration of (*R*)-glyceraldehyde and the same amount of (*S*)-glyceraldehyde?



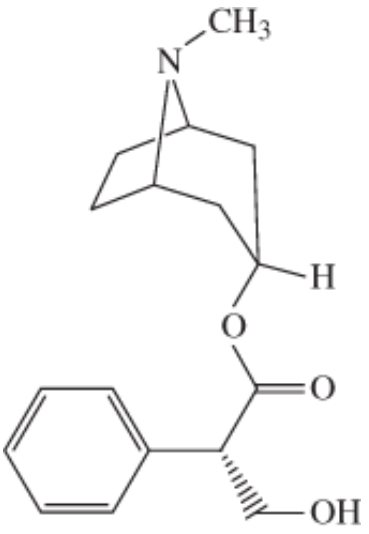
17.51 The (*S*)-enantiomer of the following molecule is (+)-carvone, which is extracted from the oil of caraway seeds:



The (*R*)-enantiomer is (-)-carvone, and it is isolated from the oil of spearmint. Draw the correct molecular structures for these molecules. If the specific rotation of a pure sample of carvone was

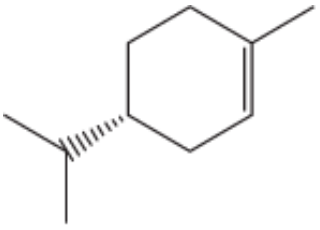
measured as +62.5° at 20 °C, which enantiomer of carvone was measured in the polarimeter?

17.52 Atropine, extracted from the plant *Atropa belladonna*, has been used in the treatment of bradycardia (low heart rate) and cardiac arrest. Draw the enantiomer of atropine.



atropine

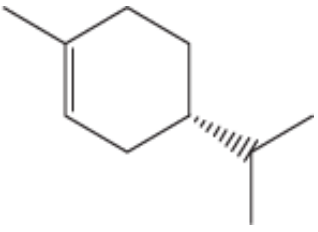
17.53 (*R*)-limonene is found in many citrus fruits, including oranges and lemons.



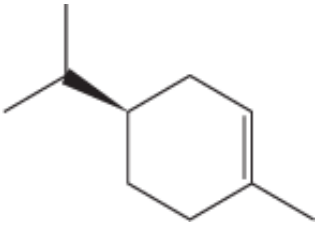
(*R*)-limonene

For each of the following compounds, identify whether it is (*R*)-limonene or its enantiomer, (*S*)-limonene.

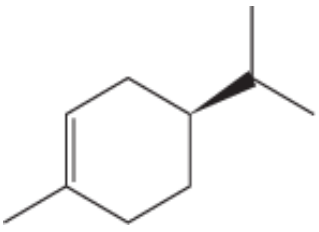
(a)

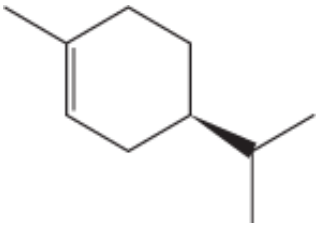


(b)



(c)



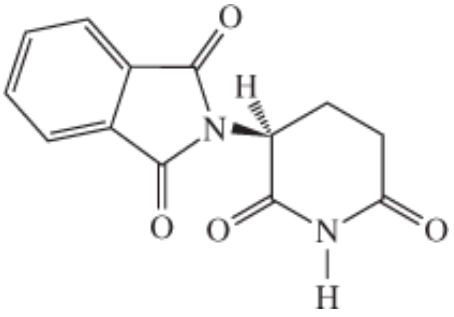
(d) 

17.54 Draw *all* possible stereoisomers of hex-4-en-2-ol.

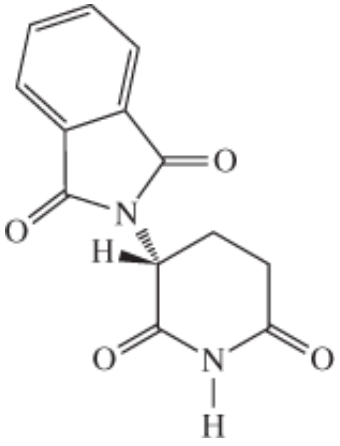
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17.55 State whether each of the following statements is true for molecules (i) and (ii).

i.



ii.



(a) Molecules (i) and (ii) are the same.

(b) Molecules (i) and (ii) are diastereomers of each other.

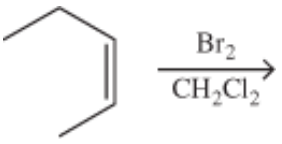
(c) Gentle heating of molecule (i) converts it to molecule (ii), so these compounds are thermal isomers.

(d) Both molecules (i) and (ii) have cyclic imide functional groups so cannot have enantiomeric isomers.

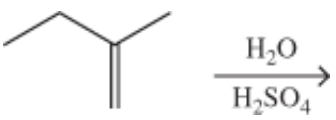
(e) Molecule (i) would rotate a plane of polarised light in the opposite direction to molecule (ii).

17.56 Predict the product(s) of the following reactions (where more than one stereoisomer is possible, show each stereoisomer).

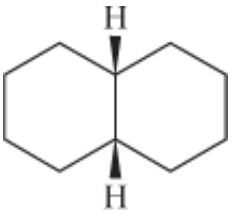
(a)



(b)

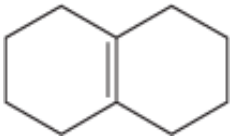


17.57 Which alkene, (a) or (b), when treated with H_2/Pd will ensure a high yield of the following stereoisomer, *cis*-decalin.

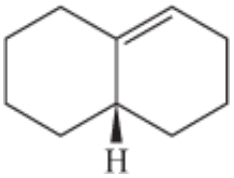


cis-decalin

(a)

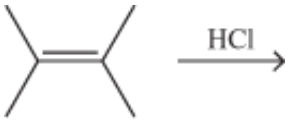


(b)

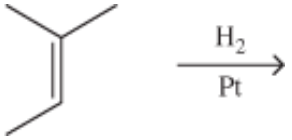


17.58 Which of the following reactions will yield a racemic mixture of products?

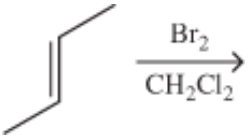
(a)



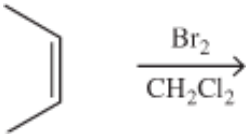
(b)



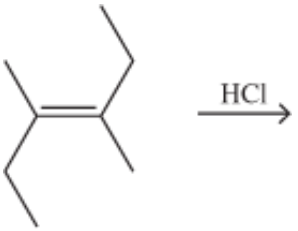
(c)



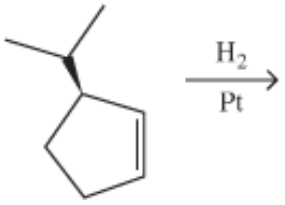
(d)



17.59 Draw all the stereoisomers that can be formed in the following reaction. Comment on how useful this particular reaction would be as a synthetic method.



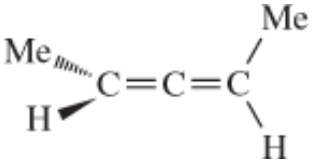
17.60 Explain why the product of the following reaction does not rotate plane-polarised light.



17.61 Using only ethylenediamine (en = $H_2NCH_2CH_2NH_2$) and bromide anions as ligands, construct a cationic octahedral complex of cobalt(III); your complex cation should have a charge of +1 and it should be chiral. Draw a three-dimensional structure for this coordination complex. Then draw the structure of a diastereomer of this complex.

17.62 Draw all possible stereoisomers of $[CoCl_2(en)(NH_3)_2]^+$. Which of these stereoisomers are chiral? (en = $H_2NCH_2CH_2NH_2$)

17.63 It is possible for a compound to be chiral even though it lacks a carbon atom with four different groups. For example, consider the structure of the following compound, which belongs to the class of compounds called allenes. This allene is chiral. Draw its enantiomer, and explain why this compound is chiral.



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KEY TERMS

achiral
asymmetric synthesis
chiral
constitutional isomers
dextrorotatory
diastereomers
enantiomers
isomers
levorotatory
meso compound
observed rotation
optical activity
plane of symmetry
plane polarised
polarimeter
R
R, S system
racemic mixture
resolution
S
specific rotation [α]
stereocentre
stereoisomers

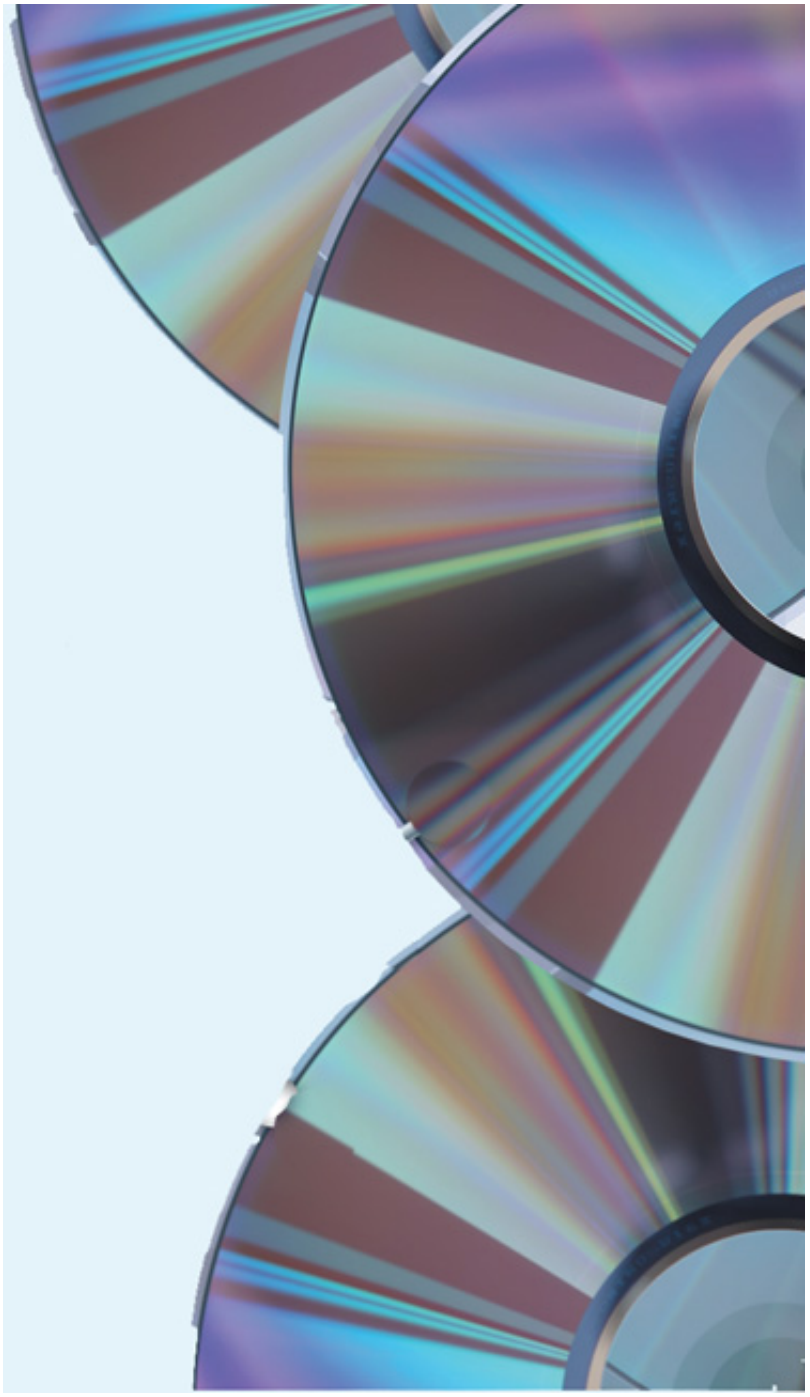
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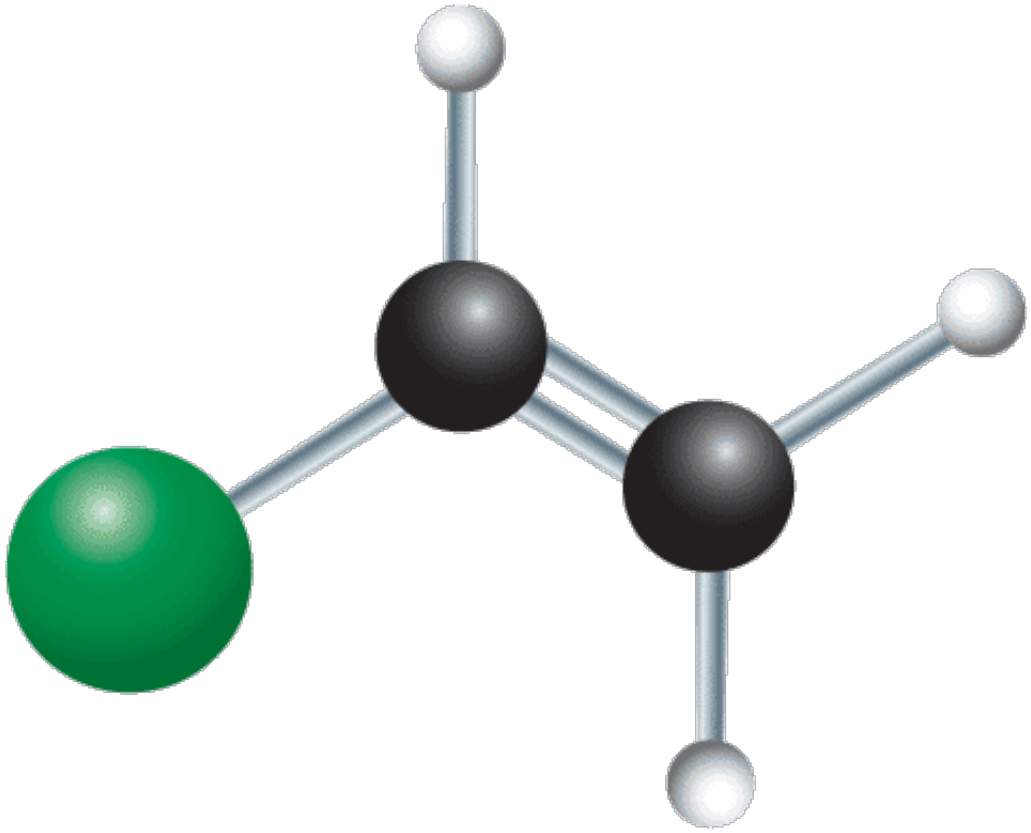
CHAPTER

18 Haloalkanes

Haloalkanes are compounds that contain a halogen atom covalently bonded to an sp^3 hybridised carbon atom. The carbon–halogen bond can be very strong, especially for fluorine, and the properties that halogen atoms impart on the molecule can be very useful. As an indication of this, almost one-fifth of all drugs contain fluorine, and haloalkanes are also used as flame retardants, in fire extinguishers and as refrigerants and solvents. While these applications arise from the low reactivity of haloalkanes, under the right chemical conditions haloalkanes can be converted to alcohols, ethers, thiols, amines and alkenes, and so they are very versatile molecules. Indeed, haloalkanes are often used as starting materials for the synthesis of many useful compounds found in all walks of life, including medicine, food chemistry and agriculture. For example, starting with the haloalkane 1,2-dichloroethane, we can produce polyvinyl chloride (the diagram below is a representation of one molecule of vinyl chloride, or chloro ethene). Polyvinyl chloride is one of the main substances that make up the CDs and DVDs in your music, software or video game collection.

Understanding how haloalkanes are transformed allows great control over the transformation of simple molecules into more valuable products. In this chapter, we study two characteristic reactions of haloalkanes: nucleophilic substitution and β-elimination.





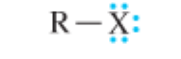
KEY TOPICS

18.1 Haloalkanes
18.2 Nucleophilic substitution
18.3 β-elimination
18.4 Substitution versus elimination

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18.1 Haloalkanes

Haloalkanes are compounds containing a halogen atom covalently bonded to an sp^3 hybridised carbon atom. The general symbol for a haloalkane is R—X, where X may be F, Cl, Br or I:



a haloalkane
(an alkyl halide)

Of all the haloalkanes, the chlorofluorocarbons (CFCs) manufactured under the trade name Freon® are the most widely known. CFCs are nontoxic, nonflammable, noncorrosive and odourless. Originally, they seemed to be ideal replacements for the hazardous compounds, such as ammonia and sulfur dioxide, formerly used in refrigeration systems. Among the CFCs most widely used for this purpose were trichlorofluoromethane (CCl_3F, Freon-11) and dichlorodifluoro-methane (CCl_2F_2, Freon-12). The CFCs also found wide use as industrial cleaning solvents. In addition, they were employed as propellants in aerosol sprays such as spray-on deodorants and spray paint (figure 18.1). However, it was theorised as early as 1974 that CFCs were responsible for damaging the stratospheric ozone layer. The ozone layer shields the Earth from short-wavelength ultraviolet radiation from the Sun. It was thought that an increase in this radiation would increase the incidence of skin cancer, as well as having a host of potentially catastrophic environmental effects. By 1987, the members of the United Nations had agreed to phase out the use of CFCs. Hydrochlorofluorocarbons (HFCs) are now used as a replacement for CFCs in many applications, including airconditioners, refrigerators and portable fire extinguishers. HFCs have much less potential to deplete the ozone layer, but their use is also being phased out.



FIGURE 18.1 In 1989, Australia banned the use of CFCs in aerosol cans. New Zealand stopped their use in 1990.

Nomenclature

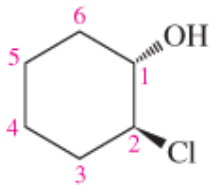
IUPAC names for haloalkanes are derived by naming the parent alkane according to the rules given in section 2.3.

- Locate and number the parent chain from the direction that gives the substituent encountered first the lower number.
- Show halogen substituents by the prefixes *fluoro-*, *chloro-*, *bromo-* and *iodo-*, and list them in alphabetical order, along with other substituents.
- Use a number preceding the name of the halogen to locate each halogen on the parent chain.



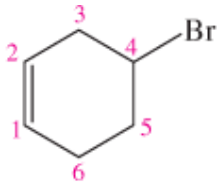
3-bromo-2-methylpentane

In molecules containing functional groups designated by a suffix (such as *-ol* for alcohols, *-al* for aldehydes, *-one* for ketones and *-oic acid* for carboxylic acids), the functional groups take precedence in the nomenclature. The location of the functional group indicated by the suffix then determines the numbering, and the halogen is simply classed as a substituent akin to an alkyl side-chain.



trans-2-chlorocyclohexanol

In haloalk*e*nes, the location of the double bond determines the numbering of the parent hydrocarbon; again, the halogen is classed as a substituent.



4-bromocyclohexene

Common names of haloalkanes consist of the common name of the alkyl group, followed by the name of the halide as a separate word. Hence, the term *alkyl halide* is a common name for this class of compounds. In the following examples, the IUPAC name of the compound is given first, followed by its common name in parentheses.



2-fluorobutane (*sec*-butyl fluoride)

chloroethene (vinyl chloride)

Methane may have one or more hydrogen atoms replaced by halogen atoms. Halogenated methanes containing more than one halogen atom are useful solvents and are generally referred to by their common names. Dichloromethane (methylene chloride) is the most widely used haloalkane solvent (see figure 18.2). Compounds of the type CHX_3 are called **haloforms**. The common name for $CHCl_3$, for example, is *chloroform*. The common name for CH_3CCl_3 is *methyl chloroform*.



FIGURE 18.2 Methyl chloroform and trichloroethene are solvents used for commercial dry-cleaning.

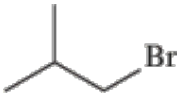
CH_2Cl_2	$CHCl_3$	CH_3CCl_3	$CCl_2{=}CHCl$
dichloromethane (methylene chloride)	trichloromethane (chloroform)	1,1,1-trichloroethane (methyl chloroform)	trichloroethene (trichloroethylene or trichlor)

WORKED EXAMPLE 18.1

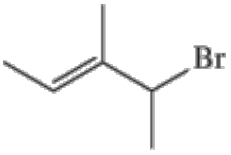
Naming Haloalkanes

Write the IUPAC name for each of the following compounds.

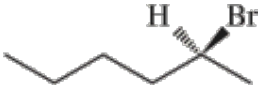
(a)



(b)



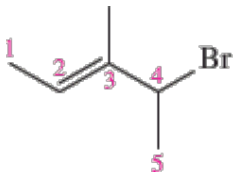
(c)



Analysis and solution

(a) The longest continuous carbon chain has three carbon atoms. There are no functional groups apart from the halogen, so the correct solution involves numbering these three carbon atoms to give the carbon atom bonded to the bromine atom the lowest number: in this case, 1. Consequently, the methyl substituent is on the second carbon atom of the chain. The IUPAC name is 1-bromo-2-methylpropane. Its common name is isobutyl bromide.

(b) There is an alkene functional group present, and this is indicated by using the suffix *–ene*. The first step involves finding the longest carbon chain that includes the double bond. Then we number this chain so that the first carbon atom of the double bond has the lowest possible number.



We then prioritise the groups present on the alkene. Of the groups bound to C(3), bromoethyl has priority over methyl (see the CIP rules in chapter 16 on p. 706). On C(2), the methyl group has priority over the hydrogen atom, which is present but not shown. The two priority groups are on opposite sides of the double bond, and this is designated *E*. Therefore, the IUPAC name is (*E*)-4-bromo-3-methylpent-2-ene. Note that C(4) is a stereocentre but, as the configuration is not shown, we cannot designate it as either *R* or *S*.

(c) There are no functional groups apart from the halogen; we number the six carbon atoms present so that the bromine atom is on C(2). In this case, C(2) is a stereocentre and there are two possible three-dimensional structures. Recall from chapter 17 that we have to prioritise the groups present on this chiral carbon atom. The bromine atom, which has the highest atomic number, has the highest priority, followed by C(3), C(1) and the hydrogen atom. Viewed with this hydrogen atom directed away from the eye, the priority groups are arranged in an anticlockwise sequence and the molecule is given the designation *S*. Therefore, the IUPAC name is (*S*)-2-bromohexane.

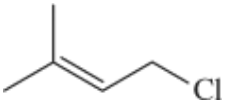
Is our answer reasonable?

Remember that, when an alkene is present, there can be two ways of constructing a molecule, so the name must include a descriptor to specify which isomer is involved. There are two ways of representing the groups on a stereocentre and the name must describe the specific isomer present.

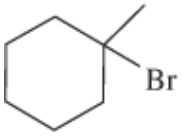
PRACTICE EXERCISE 18.1

Write the IUPAC name for each of the following compounds.

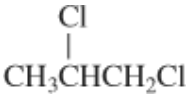
(a)



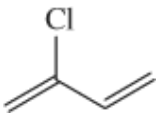
(b)



(c)



(d)



Synthesis of Haloalkanes

We learned in chapter 16 that alkanes are described as being unfunctionalised because of their very unreactive nature. Alkanes possess only strong σ bonds. Furthermore, as the electronegativities of carbon and hydrogen are so similar,

the electrons that are shared in these σ bonds are evenly distributed. This means that there are no regions of increased partial charge in alkanes; without such dipoles, neither nucleophiles nor electrophiles are attracted. This lack of reactivity led early chemists to classify alkanes as *paraffins* after the Latin term *parum affinis*, which means 'little affinity'. Alkanes can react under extreme conditions; in chapter 16 we described how complete oxidation of alkanes generates heat, CO_2 and water. In this chapter we will learn how, again under extreme reaction conditions, alkanes can be pushed to undergo a reaction called halogenation. **Halogenation** describes a reaction where some of the hydrogen atoms in alkanes are substituted by halogen atoms, most commonly chlorine or bromine.

Chlorination and Bromination

If chlorine, Cl_2, and methane gas, CH_4, are mixed together at room temperature in the absence of strong light, no reaction occurs. However, if the two gases are heated to a high temperature, or if they are exposed to an intense light source, a reaction begins and heat is liberated. As well as unreacted chlorine and methane gas, two new substances can be detected: chloromethane and hydrogen chloride. If the reaction is allowed to progress further with more chlorine gas being added, chloromethane itself begins to react and a mixture of dichloromethane, CH_2Cl_2, trichloromethane, $CHCl_3$ (also known as chloroform), and tetrachloromethane, CCl_4 (also known as carbon tetrachloride), is generated.

$$\underset{\text{methane}}{CH_4} + \underset{\text{chlorine}}{Cl_2} \xrightarrow[\text{heat}]{\text{light or}} \underset{\text{chloromethane}}{CH_3Cl} + HCl$$

$$\underset{\text{chloromethane}}{CH_3Cl} + \underset{\text{chlorine}}{Cl_2} \xrightarrow[\text{heat}]{\text{light or}} \underset{\text{dichloromethane}}{CH_2Cl_2} + HCl$$

$$\underset{\text{dichloromethane}}{CH_2Cl_2} + \underset{\text{chlorine}}{Cl_2} \xrightarrow[\text{heat}]{\text{light or}} \underset{\text{chloroform}}{CHCl_3} + HCl$$

$$\underset{\text{chloroform}}{CHCl_3} + \underset{\text{chlorine}}{Cl_2} \xrightarrow[\text{heat}]{\text{light or}} \underset{\text{carbon tetrachloride}}{CCl_4} + HCl$$

The strong conditions required for the reaction make it difficult to control, and only by using a very large excess of alkane or halogen can the reaction be limited to a single substitution product.

The mechanism by which the substitution reaction occurs is well understood and it occurs in three stages: initiation, propagation and termination. We will illustrate this process for the monochlorination of methane mentioned above:

$$\underset{\text{methane}}{CH_4} + \underset{\text{chlorine}}{Cl} \xrightarrow[\text{heat}]{\text{light or}} \underset{\text{chloromethane}}{CH_3Cl} + HCl$$

Initiation

The first stage involves breaking a bond in a chlorine molecule as a result of high temperature or absorption of light. This bond cleavage occurs evenly (homolytically) to give two chlorine atoms, 2Cl•, each with an unpaired electron in its outer shell.

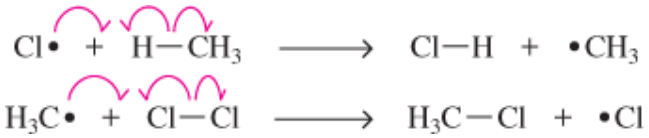
$$Cl—Cl \xrightarrow[\text{heat}]{\text{light or}} 2Cl\bullet$$

Such odd-numbered electron species are called **radicals** (or free radicals) and the overall reaction to give the chlorinated alkane is defined as a **radical substitution** reaction.

Propagation

The second stage involves formation of the product and regeneration of the radical. The initially formed chlorine radicals are extraordinarily reactive and can remove (or abstract) hydrogen atoms from other molecules to re-acquire the stable, filled, outer electron shell. In this case, the chlorine atom radical reacts with methane to give rise to HCl. (We use single-headed arrows rather than double-headed arrows to indicate that the movement of only one electron is involved.) The other product of the reaction is also a radical, in this case, a methyl radical, $\bullet CH_3$, and it is reactive enough to abstract a chlorine atom from Cl_2. This, in turn, produces another radical, and so on. We call this sequence

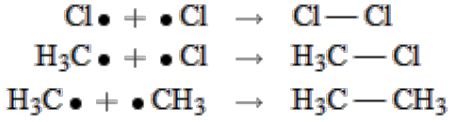
of events, where the product of one step is the reactant in the next step, a chain reaction.



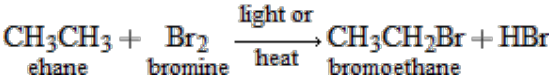
In this manner, the generation of only a few radicals in the initial homolytic stage gives rise to a substantial number of reactions with the alkane, CH_4, and, consequently, conversion to the haloalkane, CH_3Cl.

Termination

The reaction is stopped when two radicals encounter each other to produce nonradical species. Note that, because the concentration of radicals generated at any one time is so low, the chances of two radicals encountering each other are much lower than that of a radical encountering an alkane molecule.

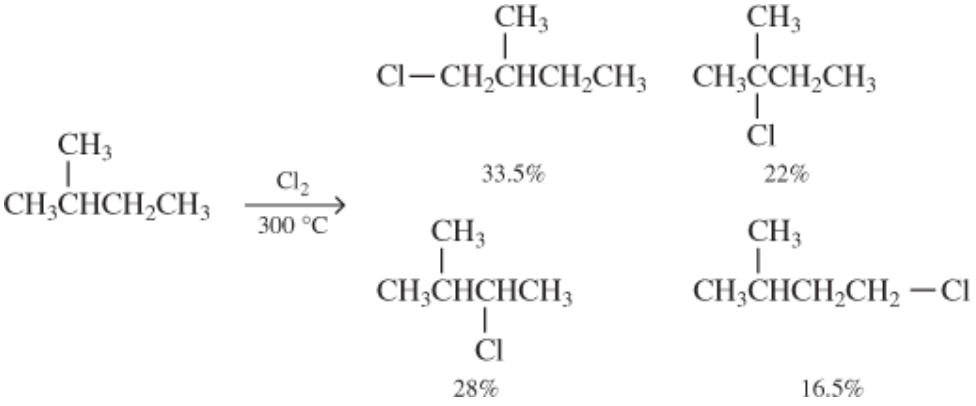


Bromine can also undergo this radical substitution reaction. For example, bromine can react with ethane to generate bromoethane and, if the reaction is not controlled, dibromoethane and tribromoethane.



While this substitution reaction can occur for the other halogens as well, it is generally used only with chlorine or bromine for a number of purely practical reasons. Fluorine, F_2, reacts with alkanes under these conditions, but the reactions are highly exothermic (reflecting the strength of the C—F bond) and so are very difficult to control. Iodine, I_2, on the other hand is seldom used because the reaction is endothermic and too much energy is required to initiate the reaction, making it difficult to control.

When an alkane with different types of C—H bonds is reacted with a halogen under these conditions, all of the possible substitution products may be detected. For instance, reacting 2-methylbutane with chlorine at 300 °C gives the following mixture of four products:



This is not a statistical distribution. As there are nine C—H bonds that are part of —CH_3 groups, two C—H bonds from —CH_2— groups and only one C—H bond on the tertiary carbon atom, the statistical distribution would be 75%, 16.7% and 8.3%. Clearly some types of C—H bonds are more susceptible to reaction than others. The products of the reaction are determined both by the numbers of C—H bonds and by the stability of the radicals that would be formed by the abstraction. For this chlorination reaction, a 3° hydrogen atom is about 4 times more likely to be substituted than a 1° C—H, and a 2° C—H is about 2.5 times more likely to be substituted than a 1° C—H. This arises from the different stability of the radicals generated by the abstraction. The halogen atom radicals Cl• and Br• have different reactivities, but the different stabilities of the carbon-centred radicals that may be formed also influence the reaction outcome. The more stable the radical, the more easily it is formed. This is because the stability of the radical is

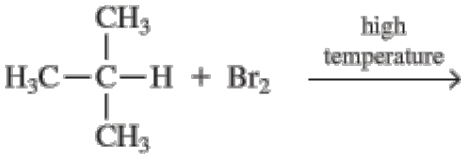
reflected in the stability of the transition state leading to its formation. Therefore, it is easier to remove a hydrogen atom from a 2° carbon atom to generate a 2° radical than it is to remove a hydrogen atom from a 1° carbon atom to produce a 1° radical. Tertiary radicals are more stable than 2° radicals. Other radicals, especially some that involve heteroatoms such as those derived from phenols, are even more stable and are important antioxidants used to interrupt the damage that more reactive radicals can generate.

WORKED EXAMPLE 18.2

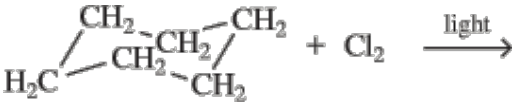
Determining the Products of Radical Substitution Reactions

Give the structures and IUPAC names of the products of the following radical substitution reactions (ignoring stereochemistry and assuming monosubstitution).

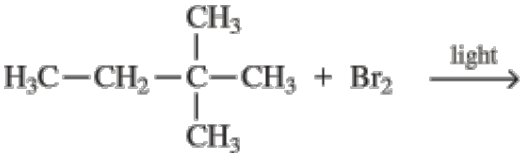
(a)



(b)

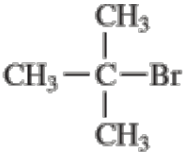


(c)

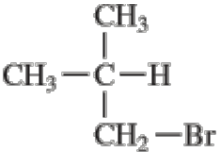


Analysis and solution

(a) The compound to be reacted with bromine is called 2-methylpropane. There are only two types of C—H bonds present in this compound. There is a single 3° C—H present, and the rest of the hydrogen atoms are part of methyl groups. This means that only two possible monosubstituted haloalkanes can arise.



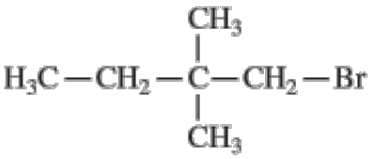
2-bromo-2-methylpropane



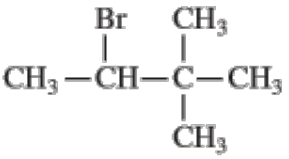
1-bromo-2-methylpropane

(b) The compound to be reacted with chlorine is called cyclohexane. As the molecule is flexible (only one monosubstitution product is possible, and no stereochemistry issues are involved), we consider that there is only one type of C—H bond present, so the product of monosubstitution with chlorine would be called chlorocyclohexane.

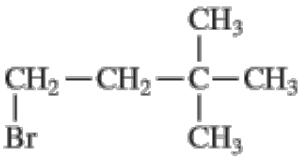
(c) The compound to be reacted with bromine is called 2,2-dimethylbutane, and there are three positions where hydrogen can be substituted by bromine.



1-bromo-2,2-dimethylbutane



3-bromo-2,2-dimethylbutane



1-bromo-3,3-dimethylbutane

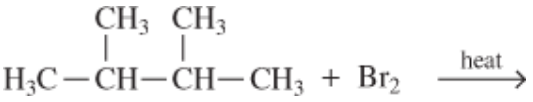
Is our answer reasonable?

Remember that single bonds are all freely rotatable, so all three CH_3 groups bound to a single carbon atom are equivalent. Under the strong conditions used for halogenation of alkanes, all possible hydrogen atoms can be substituted. The presence of halogens in an alkane is indicated by adding the prefix *chloro-* or *bromo-* to the parent alkane name. The position numbers should be chosen to give the smallest total.

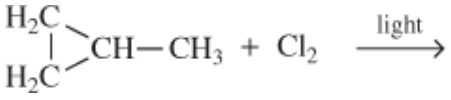
PRACTICE EXERCISE 18.2

Give the structures and write the IUPAC names for all of the possible products of the following substitution reactions (ignoring stereochemistry and assuming monosubstitution).

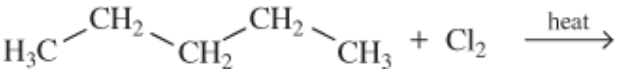
(a)



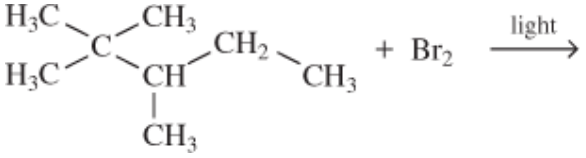
(b)



(c)



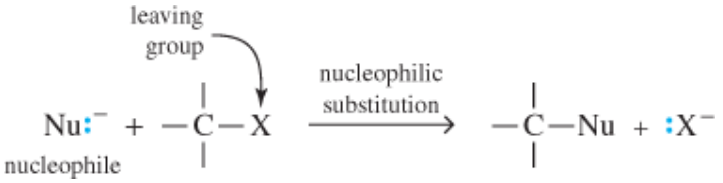
(d)



Principal Reactions of Haloalkanes

Haloalkanes are useful in the synthesis of more complicated organic molecules. This is because the polarised carbon–halogen bond is readily attacked by species with a negative character. Such species are called **nucleophiles** (which literally means ‘attracted to the nucleus’). A nucleophile is, in fact, any reagent with an unshared pair of electrons that can be donated to another atom or ion to form a new covalent bond — ‘nucleophile’ is another name for a Lewis base. **Nucleophilic substitution** is any reaction in which one nucleophile is substituted for another. In the following general equation, $Nu:^-$ is the nucleophile, X is the leaving group, and substitution takes place on an sp^3 hybridised carbon

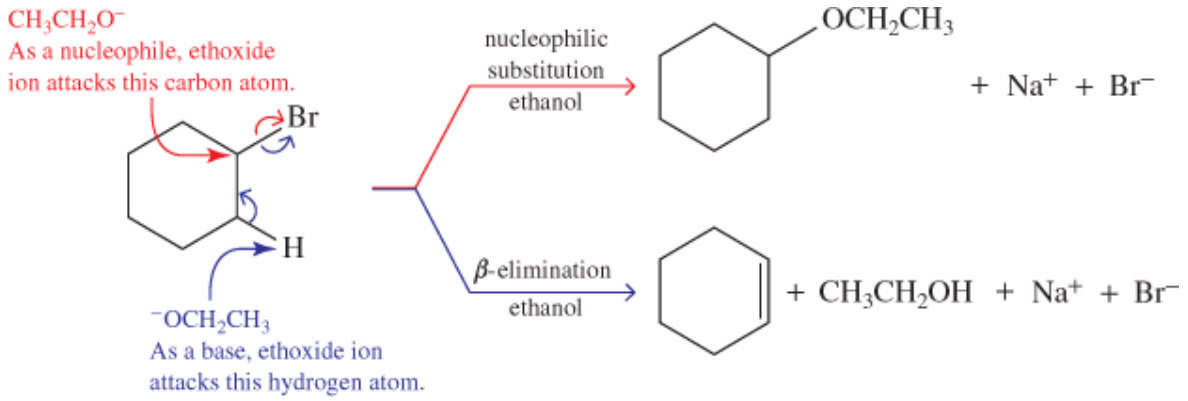
atom.



Halide ions, with a filled outer electron shell equivalent to the noble gases, make excellent leaving groups, which explains the value of haloalkanes for the synthesis of other molecules.

The process of nucleophilic substitution is evident from the name; an atom or group is replaced (substituted) by another. This is not so clear with **β-elimination**, where atoms or groups are removed from two adjacent carbon atoms. For example, H and X could be removed from a haloalkane, or H and OH from an alcohol, to give a carbon–carbon double bond in both cases.

Because all nucleophiles are also bases, nucleophilic substitution and base-catalysed β-elimination are competing reactions. (The degree to which each occurs is governed by subtle variations in structure and reaction conditions; you may encounter more on this topic in later courses.) The ethoxide ion, $CH_3CH_2O^-$, for example, is both a nucleophile and a base. With bromocyclohexane, it reacts as a nucleophile (pathway shown in red) to give ethoxycyclohexane (cyclohexyl ethyl ether) and as a base (pathway shown in blue) to give cyclohexene and ethanol.



In this chapter, we study both of these organic reactions. Using them, we can convert haloalkanes to compounds with other functional groups including alcohols, ethers, thiols, sulfides, amines, nitriles, alkenes and alkynes. Molecules with these functional groups are important as medicines, industrial chemicals and modern materials. An understanding of the nucleophilic substitution and β-elimination reactions of haloalkanes enables chemists to create some of the complex organic molecules we use in our modern society.

Chemical Connections

Fighting Fire Ants with Haloalkanes

Until recently, organochlorine compounds were used worldwide as insecticides. They are part of a group of substances referred to as persistent organic pollutants (or POPs), and many people have concerns about their environmental impact. Although these compounds are generally harmless to humans, this concern largely arises from their persistence — they remain unchanged in the environment so long that they have been detected in the breast milk of women living in the arctic tundra thousands of kilometres away from any application to control insects. Apart from their insecticidal action, organochlorines have little chemical reactivity so they are not easily degraded and can be detected in soil decades after application.

Organochlorines were used widely in Australia, especially as insecticides (most commonly DDT, heptachlor (figure 18.3), chlordane (figure 18.4), dieldrin, aldrin and lindane (figure 18.5). Dieldrin was used for treating crops to control root fly larvae, locusts, crickets and grasshoppers; in building and industry to control termites; and to control disease vectors such as cockroaches, fleas and mosquito larvae. The use of dieldrin was banned

in 1994. Heptachlor was used as a soil treatment to control ants and grubs in sugarcane, banana weevil borer (*Cosmopolites sordidus*) in banana plantations and termites in buildings and other structures. Agricultural use of heptachlor ceased in 1987, but it was still used for termite control in Queensland until 1995. Lindane has similar applications to dieldrin and heptachlor and, although its use was quickly banned in all other states of Australia, it was still used in Queensland to control white grubs and symphylids on pineapples until 2010.

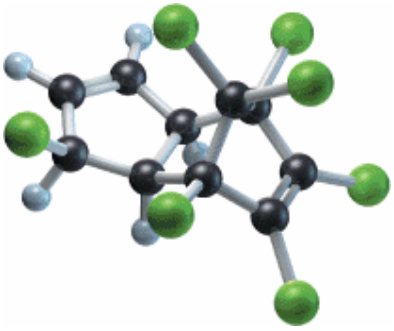


FIGURE 18.3 Heptachlor (banned in most countries, including Australia and New Zealand).

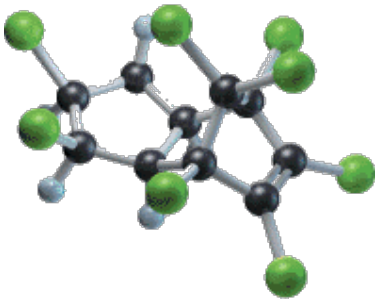


FIGURE 18.4 Chlordane.

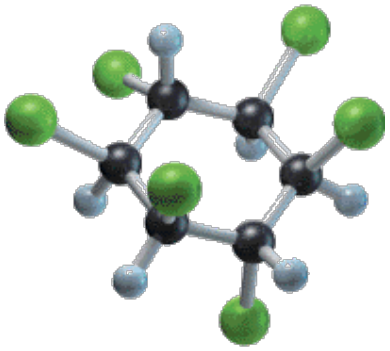


FIGURE 18.5 Lindane.

Although there is mounting evidence on the environmental impact of organochlorines, it is important to understand that, on balance, these insecticides have played very beneficial roles for humanity. Reduction in malaria deaths due to mosquito control is just one major impact of these compounds. Although chemists are now developing other insecticides to replace the banned organochlorines, these compounds still represent our most powerful weapons for controlling insects. This is evident from their recent limited approval for use in Northern Territory and Queensland in attempts to eradicate the imported red fire ant (figure 18.6), which was discovered in Brisbane in early 2001 and subsequently in Victoria and other places including Auckland.



FIGURE 18.6 A red fire ant.

Queensland's Department of Primary Industries and Fisheries described fire ants (*Solenopsis invicta*) as the greatest ecological threat to Australia's environment since the introduction of the rabbit. Fire ants are a recognised problem in the USA where they have a multibillion-dollar impact on the economy. Fire ants inflict a painful sting that often causes the skin to blister (figure 18.7). The blistering is caused by the ants using their jaws to grip the flesh while injecting a toxin called solenopsin A (figure 18.8).



FIGURE 18.7 Fire ant bites.

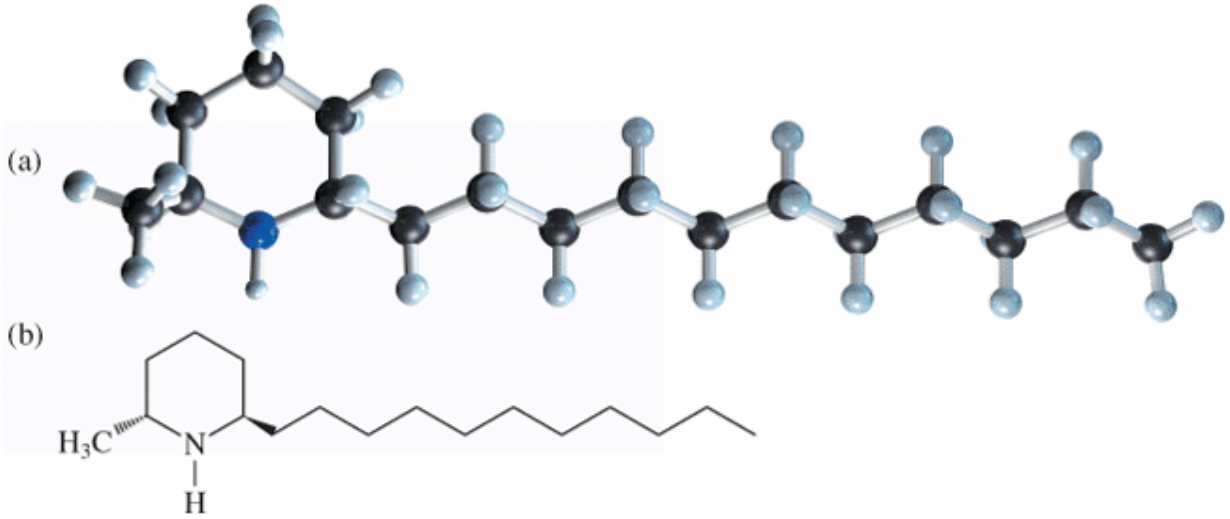


FIGURE 18.8 The structure of solenopsin A, the venom of the imported red fire ant represented as
(a) a ball-and-stick model and
(b) as a condensed line structure.

Despite some people's concerns about their environmental persistence, governments have judged that application of these powerful haloalkane insecticides is warranted to protect Australian and New Zealand flora and fauna from such imported pests.

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18.2 Nucleophilic Substitution

Nucleophilic substitution is one of the most important reactions of haloalkanes and can lead to a wide variety of new functional groups, several of which are illustrated in table 18.1.

TABLE 18.1 Some nucleophilic substitution reactions

Reaction: $Nu:^- + CH_3X \rightarrow CH_3Nu + :X^-$

Nucleophile		Product	Class of compound formed
$HO:^-$	→	CH_3OH	alcohol
$RO:^-$	→	CH_3OR	ether
$HS:^-$	→	CH_3SH	thiol (mercaptan)
$RS:^-$	→	CH_3SR	sulfide (thioether)
$:I:^-$	→	$CH_3I:$	alkyl iodide
$:NH_3$	→	$CH_3NH_3^+$	alkylammonium ion
HOH	→	$CH_3O^+(H)H$	alcohol (after proton transfer)
CH_3OH	→	$CH_3O^+(CH_3)H$	ether (after proton transfer)

Note the following points from table 18.1.

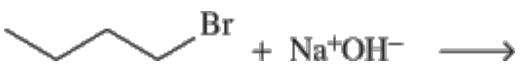
1. While the symbol $Nu:^-$ is used to represent any nucleophile, not all nucleophiles are negatively charged.
2. If the nucleophile is negatively charged, as for OH^- and RS^-, the atom donating the pair of electrons in the substitution reaction becomes neutral in the product.
3. If the nucleophile is uncharged, as for NH_3 and CH_3OH, the atom donating the pair of electrons in the substitution reaction becomes positively charged in the product. Often, the product then undergoes a second step involving proton transfer to yield a neutral substitution product.

WORKED EXAMPLE 18.3

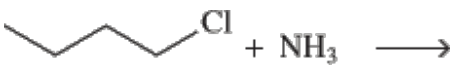
Determining the products of nucleophilic substitution

Complete the following nucleophilic substitution reactions.

(a)



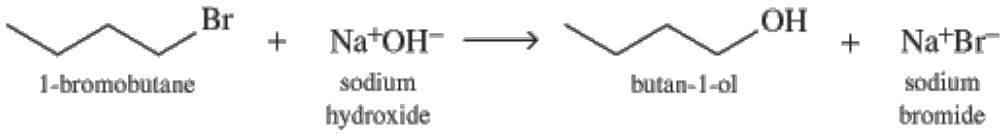
(b)



Analysis and solution

The nucleophile attacks the haloalkane and a halide ion, X^-, is ejected. (a) Hydroxide ion is the nucleophile and bromine is the leaving group:

(a)



1-bromobutane | sodium hydroxide | butan-1-ol | sodium bromide

(b) Ammonia is the nucleophile and chlorine is the leaving group:



1-chlorobutane | ammonia | butylammonium chloride

Is our answer reasonable?

Check the structures to be sure each atom has the correct valency; that is, they are bound to the appropriate number of groups and have charges as required.

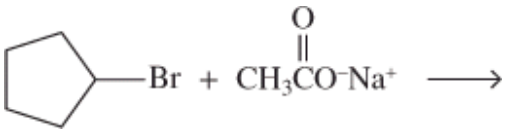
PRACTICE EXERCISE 18.3

Complete the following nucleophilic substitution reactions.

(a)



(b)



Mechanisms of Nucleophilic Substitution

On the basis of decades of experimental observations, chemists have proposed two controlling mechanisms for nucleophilic substitutions. A fundamental difference between them is the timing of bond breaking between carbon and the leaving group and of bond forming between carbon and the nucleophile.

S_N2 Mechanism

At one extreme, bond breaking and bond forming occur simultaneously. Thus, the departure of the leaving group is assisted by the incoming nucleophile. This mechanism is designated **S_N2**, where S stands for substitution, N for nucleophilic and 2 for a bimolecular reaction. A **bimolecular reaction** is one in which two species are involved in the transition state of the rate-determining step. This type of substitution reaction is classified as bimolecular because both the haloalkane and the nucleophile are involved in the rate-determining step and contribute to the rate law of the reaction:

$$\text{rate of reaction} = k[\text{haloalkane}][\text{nucleophile}]$$

Figure 18.9 shows the S_N2 mechanism for the reaction of a hydroxide ion and bromomethane to form methanol and a bromide ion. The nucleophile attacks the reactive centre from the side opposite the leaving group, as shown

in the figure below. You can see that, for a chiral compound, an S_N2 reaction at a stereocentre gives rise to a chiral product. This occurs with inversion of the configuration around the stereocentre.

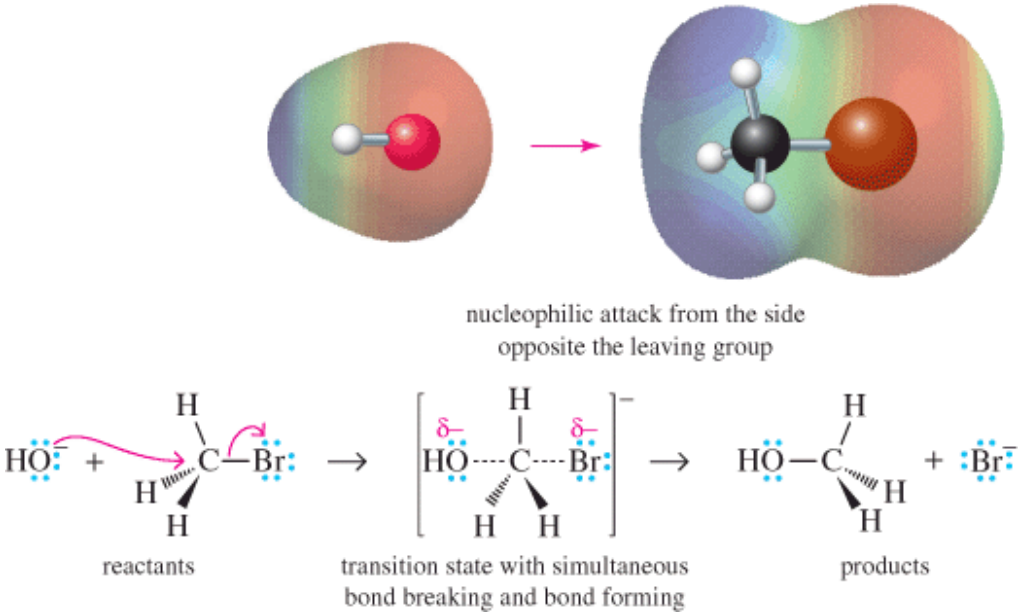


FIGURE 18.9 The S_N2 reaction is driven by the attraction between the negative charge of the nucleophile (in this case, the negatively charged oxygen atom of the hydroxide ion) and the centre of positive charge of the electrophile (in this case, the partial positive charge on the carbon atom bearing the bromine leaving group).

Figure 18.10 shows an energy diagram for an S_N2 reaction. There is a single transition state and no reactive intermediate.

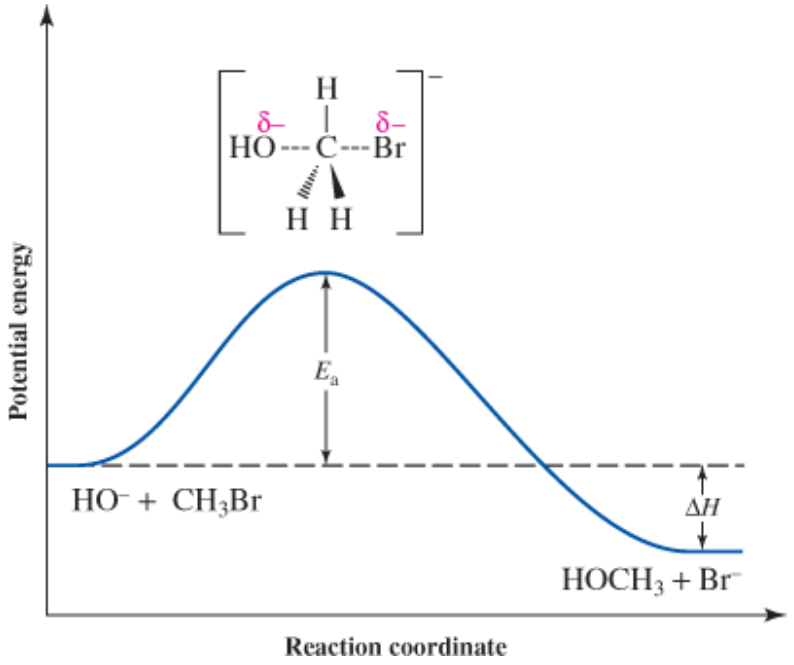


FIGURE 18.10 An energy diagram for an S_N2 reaction. There is one transition state and no reactive intermediate.

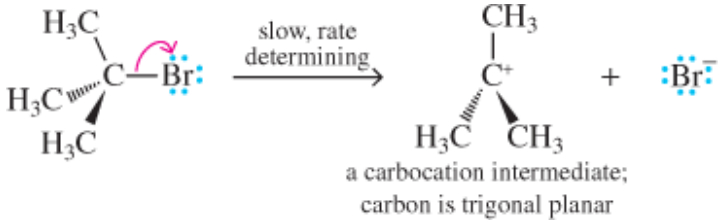
S_N1 Mechanism

In the other limiting mechanism, called **S_N1**, bond breaking between carbon and the leaving group is completed before bond forming with the nucleophile begins. In the designation S_N1, S stands for substitution, N for nucleophilic and 1 for a unimolecular reaction. A **unimolecular reaction** is one in which only one species is involved in the transition state of the rate-determining step. This type of substitution is unimolecular because only the haloalkane is involved in the rate-determining step and contributes to the rate law:

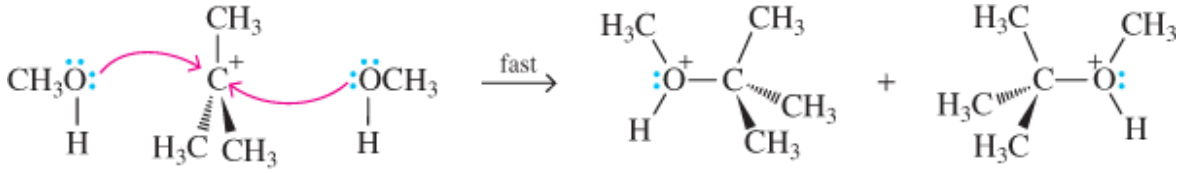
$$\text{rate of reaction} = k[\text{haloalkane}]$$

The S_N1 mechanism is illustrated by the reaction of 2-bromo-2-methylpropane (*tert*-butyl bromide) in methanol, CH_3OH, to form 2-methoxy-2-methylpropane (*tert*-butyl methyl ether). This is an example of a **solvolysis** reaction — a reaction in which the solvent plays the role of the nucleophile in the substitution reaction.

Step 1: The ionisation of a C—X bond forms a 3° carbocation intermediate:



Step 2: Reaction of methanol at either face of the planar carbocation intermediate gives an oxonium ion:



Step 3: Proton transfer from the oxonium ion to methanol (the solvent) completes the reaction and gives *tert*-butyl methyl ether:

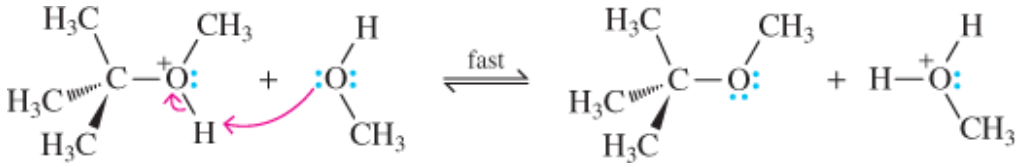


Figure 18.11 shows an energy diagram for the S_N1 reaction of 2-bromo-2-methylpropane and methanol. There is one transition state leading to formation of the carbocation intermediate in step 1 and a second transition state for the reaction of the carbocation intermediate with methanol in step 2 to give the oxonium ion. The reaction leading to formation of the carbocation intermediate has the higher energy barrier (E_{a1}), so it is the rate-determining step. Recall that you have previously encountered this type of energy diagram in chapter 15 (p. 653).

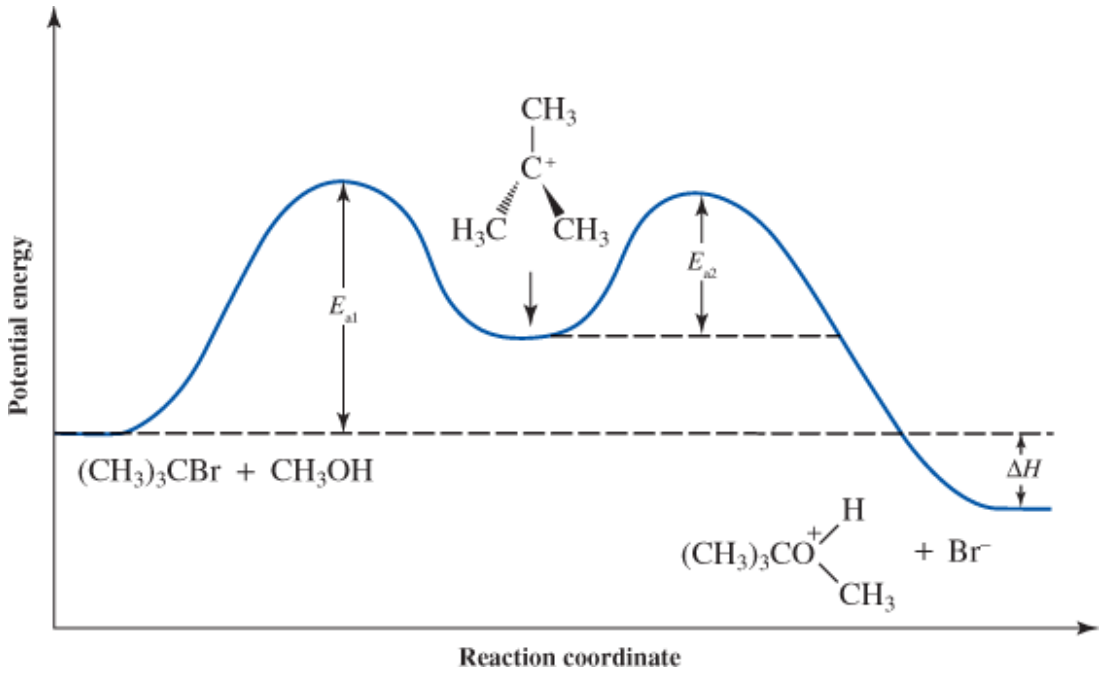
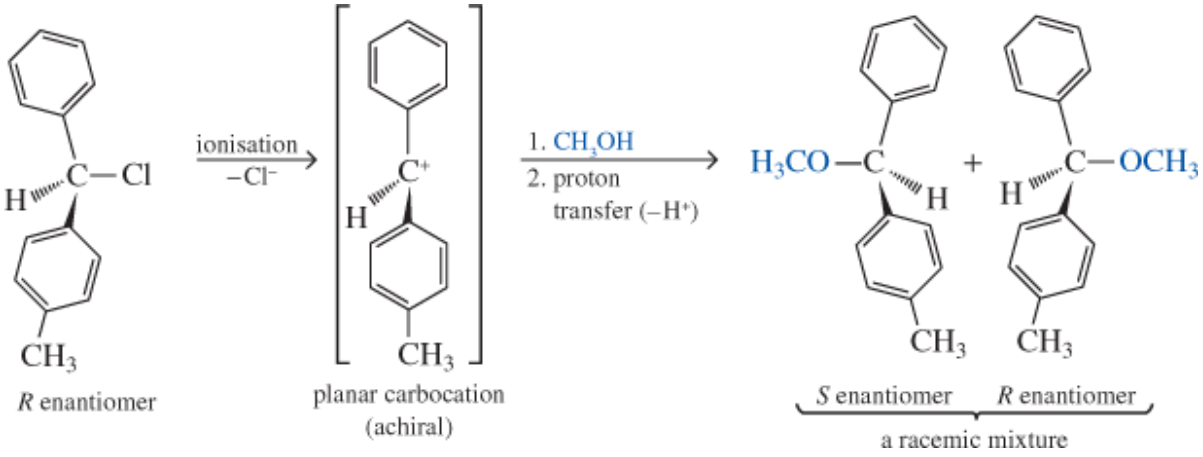


FIGURE 18.11 An energy diagram for the S_N1 reaction of 2-bromo-2-methylpropane and methanol. There is one transition state leading to formation of the carbocation intermediate in step 1 and a second transition state for the reaction of the carbocation intermediate with methanol in step 2. Step 1 crosses the higher energy barrier and so is rate determining.

If an S_N1 reaction is carried out at a tetrahedral stereocentre, the product is a racemic mixture (see chapter 17). We can illustrate this result with the following example. Upon ionisation, the *R* enantiomer forms an achiral carbocation intermediate. Attack by the nucleophile from the left face of the carbocation intermediate gives the *S* enantiomer; attack from the right face gives the *R* enantiomer. Because attack by the nucleophile occurs with equal probability from either face of the planar carbocation intermediate, the *R* and *S* enantiomers are formed in equal amounts, and the product is a racemic mixture.



Experimental Evidence for S_N1 and S_N2 Mechanisms

Let us now examine some of the experimental evidence on which these two contrasting mechanisms are based. As we do, we consider the following questions:

1. What effect does the nature of the nucleophile have on the rate of reaction?
2. What effect does the structure of the haloalkane have on the rate of reaction?
3. What effect does the structure of the leaving group have on the rate of reaction?
4. What is the role of the solvent?

Nature of the Nucleophile

Nucleophilicity is a kinetic property, which we measure by relative rates of reaction. We can establish the relative nucleophilicities for a series of nucleophiles by measuring the rate at which each displaces a leaving group from a haloalkane under defined conditions. For example, we could measure the rate at which various nucleophiles displace bromide from bromoethane in ethanol at 25 °C. The following equation shows this reaction with ammonia, NH_3, as the nucleophile:

$$CH_3CH_2Br + NH_3 \xrightarrow[25\,^\circ C]{\text{ethonol}} CH_3CH_2NH_3^+ + Br^-$$

Comparing the rate of reaction of bromoethane under these defined conditions with the nucleophiles listed in table 18.2 allows us to define their relative nucleophilicity. The more effective nucleophiles are those that react more rapidly. The nucleophiles in table 18.2 are those we deal with most commonly in this text.

TABLE 18.2 Examples of common nucleophiles and their relative effectiveness

Effectiveness as a nucleophile	Nucleophile
good	Br^-, I^-
	CH_3S^-, RS^-
	HO^-, CH_3O^-, RO^-
moderate	$CH_3\overset{O}{\overset{\|}{C}}O^-$, $R\overset{O}{\overset{\|}{C}}O^-$
	CH_3SH, RSH, R_2S
	NH_3, RNH_2, R_2NH, R_3N
poor	H_2O
	CH_3OH, ROH
	$CH_3\overset{O}{\overset{\|}{C}}OH$, $R\overset{O}{\overset{\|}{C}}OH$

Increasing nucleophilicity

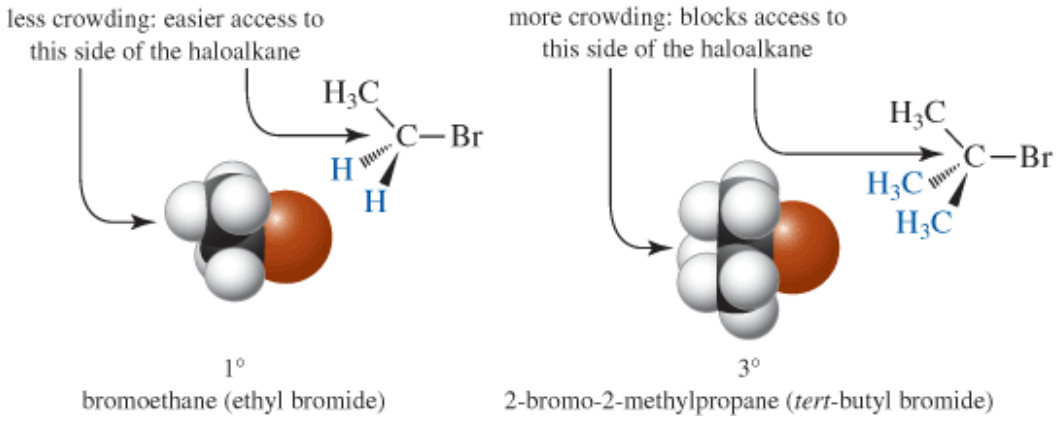
Because the nucleophile participates in the rate-determining step in an S_N2 reaction, the better the nucleophile, the more likely it is that the reaction will occur by that mechanism. The nucleophile does not participate in the rate-determining step in an S_N1 reaction. Thus, an S_N1 reaction can, in principle, occur at approximately the same rate with any of the common nucleophiles, regardless of their relative nucleophilicities.

Structure of the Haloalkane

S_N1 reactions are governed mainly by the relative stabilities of carbocation intermediates. S_N2 reactions, by contrast, are governed mainly by factors involving the size and bulkiness of the molecules involved. We describe

these factors as **steric hindrance**, which refers to the ability of groups, because of their size and shape, to hinder access to a reaction site within a molecule. S_N2 transition states are particularly sensitive to crowding around the site of reaction. The distinction is as follows:

1. *Relative stabilities of carbocations:* As we learned in section 16.5 (figure 16.29), 3° carbocations are the most stable carbocations, requiring the lowest activation energy for their formation; 1° carbo cations are the least stable, requiring the highest activation energy for their formation. In fact, 1° carbocations are so unstable that they have never been observed in solution. Therefore, 3° haloalkanes are the most likely to react by carbocation formation; 2° haloalkanes are less likely to react in this manner; and methyl and 1° haloalkanes never react in this manner.
2. *Steric hindrance:* In an S_N2 reaction, the nucleophile begins to form a new covalent bond to the substitution centre by approaching at 180° to the leaving group. If we compare the ease of approach by the nucleophile to the substitution centre of a 1° haloalkane with that of a 3° haloalkane, we see that this approach is considerably easier in the case of the 1° haloalkane. Two hydrogen atoms and one alkyl group shield the substitution centre of a 1° haloalkane. In contrast, three alkyl groups shield the substitution centre of a 3° haloalkane. This centre in bromoethane is easily accessed by a nucleophile, while there is extreme crowding around it in 2-bromo-2-methylpropane:



Given the competition between electronic and steric factors, we find that 3° haloalkanes react by the S_N1 mechanism because 3° carbocation intermediates are particularly stable and because the approach of a nucleophile to the substitution centre in a 3° haloalkane is hindered by the three groups surrounding it; 3° haloalkanes never react by the S_N2 mechanism. Halomethanes and 1° haloalkanes have little crowding around the substitution centre and react by the S_N2 mechanism; they never react by the S_N1 mechanism, because methyl and 1° carbocations are so unstable. Secondary haloalkanes may react by either the S_N1 or the S_N2 mechanism, depending on the nucleophile and solvent. The competition between electronic and steric factors and their effects on relative rates of nucleophilic substitution reactions of haloalkanes are summarised in figure 18.12.

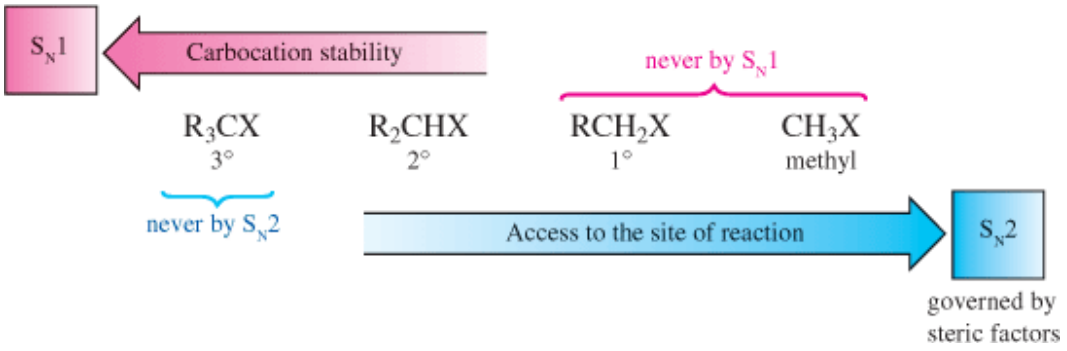
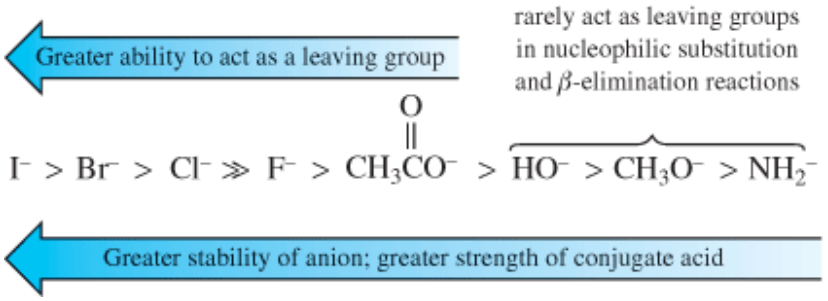


FIGURE 18.12 Effect of electronic and steric factors in competition between S_N1 and S_N2 reactions of haloalkanes.

The Leaving Group

In the transition state for nucleophilic substitution on a haloalkane, the leaving group develops a partial negative charge in both S_N1 and S_N2 reactions; therefore, the ability of a group to function as a leaving group is related to

how stable it is as an anion. The most stable anions and the best leaving groups are the conjugate bases of strong acids. Thus, we can use information on the relative strengths of organic and inorganic acids in appendix E to determine which anions are the best leaving groups:



The best leaving groups in this series are the halide ions I^-, Br^- and Cl^-. Hydroxide ions, OH^-, methoxide ions, CH_3O^-, and amide ions, NH_2^-, are such poor leaving groups that they rarely, if ever, are displaced in nucleophilic substitution reactions.

The Solvent

Solvents provide the medium in which reactants are dissolved and in which nucleophilic substitution reactions take place. Common solvents for these reactions are divided into two groups: protic and aprotic.

Protic solvents contain —OH groups and are hydrogen-bond donors. Common protic solvents for nucleophilic substitution reactions are water, low-molar-mass alcohols and low-molar-mass carboxylic acids (table 18.3). Each can solvate (see chapter 10, p. 396) both the anionic and cationic components of ionic compounds by electrostatic interaction between its partially negatively charged oxygen atom(s) and the cation and between its partially positively charged hydrogen atom and the anion. These same properties aid in the ionisation of C—X bonds to give an X^- anion and a carbocation; thus, protic solvents are good solvents in which to carry out S_N1 reactions.

TABLE 18.3 Common protic solvents

Protic solvent	Structure	Polarity of solvent	Notes
water	H_2O	Increasing	These solvents favour S_N1 reactions. The greater the polarity of the solvent, the easier it is to form carbocations in it, because both the carbocation and the negatively charged leaving group can be solvated.
formic acid	HCOOH		
methanol	CH_3OH		
ethanol	CH_3CH_2OH		
acetic acid	CH_3COOH		

Aprotic solvents do not contain —OH groups and cannot function as hydrogen-bond donors. Table 18.4 lists the aprotic solvents most commonly used for nucleophilic substitution reactions. Dimethyl sulfoxide and acetone are polar aprotic solvents; dichloromethane and diethyl ether are relatively nonpolar aprotic solvents. The aprotic solvents listed in table 18.4 are particularly good for S_N2 reactions. Polar aprotic solvents can solvate cations only; they cannot solvate anions (i.e. the anions are not closely surrounded by solvent molecules), so anions in aprotic solvents are much more reactive as nucleophiles.

TABLE 18.4 Common aprotic solvents

Aprotic solvent	Structure	Polarity of solvent	Notes
dimethyl sulfoxide (DMSO)	CH_3SCH_3 (O)	Increasing	These solvents favour S_N2 reactions. Although solvents at the top of this list are polar, the formation of carbocations in them is far more difficult than in protic solvents, because the anionic leaving group cannot be solvated by these solvents.
acetone	CH_3CCH_3 (O)		
dichloromethane	CH_2Cl_2		
diethyl ether	$(CH_3CH_2)_2O$		

Table 18.5 summarises the factors favouring S_N1 and S_N2 reactions; it also shows the change in configuration when nucleophilic substitution takes place at a stereocentre.

TABLE 18.5 Comparison between S_N1 and S_N2 reactions of haloalkanes

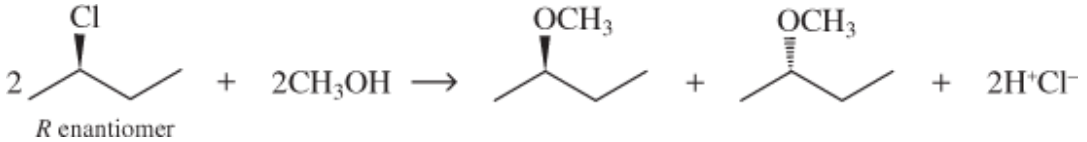
Type of haloalkane	S_N2	S_N1
methyl, CH_3X	S_N2 is favoured.	S_N1 does not occur. The methyl cation is so unstable that it is never observed in solution.
primary, RCH_2X	S_N2 is favoured.	S_N1 does not occur. Primary carbocations are so unstable that they are never observed in solution.
secondary, R_2CHX	S_N2 is favoured in aprotic solvents with good nucleophiles.	S_N1 is favoured in protic solvents with poor nucleophiles.
tertiary, R_3CX	S_N2 does not occur because of steric hindrance around the substitution centre.	S_N1 is favoured because of the ease of formation of 3° carbocations.
substitution at a stereocentre	Inversion of configuration — the nucleophile attacks the stereocentre from the side opposite the leaving group.	Racemisation — the carbocation intermediate is planar, and an attack by the nucleophile occurs with equal probability from either side.

Analysis of Several Nucleophilic Substitution Reactions

Predictions about the mechanism of a particular nucleophilic substitution reaction must be based on considerations of the structure of the haloalkane, the nucleophile, the leaving group and the solvent. The following are analyses of three such reactions.

Example 1

Methanol is a polar protic solvent and a good one in which to form carbocations. For example, 2-chlorobutane ionises in methanol to form a 2° carbocation intermediate. Methanol is a weak nucleophile. From this analysis, we predict that reaction occurs by the S_N1 mechanism. The 2° carbocation intermediate (an electrophile) then reacts with methanol (a nucleophile) followed by proton transfer to give the observed product. The product is formed as a 50 : 50 mixture of *R* and *S* configurations; that is, it is formed as a racemic mixture.



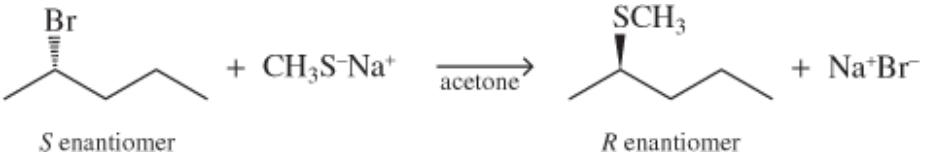
Example 2

The equation below shows a 1° bromoalkane in the presence of an iodide ion, a good nucleophile. Because 1° carbocations are so unstable, they never form in solution, and an S_N1 reaction is not possible. Dimethyl sulfoxide (DMSO), a polar aprotic solvent, is a good solvent in which to carry out S_N2 reactions. From this analysis, we predict that reaction occurs by the S_N2 mechanism.



Example 3

Bromide is a good leaving group on a 2° carbon atom. The methylsulfide ion is a good nucleophile. Acetone, a polar aprotic solvent, is a good medium in which to carry out S_N2 reactions, but a poor medium in which to carry out S_N1 reactions. Therefore, we predict that the reaction below occurs by the S_N2 mechanism, and that the product formed has the *R* configuration.

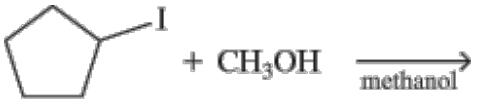


WORKED EXAMPLE 18.4

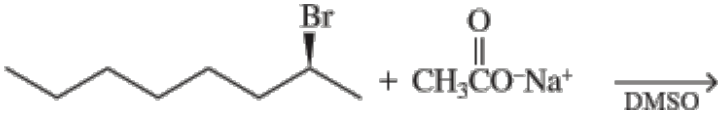
Predicting Reaction Products and Mechanisms

Write the expected product of each of the following nucleophilic substitution reactions and predict the mechanism by which the product is formed.

(a)



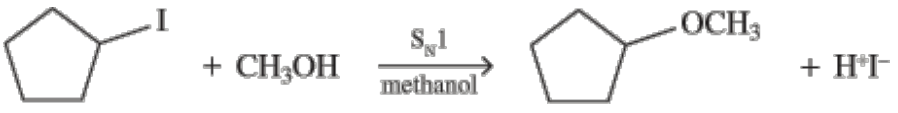
(b)



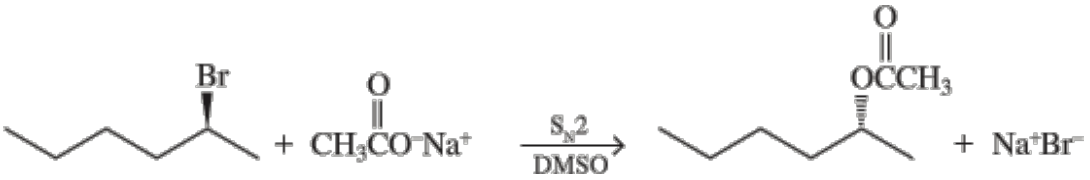
Analysis and solution

With our knowledge of the factors that control the reaction mechanisms of haloalkanes, we can predict the products and the manner in which they are formed.

(a) Methanol is a poor nucleophile. It is also a polar protic solvent that can solvate carbocations. Ionisation of the carbon–iodine bond forms a 2° carbocation intermediate. We predict that the reaction occurs by the S_N1 mechanism:



(b) Bromide is a good leaving group on a 2° carbon atom. The acetate ion is a moderate nucleophile. DMSO is a particularly good solvent for S_N2 reactions. We predict substitution by the S_N2 mechanism with inversion of configuration at the stereocentre:



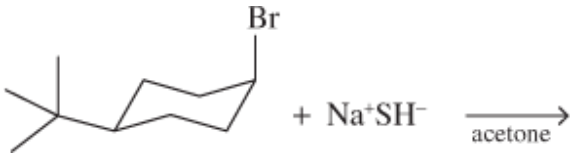
Is our answer reasonable?

Check your answer by answering these two questions: Are the products sensible in terms of the groups and bonding? Do the products have poorer leaving groups than the starting materials?

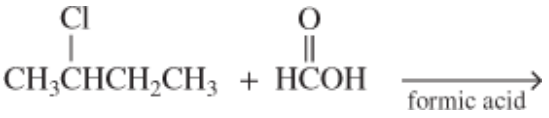
PRACTICE EXERCISE 18.4

Write the expected product of each of the following nucleophilic substitution reactions and predict the mechanism by which the product is formed.

(a)



(b)



Chemistry Research

Green Solvents

Dr Jason Harper, University of New South Wales

Solvents clearly affect the outcome of reactions, particularly by changing the free energies of starting materials and transition state complexes. This is useful synthetically as the rate, and often the utility of a process, can be modified by changing the solvent. Our group is investigating ways of affecting reaction progress using novel solvent systems.

Recently, there has been a great push towards environmentally friendly or ‘green’ chemistry. One area has been reducing the use of volatile organic solvents and replacing them with ionic liquids (see figure 18.13). Ionic liquids are salts that, unlike those simple salts made up of a metal cation and a nonmetal anion, are made up of complex ionic components; the result is that they are liquid at room temperature. While they are liquid, the forces between the components are electrostatic and very strong, so that they do not evaporate. These unique properties mean that they are not lost to the environment and are hence considered as green alternatives to conventional solvents.



FIGURE 18.13 An example of an ionic liquid; both the
(a) cation and
(b) anion are large and the charge is diffuse.

The electrostatic interactions are not just between the anion and cation components of an ionic liquid but also between the solutes dissolved in them; this solvation (see section 10.3) is typically more significant than in molecular solvents. We have shown that this can dramatically affect substitution reactions, such as those shown in figure 18.14, not only by stabilising the developing charges in the transition state but also through ordering of the solvent around the components of the reaction mixture. By changing the relative contributions of these two factors, which can be done by changing the proportion of ionic liquid in the solvent, the rate of reaction can be optimised. The ultimate goal is to develop systems in which the rate of reaction is maximised using only these environmentally friendly solvents.

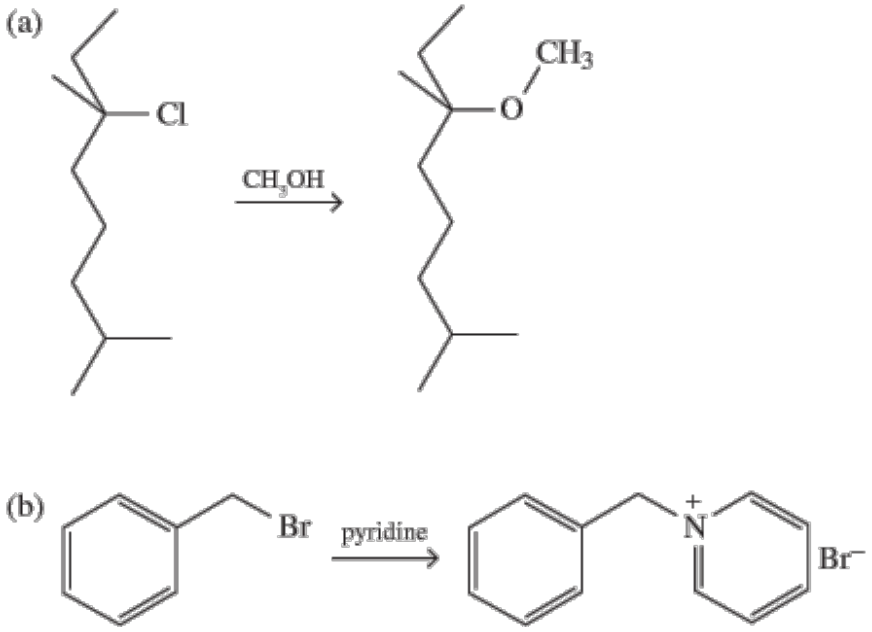
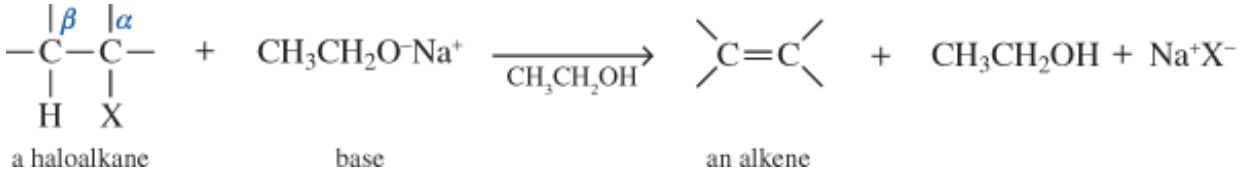


FIGURE 18.14 (a) S_N1 and
(b) S_N2 processes that are changed dramatically by moving to an ionic liquid solvent.

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18.3 β-elimination

Earlier in this chapter (p. 783), we described one of the reactions of haloalkanes as elimin ation to produce alkenes. These are called β-eliminations and, in this section, we study a type of β-elimination called **dehydrohalogenation**. In this process, in the presence of a strong base such as hydroxide ions or ethoxide ions, hydrogen can be removed from a carbon atom adjacent to the halogen, followed by removal of the halogen, to form a carbon–carbon double bond:

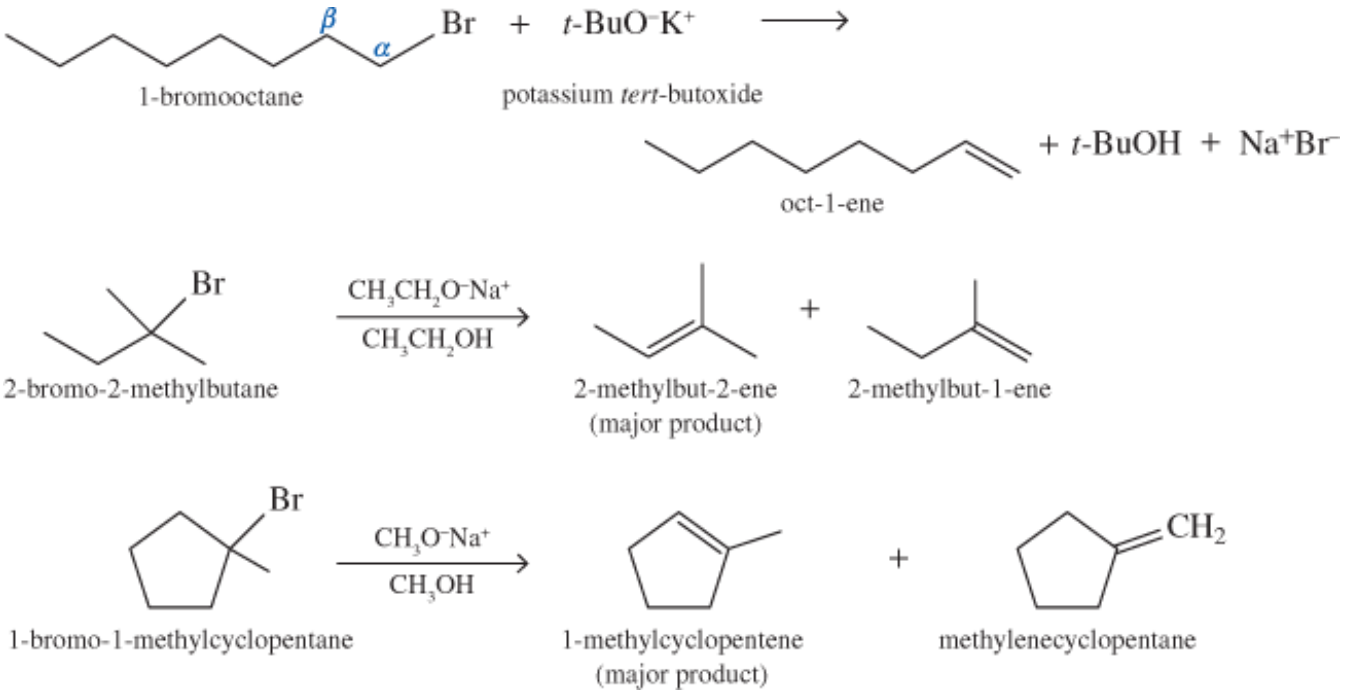


a haloalkane base an alkene

As the equation shows, we call the carbon atom bearing the halogen the α-carbon atom and the adjacent carbon atom the β-carbon atom.

Because most nucleophiles can also act as bases and vice versa, it is important to keep in mind that β-elimination and nucleophilic substitution are competing reactions. At this level, it is not necessary to explore which is more favoured, although we will deal with some of the principles that govern the outcome in section 18.4. At this stage, note that both processes may occur in the reaction of some molecules.

Common strong bases used for β-elimination are OH^-, OR^- and NH_2^-. The following are three examples of base-promoted reactions:

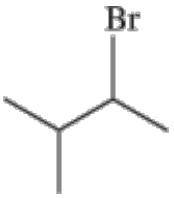


In the first example, the base is shown as a reactant on the left-hand side of the arrow and the reaction equation is balanced. In the second and third examples, although the base is still a reactant, it is shown over the reaction arrow and the equation is not balanced. In organic chemistry, we focus primarily on changes to the organic structure and we do not necessarily show the presence of reactants and spectator ions. The second and third examples are more complicated than the first; there are nonequivalent β-carbon atoms, each bearing a hydrogen atom. Therefore, two alkenes are possible from each β-elimination reaction. In each case, the major product of these and most other β-elimination reactions is the more substituted alkene (it is also the more stable alkene). This is known as **Zaitsev's rule** (or Zaitsev elimination) in honour of the chemist who first made this generalisation.

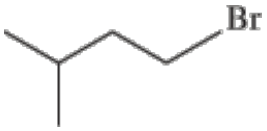
Predicting β-elimination Products

Predict the β-elimination product(s) formed when each of the following bromoalkanes is treated with sodium ethoxide in ethanol (if two products might be formed, predict the major product).

(a)



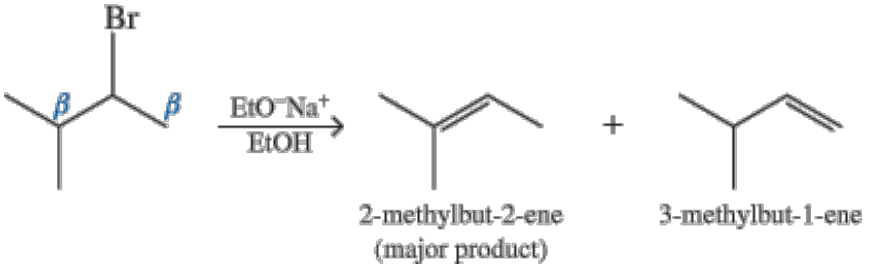
(b)



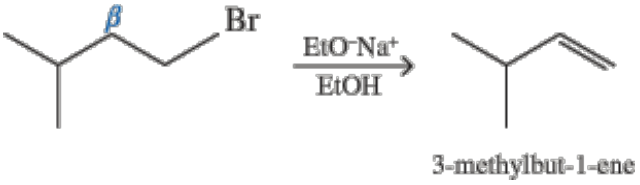
Analysis and solution

When strong bases can remove a hydrogen atom to form a relatively stable carbocation, β-elimination becomes possible.

(a) There are two nonequivalent β-carbon atoms in this bromoalkane, so two alkenes are possible. The major product is 2-methylbut-2-ene, the more substituted alkene.



(b) There is only one β-carbon atom in this bromoalkane, so only one alkene is possible.



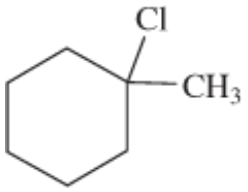
Is our answer reasonable?

You should check your answer to ensure that the newly formed double bond involves the carbon atom that was bonded to the halogen. Also, ensure that the valencies of all the atoms in the products are correct. Remember that a neutral carbon atom must always have four bonds.

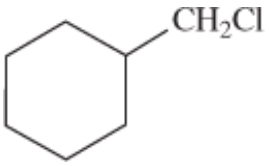
PRACTICE EXERCISE 18.5

Predict the β-elimination products formed when each of the following chloroalkanes is treated with sodium ethoxide in ethanol (if two products might be formed, predict which is the major product).

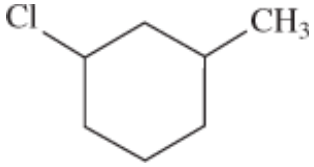
(a)



(b)



(c)



Mechanisms of β-elimination

There are two types of mechanisms for β-elimination reactions. A fundamental difference between them is the timing of the bond-breaking and bond-forming steps. Recall that we made this same statement about the two limiting mechanisms for nucleophilic substitution reactions in section 18.2.

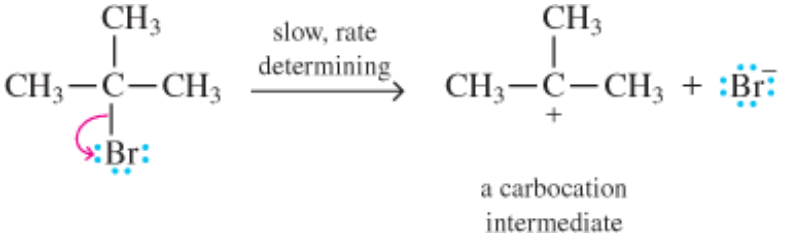
E1 Mechanism

When the carbon–halogen bond is completely broken before the base removes a hydrogen atom to give the carbon–carbon double bond, the mechanism is designated **E1**. E stands for elimination and 1 for a unimolecular reaction; only one species, in this case the haloalkane, is involved in the rate-determining step. The rate law for an E1 reaction has the same form as that for an S_N1 reaction:

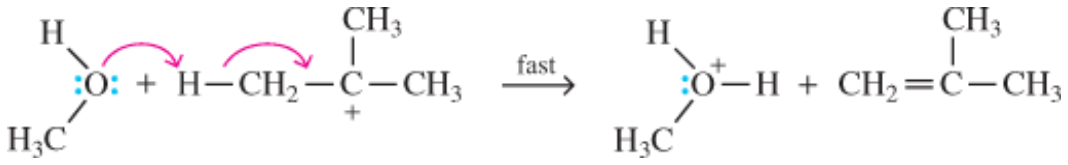
$$\text{rate of reaction} = k[\text{haloalkane}]$$

The mechanism for an E1 reaction is illustrated by the reaction of 2-bromo-2-methylpropane to form 2-methylpropene. In this two-step mechanism, the rate-determining step is the breaking of the carbon–halogen bond to form a carbocation intermediate (just as it is in the S_N1 mechanism).

Step 1: Rate-determining breaking of the C—Br bond gives a carbocation intermediate:



Step 2: Proton transfer from the carbocation intermediate to methanol (which in this instance is both the solvent and a reactant) gives the alkene:

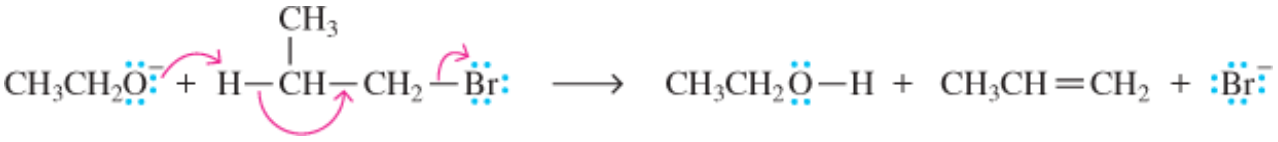


E2 Mechanism

When the base removes a β-hydrogen atom at the same time as the carbon–halogen bond is broken, it is designated an **E2** reaction. E stands for elimination and 2 for a bimolecular reaction. The rate law for the rate-determining step depends on both the haloalkane and the base:

$$\text{rate of reaction} = k[\text{haloalkane}][\text{base}]$$

The stronger the base, the more likely it is that the E2 mechanism will dominate. We illustrate the E2 mechanism by the reaction of 1-bromopropane with sodium ethoxide. In this mechanism, proton transfer to the base, formation of the carbon–carbon double bond and ejection of the bromide ion occur simultaneously; that is, all bond-forming and bond-breaking steps occur at the same time.



For both E1 and E2 reactions, the major product is that formed in accordance with Zaitsev's rule as illustrated by this E2 reaction:

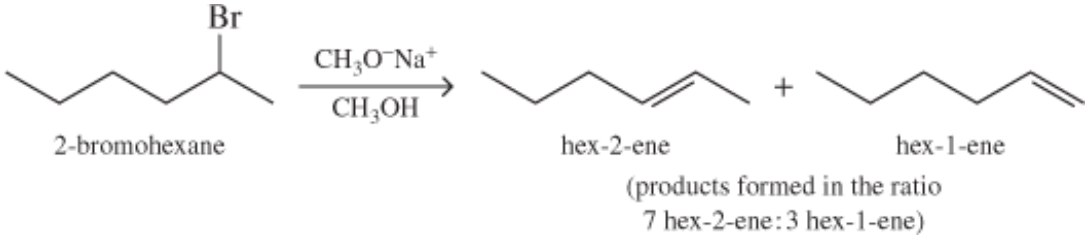


Table 18.6 summarises the generalisations made on this and the previous pages about reactions of haloalkanes.

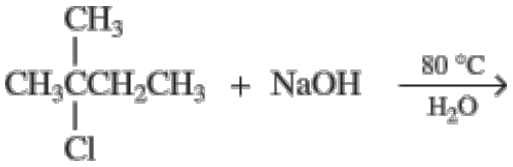
TABLE 18.6 Comparison between E1 and E2 reactions of haloalkanes

Haloalkane	E1	E2
primary, RCH_2X	E1 does not occur. Primary carbocations are so unstable that they are never observed in solution.	E2 is favoured.
secondary, R_2CHX	E1 is the main reaction with weak bases such as H_2O and ROH.	E2 is the main reaction with strong bases such as OH^- and OR^-.
tertiary, R_3CX	E1 is the main reaction with weak bases such as H_2O and ROH.	E2 is the main reaction with strong bases such as OH^- and OR^-.

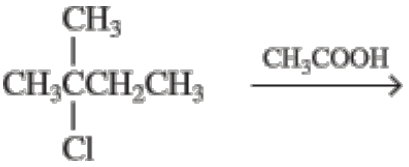
Predicting β-elimination Reaction Mechanisms

Predict whether each of the following β-elimination reactions proceeds predominantly by the E1 or E2 mechanism, and write a structural formula for the major organic product.

(a)



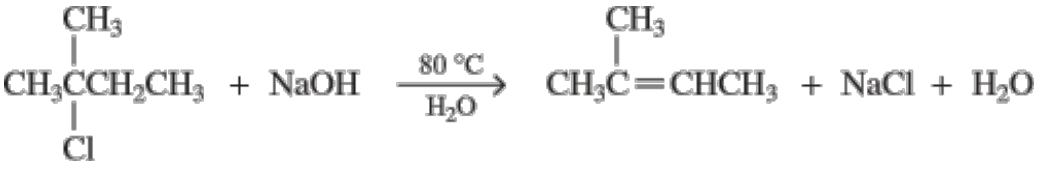
(b)



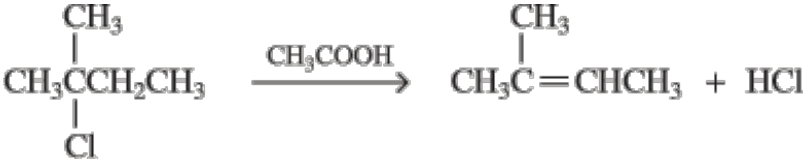
Analysis and solution

Based on the structure of the haloalkane and the strength of the acid, the likely reaction mech anism can be determined.

(a) A 3° chloroalkane is heated with a strong base. Elimination by an E2 reaction predominates, giving 2-methylbut-2-ene as the major product:



(b) A 3° chloroalkane is dissolved in acetic acid, a solvent that promotes the formation of carbocations, to form a 3° carbocation that then loses a proton to give 2-methylbut-2-ene as the major elimination product. The reaction occurs by the E1 mechanism:



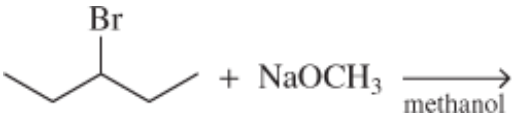
Is our answer reasonable?

Check your answer by asking these two questions: Do the structures make sense? Are the conditions and base strength sufficient for the reaction described?

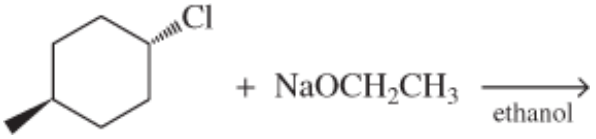
PRACTICE EXERCISE 18.6

Predict whether each of the following β-elimination reactions proceeds predominantly by the E1 or E2 mechanism, and write a structural formula for the major organic product:

(a)



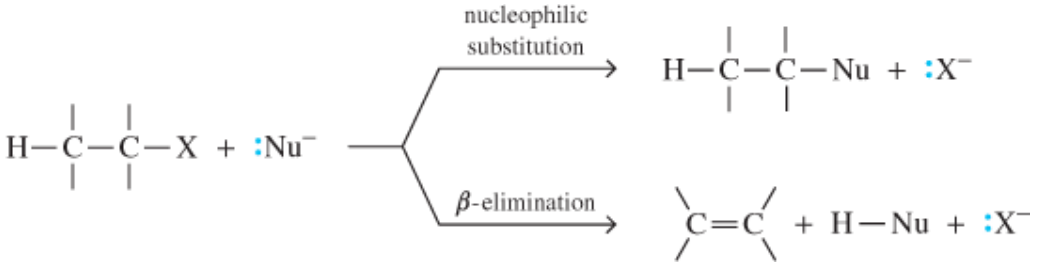
(b)



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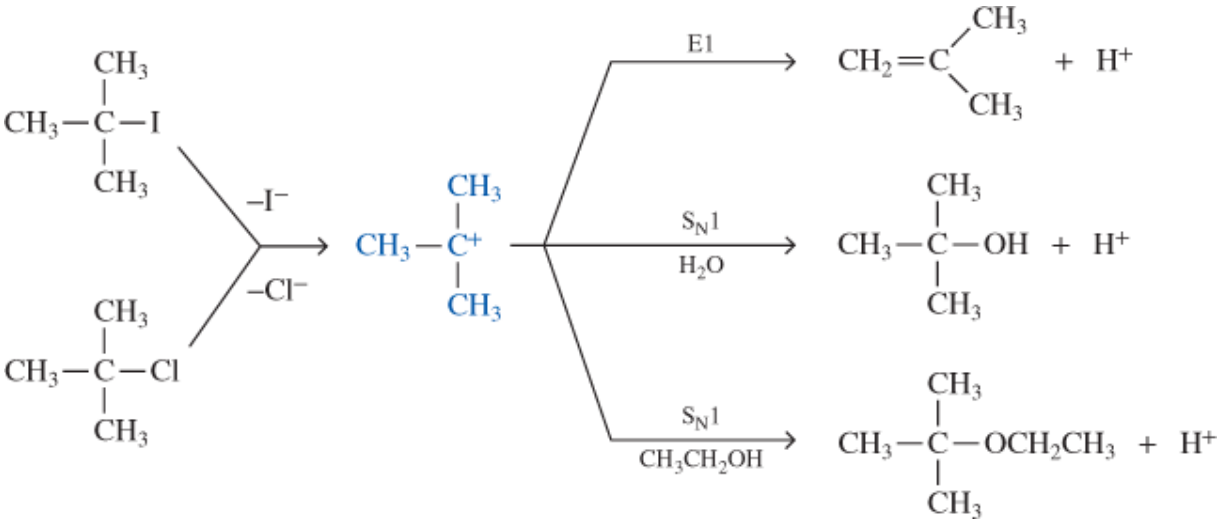
18.4 Substitution Versus Elimination

Thus far, we have considered two types of reactions of haloalkanes: nucleophilic substitution and β-elimination. Many of the nucleophiles we have examined, such as hydroxide ions and alkoxide ions, are also strong bases. Accordingly, nucleophilic substitution and β-elimination often compete with each other, and the ratio of products formed by these reactions depends on the relative rates of the two reactions:



S_N1 Versus E1 Reactions

Reactions of 2° and 3° haloalkanes in polar protic solvents give mixtures of substitution and elimination products. In both reactions, step 1 is the formation of a carbocation intermediate. This step is then followed by either (1) the loss of a hydrogen atom to give an alkene (E1), or (2) reaction with the solvent to give a substitution product (S_N1). In polar protic solvents, the products formed depend only on the structure of the particular carbocation. For example, *tert*-butyl chloride and *tert*-butyl iodide in 80% aqueous ethanol both react with the solvent, giving the same mixture of substitution and elimination products:



Because the iodide ion is a better leaving group than the chloride ion, *tert*-butyl iodide reacts over 100 times faster than *tert*-butyl chloride. However, the ratio of products is the same.

Chemistry Research

Haloalkane Chemistry

Associate Professor Roger Read, Molecular Design and Synthesis Group, University of New South Wales

Halogen atoms are generally monovalent and, in this respect, can participate in bonding in a similar way to hydrogen atoms. Haloalkanes resemble hydrocarbons and are found as small and large molecules, straight-chained and branched, saturated and unsaturated. They can also exist as singly substituted species or in multisubstituted situations. The presence of a halogen imparts reactivity to the hydrocarbons, but, because the carbon–halogen bond is relatively strong, haloalkanes are relatively stable. For example, well-known chlorinated hydrocarbons, such as dichloromethane, CH_2Cl_2, chloroform, $CHCl_3$, and trichloroethane,

CH_3CCl_3, are extremely useful solvents. They undergo reaction under sometimes mild conditions, but the ease of reaction depends on the type of halogen (iodoalkanes are the most reactive while fluoroalkanes are the least reactive) and the degree of substitution at the point of attachment.

Fully fluorinated molecules, such as perfluorohexane (tetradecafluorohexane, figure 18.15), have two extremely interesting properties. Firstly, they dissolve very large quantities of oxygen, compared with other solvents. Secondly, the perfluorocarbons do not mix well with water or regular (organic) solvents such as toluene, ethyl acetate, ethanol or acetonitrile. These features have made them suitable as short-term blood replacements. Polymers of perfluoroalkanes have also been developed and those derived from poly(tetrafluoroethylene) are well known under the trade name of Teflon®. These materials repel water and greases and are relatively heat stable. This allows the polymeric material to be applied to surfaces to give them nonstick properties. The same materials can also be incorporated into paints and cloth to make them nonstick, water resistant and dirt resistant.

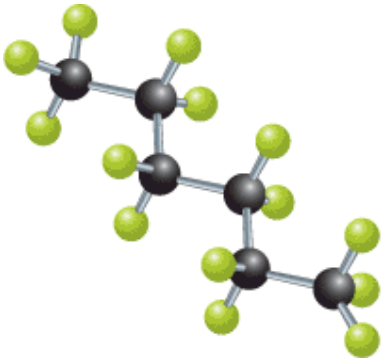


FIGURE 18.15 Perfluorohexane (see figure 18.19 for more detail).

There is also growing use for perfluorocarbons, such as perfluorohexane, C_6F_{14}, as specialist solvents in liquid–liquid separation technologies, and hybrid solvents, such as benzotrifluoride (trifluoromethylbenzene, $C_6H_5CF_3$), for reaction media. Conventional systems allow separation of solutes into water or organic solvents. For example, the separation of sugar from petrol is easily achieved by shaking the mixture with water; the sugar dissolves in the water and can be removed by separating the two layers of water and petrol. Because perfluorocarbons do not mix with aqueous or with organic solvents, they form a three-phase system: organic, aqueous and fluorous (figure 18.16), allowing an additional opportunity for separation.

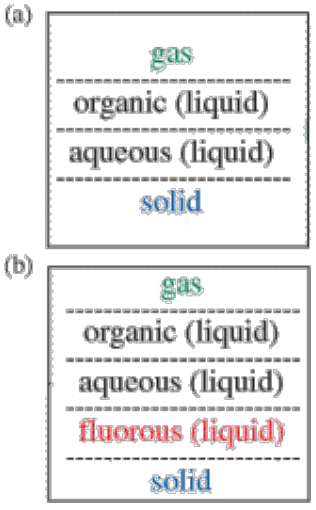


FIGURE 18.16 Comparison of
(a) 2-phase and
(b) 3-phase liquid systems for separation of reaction mixtures.

As part of this effort, the Molecular Design and Synthesis Group at the University of New South Wales has been designing tagging agents that will temporarily introduce highly fluorinated alkyl groups to molecules to aid in organic synthesis (for example, see figure 18.17). If a Teflonlike coating is applied separately to an adsorbant, this can allow separation of fluorous-tagged substances by simple filtration through the modified adsorbant. This operation takes advantage of conventional solid-phase extraction (SPE) and introduces fluorous solid-phase extraction (FSPE). After separation, the fluorous tags can be removed and the molecules returned to their normal state and behaviour. This type of chemistry is very new and there are many new tagging agents and reagents that could be developed.

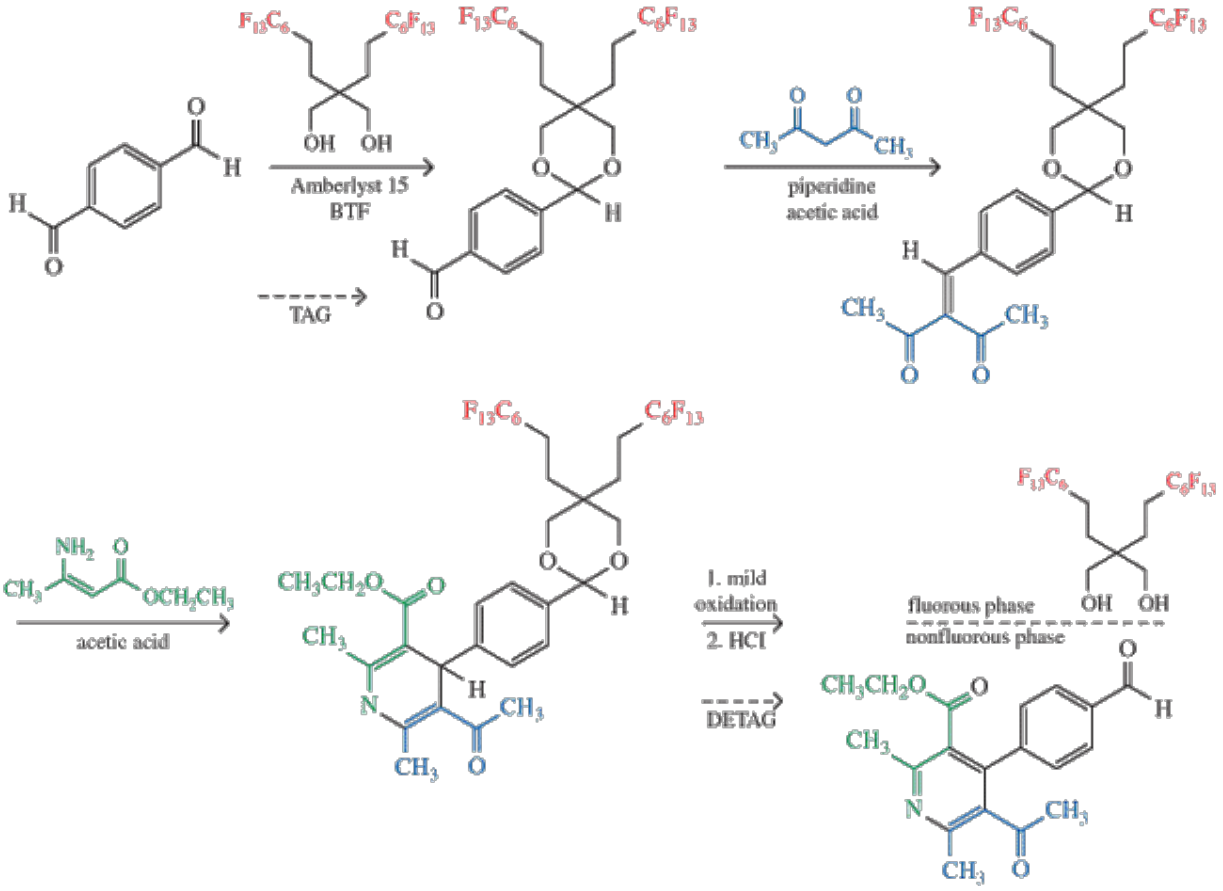


FIGURE 18.17 A typical synthesis in which a fluorous tag (in this case, a diol with polyfluoroalkyl groups, shown in red) is introduced to assist in separation events during intermediate stages of the synthetic process. Removal at the final step releases the desired nonfluorous product and again provides easy separation from the fluorous material. Note that in this synthesis the taggant also serves to protect one aldehyde group (as an acetal); the tagging agent can be recovered and recycled.

The strong dislike of nonfluorous entities for fluorine causes highly fluorinated alkyl groups to be shunned and actually aggregate together out of defence; they aggregate even more efficiently than comparable hydrocarbon systems. This has opened up further opportunities to design well-defined but totally artificial and stable multilayer, micelle and vesicle structures. We are investigating this approach in the design of functional fluorous surfactants based on small heterocyclic compounds (figure 18.18). Aggregates of the molecules could form molecular containers and special surface active materials, while substituents attached to the molecules will be designed to provide added functionality.

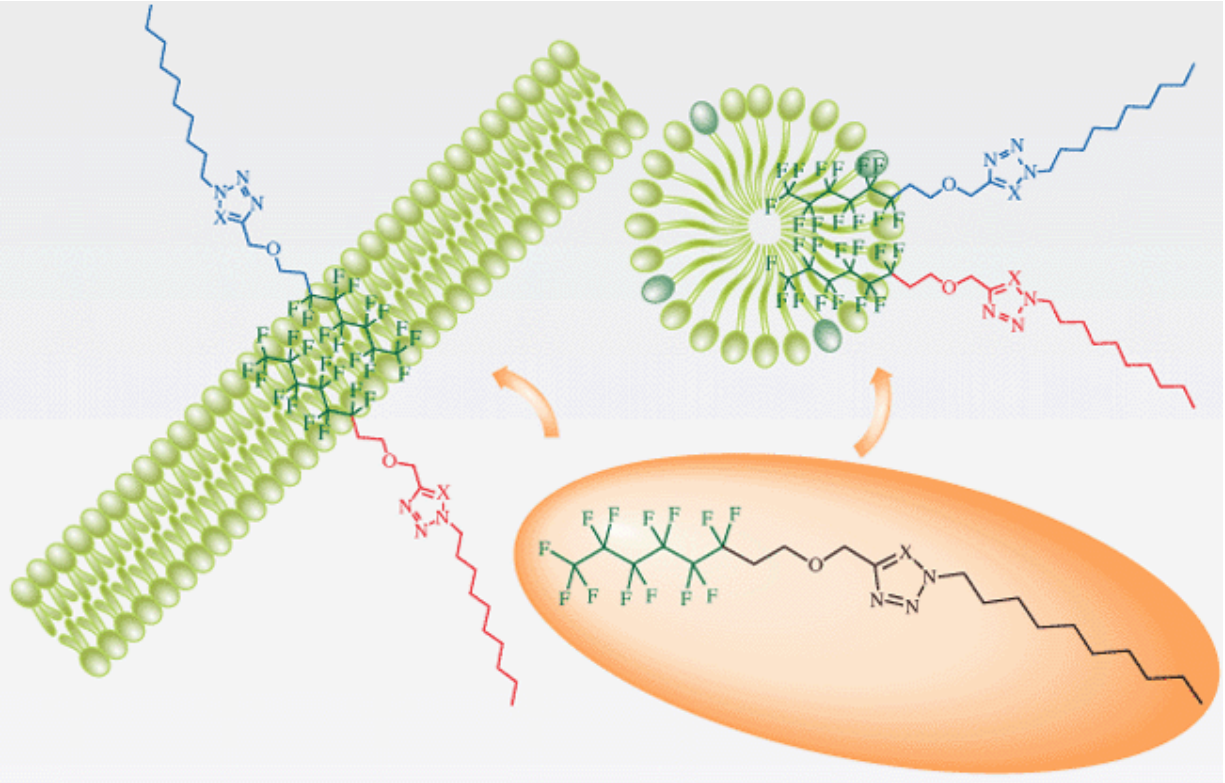


FIGURE 18.18 Fluorous molecules such as these have shown useful surface activity, but their application will depend on how they associate (for example, in opposition, as in the bilayer structure, or in concert, as in the micellar structure).

There are many opportunities and exciting discoveries yet to be made in haloalkane chemistry.

A conformational curiosity

Unlike normal alkyl chains, which are most stable in linear zigzag conformations, equivalent polyfluoroalkyl groups adopt a relatively rigid, helix-like conformation (follow the carbon framework in figure 18.19). This is due to the combined effects of the short, but highly polarised, C—F bond, and the relatively larger size of the fluorine atoms over hydrogen atoms.

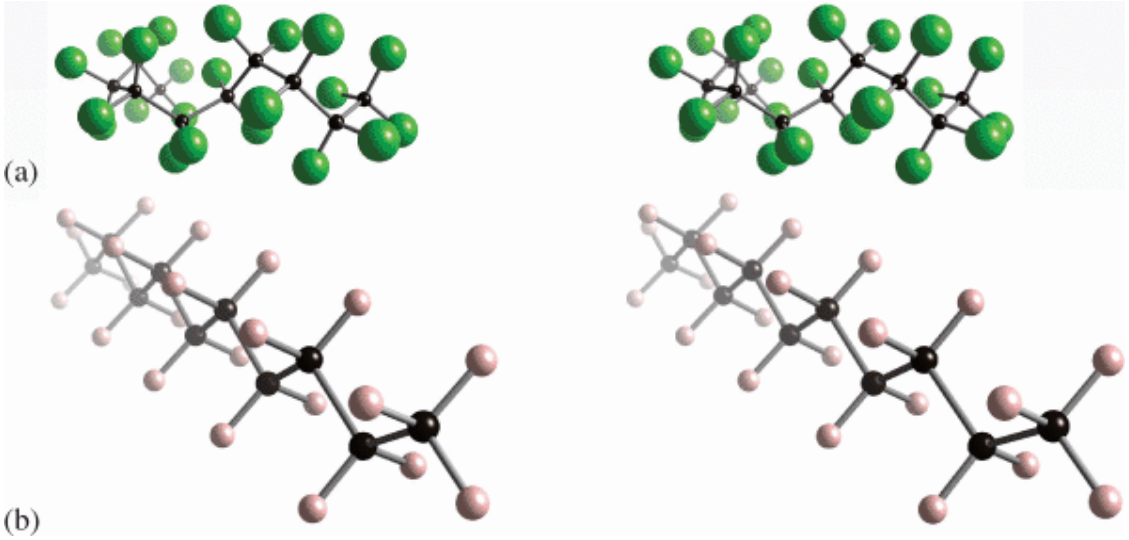


FIGURE 18.19 Stereoviews of

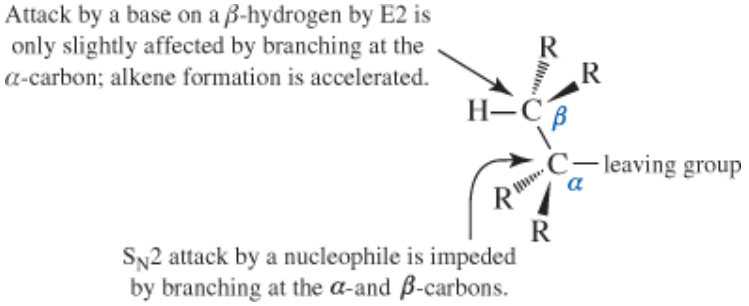
(a) perfluorodecane showing a helical twist in the carbon framework (black balls) compared with

(b) the normal zigzag arrangement in the equivalent hydrocarbon, *n*-decane. Note the relative atom sizes of fluorine (green) atoms and hydrogen (pink) atoms in the two molecules. This and the strong dipole of the C—F bond compared with the C—H bond are the driving forces behind the different preferred conformations. Both diagrams can be viewed in 3D with a little practice.

S_N2 Versus E2 Reactions

It is considerably easier to predict the ratio of substitution to elimination products for reactions of haloalkanes with reagents that act as both nucleophiles and bases. The guiding principles are as follows:

1. Branching at the α-carbon or β-carbon(s) increases steric hindrance around the α-carbon and significantly retards S_N2 reactions. By contrast, branching at the α-carbon or β-carbon(s) increases the rate of E2 reactions because of the increased stability of the alkene product.
2. The greater the nucleophilicity of the attacking reagent, the greater is the S_N2 : E2 ratio. Conversely, the greater the basicity of the attacking reagent, the lower is the S_N2 : E2 ratio.



Primary haloalkanes react with bases/nucleophiles to give predominantly substitution products. With strong bases, such as hydroxide ions and ethoxide ions, a percentage of the product is formed by an E2 reaction, but it is generally small compared with that formed by an S_N2 reaction. With strong, bulky bases, such as the *tert*-butoxide ion, the E2 product becomes the major product. Tertiary haloalkanes react with all strong bases/good nucleophiles to give only elimination products.

Secondary haloalkanes are borderline, and substitution or elimination may be favoured, depending on the particular base/nucleophile, solvent and temperature at which the reaction is carried out. Elimination is favoured with strong bases/good nucleophiles, such as hydroxide ions and ethoxide ions. Substitution is favoured with weak bases/poor nucleophiles, such as acetate ions. Table 18.7 summarises this information about substitution versus elimination reactions of haloalkanes.

TABLE 18.7 Summary of substitution versus elimination reactions of haloalkanes

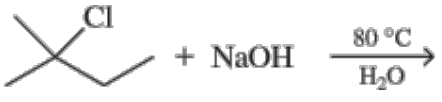
Haloalkane	Mechanism	Comments
methyl, CH_3X	S_N2	S_N2 is the only substitution reaction observed.
	~~S_N1~~	S_N1 reactions of methyl halides are never observed. The methyl cation is so unstable that it is never formed in solution.
primary, RCH_2X	S_N2	S_N2 is the main reaction with strong bases, such as OH^- and EtO^-, and with good nucleophiles/weak bases, such as I^- and CH_3COO^-.
	E2	E2 is the main reaction with strong, bulky bases, such as potassium *tert*-butoxide.
	~~S_N1/E1~~	Primary carbocations are never formed in solution so S_N1 and E1 reactions of 1° haloalkanes are never observed.
secondary, R_2CHX	S_N2	S_N2 is the main reaction with weak bases/good nucleophiles, such as I^- and CH_3COO^-.
	E2	E2 is the main reaction with strong bases/good nucleophiles, such as OH^- and $CH_3CH_2O^-$.
	S_N1/E1	S_N1 and E1 are common in reactions with weak nucleophiles in polar protic solvents, such as water, methanol and ethanol.
tertiary, R_3CX	~~S_N2~~	S_N2 reactions of 3° haloalkanes are never observed because of the extreme crowding around the 3° carbon atom.
	E2	E2 is the main reaction with strong bases, such as HO^- and RO^-.
	S_N1/E1	S_N1 and E1 are the main reactions with poor nucleophiles/weak bases.

WORKED EXAMPLE 18.7

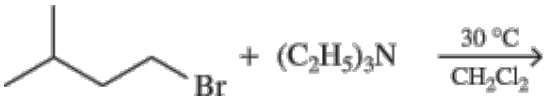
Substitution Versus Elimination

Predict whether each of the following reactions proceeds predominantly by substitution (S_N1 or S_N2) or elimination (E1 or E2) or whether the two compete. Write structural formulae for the major organic product(s).

(a)

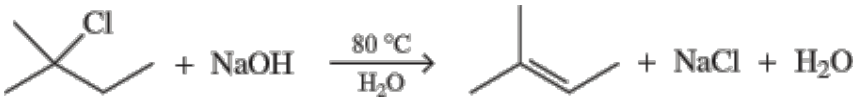


(b)

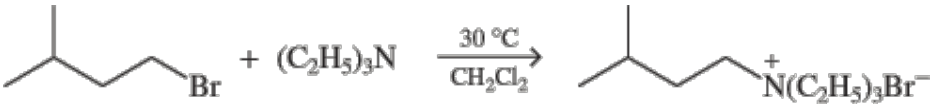


Analysis and solution

(a) A 3° chloroalkane is heated with a strong base/good nucleophile. Elimination by an E2 reaction predominates to give 2-methylbut-2-ene as the major product:



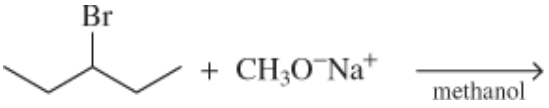
(b) Reaction of a 1° bromoalkane with triethylamine, a moderate nucleophile/weak base, gives substitution by an S_N2 reaction:



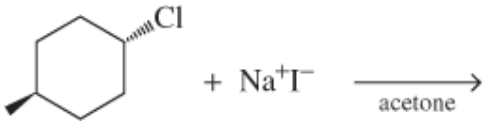
PRACTICE EXERCISE 18.7

Predict whether each of the following reactions proceeds predominantly by substitution (S_N1 or S_N2) or elimination (E1 or E2) or whether the two compete. Write structural formulae for the major organic product(s).

(a)



(b)



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SUMMARY

Haloalkanes

Haloalkanes contain a halogen atom covalently bonded to an sp^3 hybridised carbon atom. In the IUPAC system, halogen atoms are named as *fluoro-*, *chloro-*, *bromo-* or *iodo-* substituents and are listed with other substituents in alphabetical order. Haloalkanes are often called alkyl halides. Common names are derived by naming the alkyl group, followed by the name of the halide as a separate word. Compounds of the type CHX_3 are called haloforms.

Haloalkanes can be generated in several ways but one of the most important is direct halogenation of an alkane via a free radical substitution reaction. The reaction is not very selective and generally all possible monosubstitution products are formed. If the reaction is not controlled and an excess of alkane is not present, multiple substitution can occur.

A nucleophile is any reagent with an unshared pair of electrons that can be donated to another atom or ion to form a new covalent bond. Nucleophilic substitution is any reaction in which one nucleophile is substituted for another. β-elimination is any reaction in which atoms or groups are removed from two adjacent carbon atoms. Because all nucleophiles are also bases, nucleophilic substitution and base-promoted β-elimination are competing reactions.

Nucleophilic Substitution

In a nucleophilic substitution reaction, negatively charged nucleophiles become neutral after the reaction. Uncharged nucleophiles become positively charged and must undergo a second step to lose the proton.

An S_N2 reaction occurs in one step. The loss of one group is assisted by the incoming nucleophile, and both are involved in the transition state of the rate-determining step. As two species are involved, it is called a bimolecular reaction.

An S_N1 reaction occurs in two steps. The first step involves loss of a halogen to form a carbocation intermediate; this is slow so it governs the rate of the reaction. The second step is a rapid reaction with a nucleophile to complete the substitution. An S_N1 reaction is a unimolecular reaction; only one species is involved in the reaction leading to the transition state of the rate-determining step.

Solvolysis describes a reaction where the solvent plays the role of the nucleophile in the substitution reaction. For S_N1 reactions taking place at a stereocentre, the reaction occurs with racemisation.

The nucleophilicity of a reagent is measured by the rate of its reaction in a reference nucleophilic substitution. S_N1 reactions are governed by electronic factors, namely, the relative stabilities of carbocation intermediates. S_N2 reactions are governed by steric hindrance, the ability of larger groups to hinder access to the site of substitution. The ability of a group to function as a leaving group is related to its stability as an anion. The most stable anions and the best leaving groups are the conjugate bases of strong acids. Protic solvents contain —OH groups. They interact strongly with polar molecules and ions and are good solvents in which to form carbocations. Protic solvents favour S_N1 reactions. Aprotic solvents do not contain —OH groups. They do not interact as strongly with polar molecules and ions, and carbocations are less likely to form in them. Aprotic solvents favour S_N2 reactions.

β-elimination

Dehydrohalogenation, a type of β-elimination reaction, is the removal of H and X from adjacent carbon

atoms. A β-elimination that gives the most highly substituted, and therefore most stable, alkene is said to follow Zaitsev's rule.

An E1 reaction occurs in two steps: breaking the C—X bond to form a carbocation intermediate, followed by the loss of H^+ to form an alkene. An E2 reaction occurs in one step: reaction with a base to remove H^+, formation of the alkene and departure of the leaving group, all occurring simultaneously.

Substitution Versus Elimination

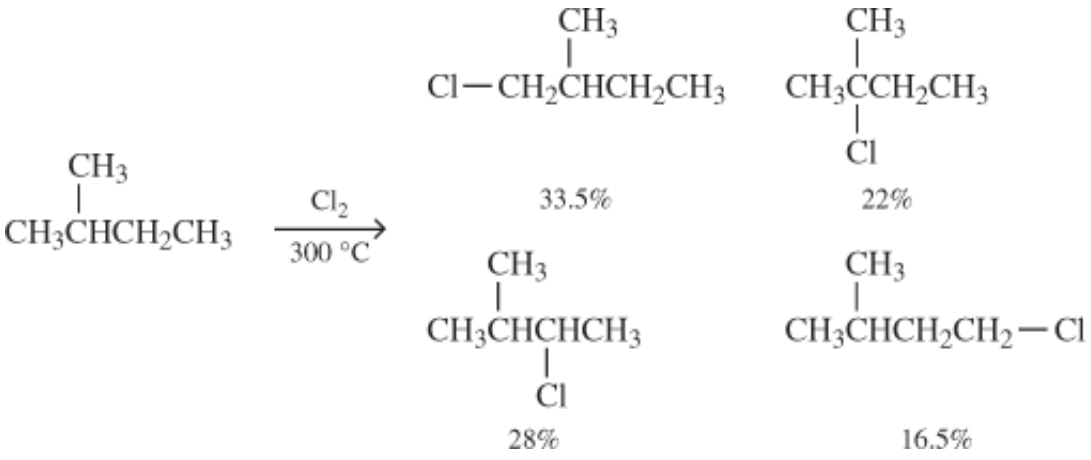
When a nucleophile is also a strong base, nucleophilic substitution and β-elimination often compete with each other. Reactions of 2° and 3° haloalkanes in polar protic solvents give mixtures of substitution and elimination products. After the formation of the carbocation intermediate, either (1) H^+ is lost to give an alkene (E1), or (2) solvent adds to give a substitution product (S_N1). In polar protic solvents, the products formed depend only on the structure of the particular carbocation. For reactions of haloalkanes with reagents that act as both nucleophiles and bases, steric hindrance significantly retards S_N2 reactions, while branching at the α-carbon or β-carbon(s) increases the rate of E2 reactions to give the alkene product. The greater the nucleophilicity of the attacking reagent, the greater is the S_N2 : E2 ratio. Conversely, the greater the basicity of the attacking reagent, the smaller is the S_N2 : E2 ratio.

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KEY CONCEPTS AND EQUATIONS

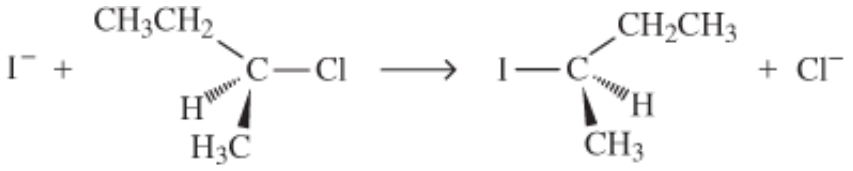
Halogenation: a radical substitution reaction *(section 18.1)*

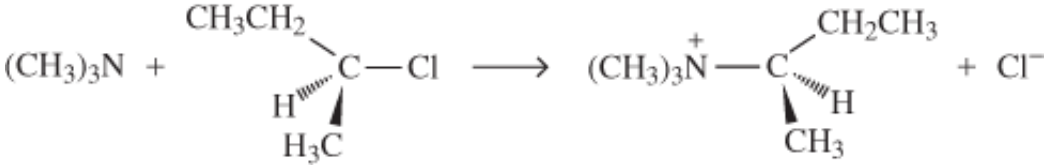
Substitution of hydrogens atoms on an alkane can be achieved using high temperatures or intense light to induce a radical chain reaction. Only bromine and chlorine are practical for this halogenation reaction.



Nucleophilic substitution: S_N2 *(section 18.2)*

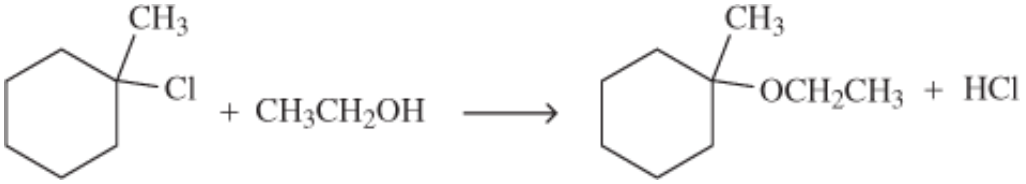
S_N2 reactions occur in one step, and both the nucleophile and the leaving group are involved in the transition state of the rate-determining step. The nucleophile may be negatively charged or neutral. S_N2 reactions result in an inversion of configuration at the reaction centre. They are accelerated in polar aprotic solvents compared with polar protic solvents. S_N2 reactions are governed by steric factors, namely, the degree of crowding around the site of reaction.





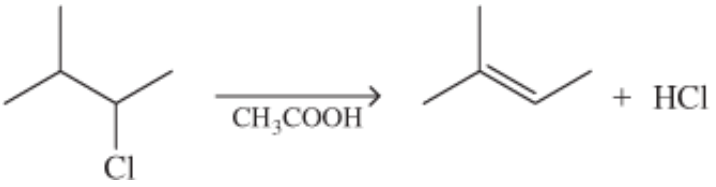
Nucleophilic substitution: S_N1 *(section 18.2)*

An S_N1 reaction occurs in two steps. Step 1 is the slow, rate-determining cleavage of the C—X bond to form a carbocation intermediate, followed in step 2 by the intermediate's rapid reaction with a nucleophile to complete the substitution. Reaction at a stereocentre gives a racemic product. S_N1 reactions are governed by electronic factors, namely, the relative stabilities of carbocation intermediates.



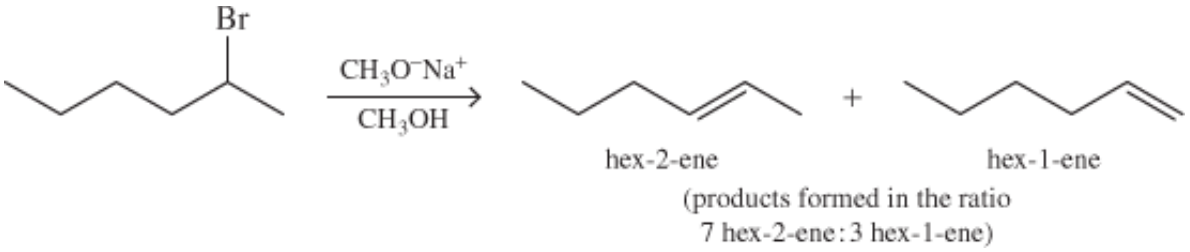
β-elimination: E1 *(section 18.3)*

E1 reactions involve the elimination of atoms or groups of atoms from adjacent carbon atoms. Reactions occur in two steps and involve the formation of a carbocation intermediate.



β-elimination: E2 *(section 18.3)*

An E2 reaction occurs in one step: reaction with base to remove a hydrogen atom, formation of the alkene and departure of the leaving group, all occurring simultaneously.



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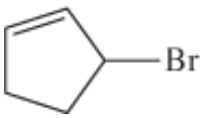
REVIEW QUESTIONS

Haloalkanes

18.1 Write the IUPAC name of each of the following compounds.

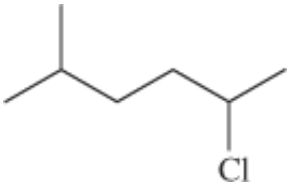
(a) $CH_2{=}CF_2$

(b)



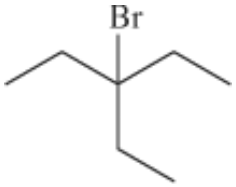
(c) $Cl(CH_2)_6Cl$

(d)



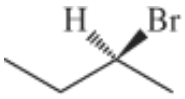
(e) CF_2Cl_2

(f)

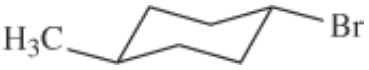


18.2 Write the IUPAC name of each of the following compounds (be certain to include a designation of configuration, where appropriate, in your answer).

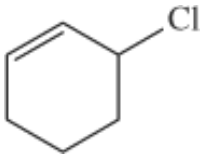
(a)



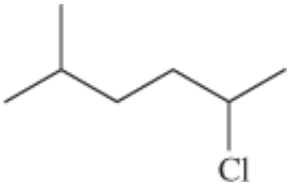
(b)



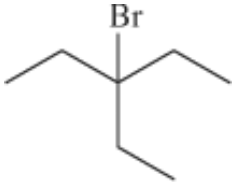
(c)



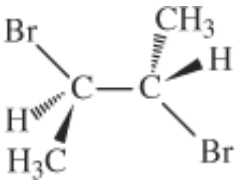
(d)



(e)



(f)



18.3 Draw a structural formula for each of the following compounds with the IUPAC name given.

(a) 3-bromopropene
(b) (*R*)-2-chloropentane
(c) *meso*-3,4-dibromohexane
(d) *trans*-1-bromo-3-isopropylcyclohexane
(e) 1,2-dichloroethane
(f) bromocyclobutane

18.4 Draw a structural formula for each of the following compounds with the common name given.

(a) isopropyl chloride
(b) *sec*-butyl bromide
(c) allyl iodide
(d) methylene chloride
(e) chloroform
(f) *tert*-butyl chloride
(g) isobutyl chloride

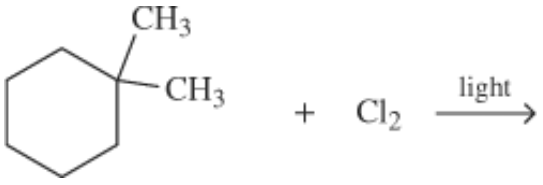
18.5 Which of the following compounds are 2° haloalkanes?

(a) isobutyl chloride
(b) 2-iodooctane
(c) *trans*-1-chloro-4-methylcyclohexane

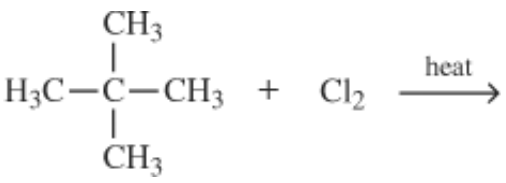
18.6 Ignoring stereochemistry, write the structural formulae and give the IUPAC names for the products of the following halogenation reactions.

(a) $H_3C-CH_2-CH_2-CH_3 + Cl_2 \xrightarrow{\text{heat}}$

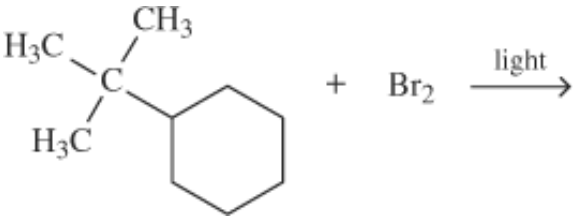
(b)



(c)



(d)



Nucleophilic Substitution

18.7 Write structural formulae for the following common organic solvents.

(a) dichloromethane

(b) acetone

(c) ethanol

(d) diethyl ether

(e) dimethyl sulfoxide

18.8 Arrange these protic solvents in order of increasing polarity: H_2O, CH_3CH_2OH, CH_3OH.

18.9 Arrange these aprotic solvents in order of increasing polarity: acetone, pentane, diethyl ether.

18.10 From each of the following pairs, select the better nucleophile.

(a) H_2O or OH^-

(b) CH_3COO^- or OH^-

(c) CH_3SH or CH_3S^-

18.11 Which statements are true for S_N2 reactions of haloalkanes?

(a) Both the haloalkane and the nucleophile are involved in the transition state of the rate-determining step.

(b) The reaction proceeds with inversion of configuration at the substitution centre.

(c) The reaction proceeds with retention of optical activity.

(d) The order of reactivity is 3° > 2° > 1° > methyl.

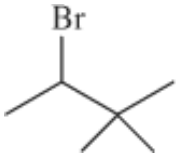
(e) The nucleophile must have an unshared pair of electrons and bear a negative charge.

(f) The greater the nucleophilicity of the nucleophile, the greater is the rate of reaction.

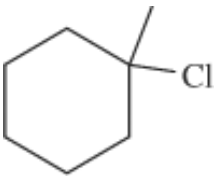
β-elimination

18.12 Draw structural formulae for the alkene(s) formed by treating each of the following haloalkanes with sodium ethoxide in ethanol. Assume that elimination occurs by the E2 mechanism. Where two alkenes are possible, use Zaitsev's rule to predict which alkene is the major product.

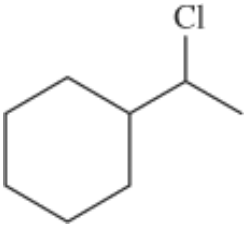
(a)



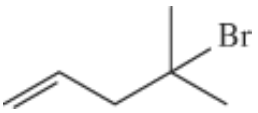
(b)



(c)



(d)



18.13 Which of the following haloalkanes undergo dehydrohalogenation to give alkenes that do not show *cis–trans* isomerism?

(a) 2-chloropentane

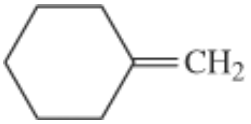
(b) 2-chlorobutane

(c) chlorocyclohexane

(d) isobutyl chloride

18.14 What haloalkane might you use as starting material to produce each of the following alkenes in high yield and uncontaminated by isomeric alkenes?

(a)



(b)



Substitution Versus Elimination

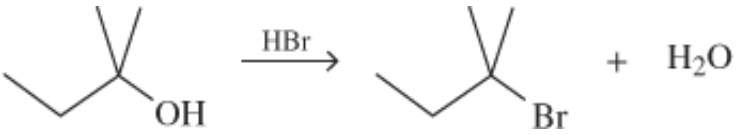
18.15 The reaction of methyl iodide with sodium hydroxide to give methanol always involves the S_N2 mechanism. Why is it that S_N1 cannot play a role in this conversion?

18.16 What is the product of the reaction of 2-bromoethane with potassium *tert*-butoxide? Why is it that little substitution occurs in this reaction?

18.17 What is the major product of the reaction of 2-iodopropane with sodium ethoxide?

18.18 The reaction of 2-bromo-2-methylpropane and sodium hydroxide occurs primarily by which mechanism, S_N1, S_N2, E1 or E2?

18.19 Consider the following substitution reaction.



(a) Determine whether this reaction proceeds via an S_N1 or S_N2 process.

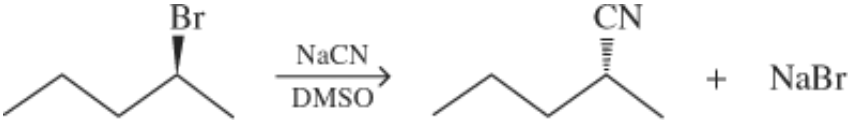
(b) Draw the mechanism for this reaction.

(c) What is the rate equation for this reaction?

(d) Would the reaction occur at a faster rate if sodium bromide were added to the reaction mixture?

(e) Draw an energy diagram for this reaction.

18.20 Consider the following substitution reaction.



(a) Determine whether this reaction proceeds via an S_N1 or S_N2 process.

(b) Draw the mechanism for this reaction.
(c) What is the rate equation for this reaction?
(d) Would the reaction occur at a faster rate if the concentration of cyanide were doubled?
(e) Draw an energy diagram for this reaction.

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18.21 Ignoring stereochemistry, write the structural formulae and give the IUPAC names for the products of the following halogenation reactions.

(a) 1, 4-dimethylcyclohexane + Cl_2 $\xrightarrow{\text{heat}}$

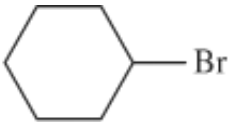
(b) 1, 1, 3, 3-tetramethylcyclopentane + Br_2 $\xrightarrow{\text{light}}$

(c) 3, 4-diethylhexane + Br_2 $\xrightarrow{\text{heat}}$

(d) 3-ethylpentane + Br_2 $\xrightarrow{\text{light}}$

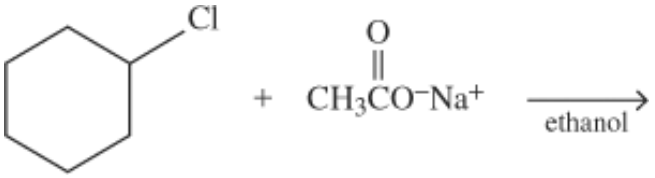
18.22 Complete the following S_N2 reactions.

(a) Na^+I^- + $CH_3CH_2CH_2Cl$ $\xrightarrow[\text{acetone}]{}$

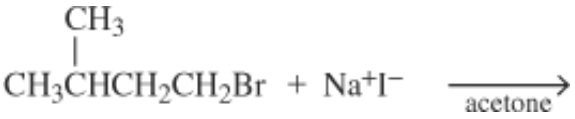
(b) NH_3 +  $\xrightarrow[\text{ethanol}]{}$

(c) $CH_3CH_2O^-Na^+ + CH_2{=}CHCH_2Cl$ $\xrightarrow[\text{ethonal}]{}$

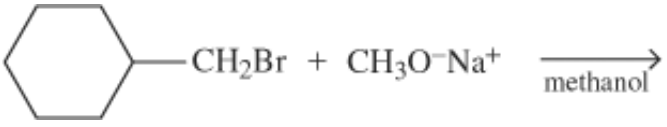
18.23 Complete the following S_N2 reactions.

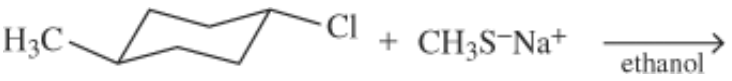
(a) 

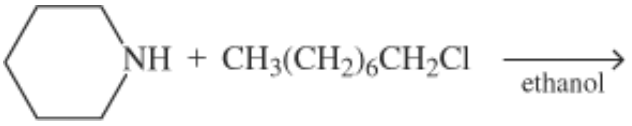
(b) 

(c) 

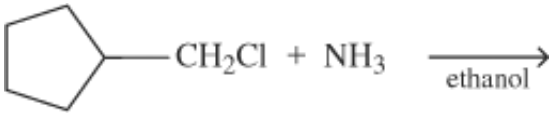
(d) $(CH_3)_3N + CH_3I$ $\xrightarrow[\text{acetone}]{}$

(e) 

(f) 

(g) 

(h)

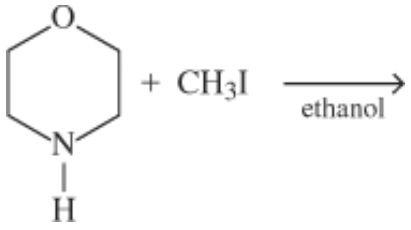


18.24 You were told that each reaction in question 18.23 proceeds by the S_N2 mechanism. Suppose you were not told the mechanism. Describe how you could conclude, from the structures of the haloalkane, the nucleophile and the solvent, that each reaction is in fact an S_N2 reaction.

18.25 In the following reactions, a haloalkane is treated with a compound that has two nucleophilic sites. Select the more nucleophilic site in each part, and show the product of each S_N2 reaction.

(a) $HOCH_2CH_2NH_2 + CH_3I \xrightarrow[\text{ethanol}]{}$

(b)



(c) $HOCH_2CH_2SH + CH_3I \xrightarrow[\text{ethanol}]{}$

18.26 Which statements are true for S_N1 reactions of haloalkanes?

(a) Both the haloalkane and the nucleophile are involved in the transition state of the rate-determining step.

(b) The reaction at a stereocentre proceeds with retention of configuration.

(c) The reaction at a stereocentre proceeds with loss of optical activity.

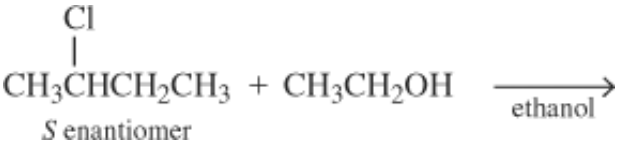
(d) The order of reactivity is 3° > 2° > 1° > methyl.

(e) The greater the steric crowding around the reactive centre, the lower is the rate of reaction.

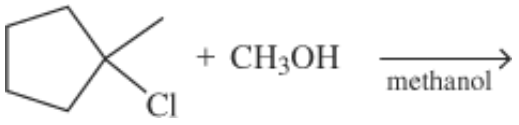
(f) The rate of reaction is greater with good nucleophiles than with poor nucleophiles.

18.27 Draw a structural formula for the product of each of the following S_N1 reactions.

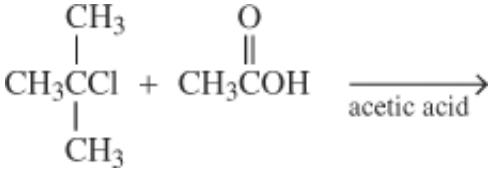
(a)



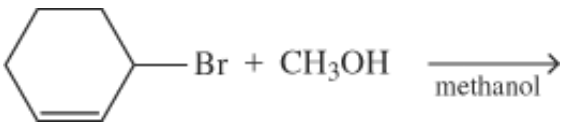
(b)



(c)



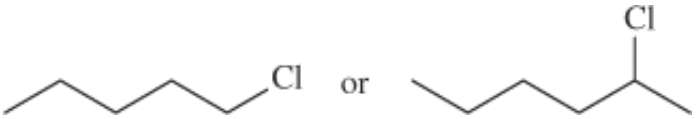
(d)



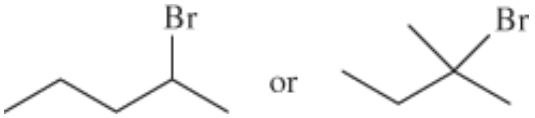
18.28 You were told that each substitution reaction in question 18.27 proceeds by the S_N1 mechanism. Suppose that you were not told the mechanism. Describe how you could conclude, from the structures of the haloalkane, the nucleophile and the solvent, that each reaction is in fact an S_N1 reaction.

18.29 Select the member of each of the following pairs that undergoes nucleophilic substitution in aqueous ethanol more rapidly.

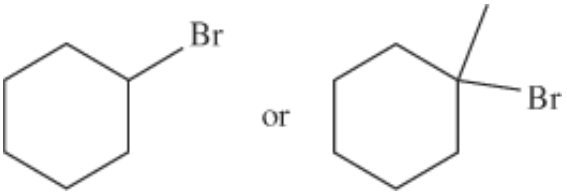
(a)



(b)



(c)



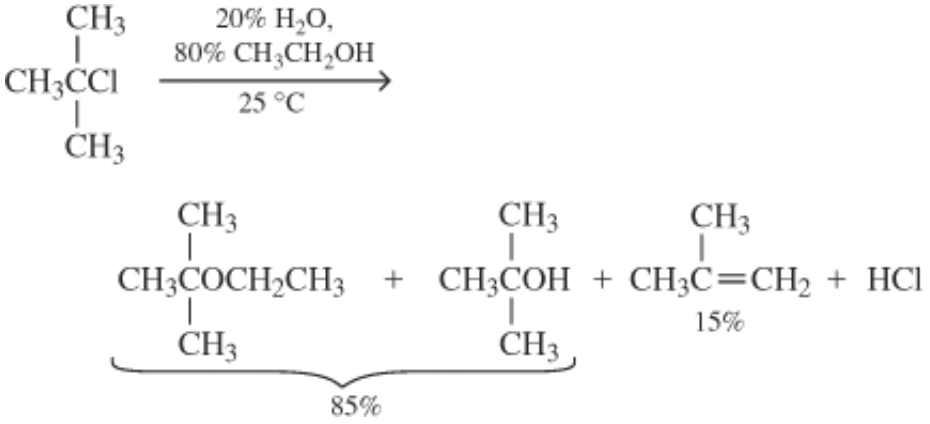
18.30 Identify the reagent you would use to accomplish each of the following transformations.

(a) cyclobutanol → bromocyclobutane

(b) *tert*-butanol → *tert*-butyl chloride

(c) ethyl → chloride

18.31 Propose a mechanism for the formation of the products (but not their relative percentages) in this reaction.



18.32 The rate of reaction in question 18.31 increases by 140 times when carried out in 80% water/ 20% ethanol compared with 40% water/ 60% ethanol. Account for this difference.

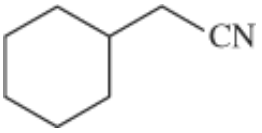
18.33 What hybridisation best describes the reacting carbon atom in the S_N2 transition state?

18.34 Haloalkenes such as vinyl bromide, $CH_2{=}CHBr$, undergo neither S_N1 nor S_N2 reactions. What factors account for this lack of reactivity?

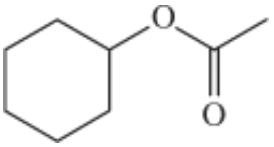
18.35 Show how you might synthesise the following compounds from a haloalkane and a nucleophile.

(a)

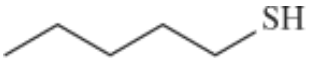
(b)



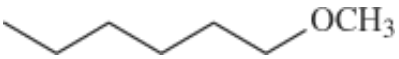
(c)



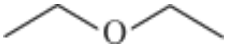
(d)



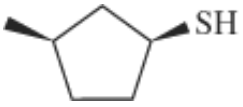
(e)



(f)

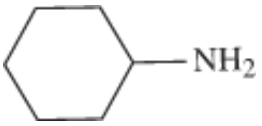


(g)

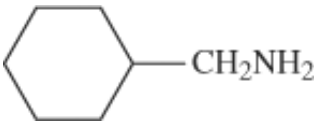


18.36 Show how you might synthesise the following compounds from a haloalkane and a nucleophile.

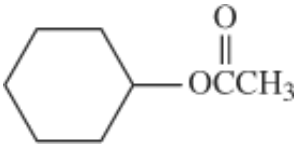
(a)



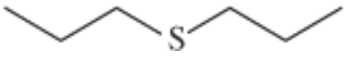
(b)



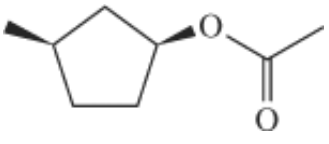
(c)



(d)



(e)

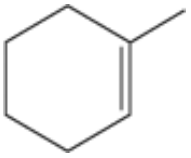


(f) $(CH_3CH_2CH_2CH_2)_2O$

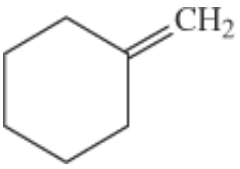
18.37 For each of the following alkenes, draw structural formulae of all chloroalkanes that undergo

dehydrohalogenation when treated with KOH to give that alkene as the major product (for some alkenes, only one chloroalkane gives the desired alkene as the major product; for other alkenes, two chloroalkanes may work).

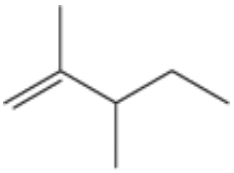
(a)



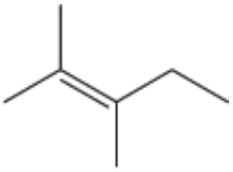
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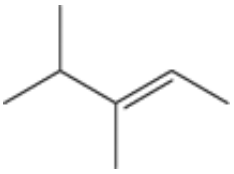
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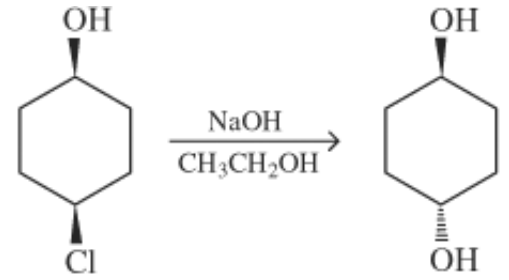
(d)



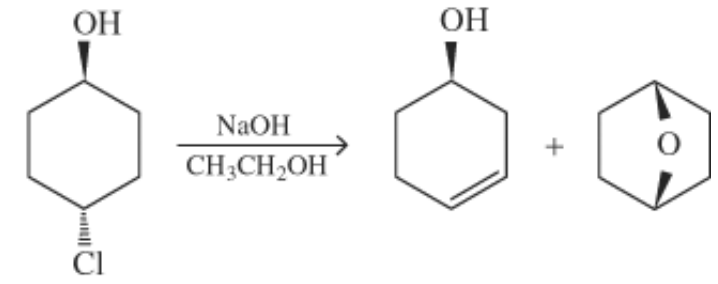
(e)



18.38 When *cis*-4-chlorocyclohexanol is treated with sodium hydroxide in ethanol, it gives only one substitution product, *trans*-1,4-cyclohexanediol (1). Under the same experimental conditions, *trans*-4-chlorocyclohexanol gives cyclohex-3-enol (2) and the bicyclic ether (3).



cis-4-chloro-cyclohexanol (1)



trans-4-chloro-cyclohexanol (2) (3)

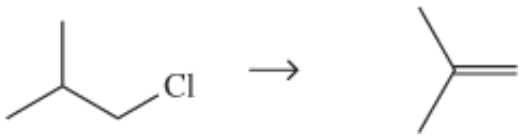
(a) Propose a mechanism for the formation of product (1), and account for its configuration.

(b) Propose a mechanism for the formation of product (2).

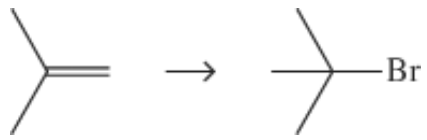
(c) Account for the fact that the bicyclic ether (3) is formed from the *trans* isomer, but not from the *cis* isomer.

18.39 In each of the following reactions, show how to convert the given starting material into the desired product (note that some syntheses require only one step, whereas others require two or more steps).

(a)



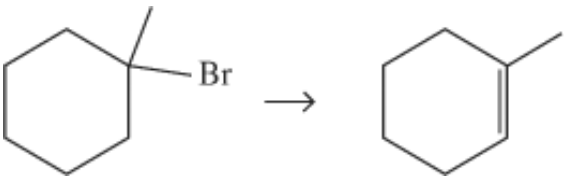
(b)



(c)

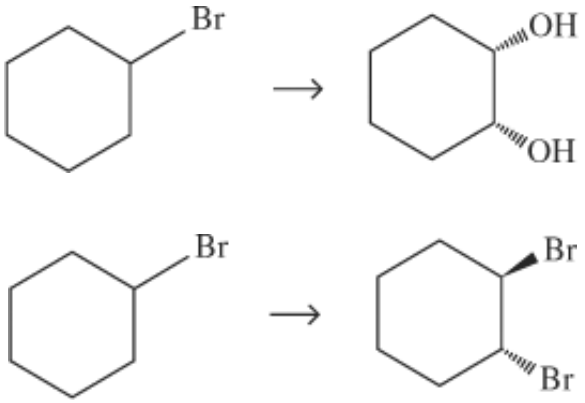


(d)



(e)

(f)



18.40 How many isomers, including *cis–trans* isomers, are possible for the major product of dehydrohalogenation of each of the following haloalkanes?

(a) 3-chloro-3-methylhexane

(b) 3-bromohexane

18.41 Give the products of the reaction of 1-iodopropane with each of the following.

(a) NaOH

(b) $NaNH_2$

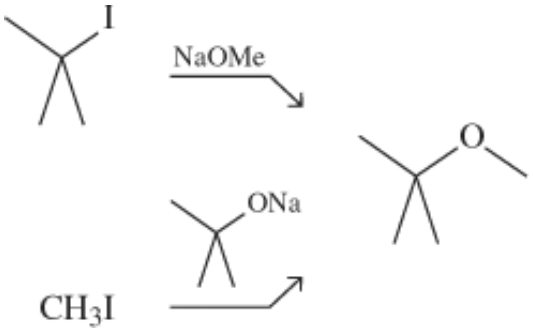
(c) NaCN

(d) $NaOOCCH_3$

(e) NaI

(f) $NaOC(CH_3)_3$

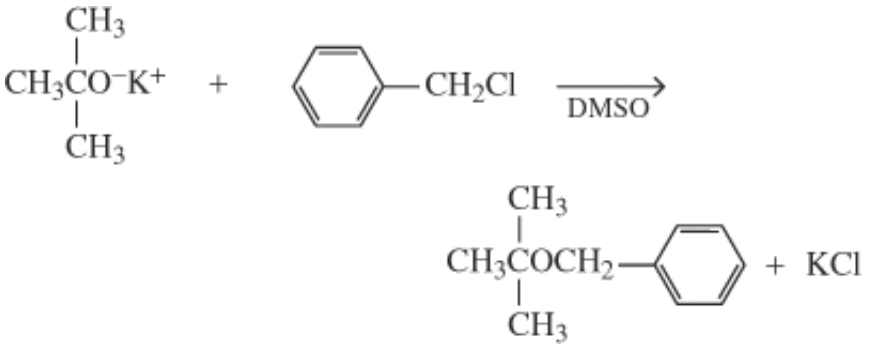
18.42 Below are two potential methods for preparing the same ether, but only one of them is successful. Identify the successful approach and explain your choice.



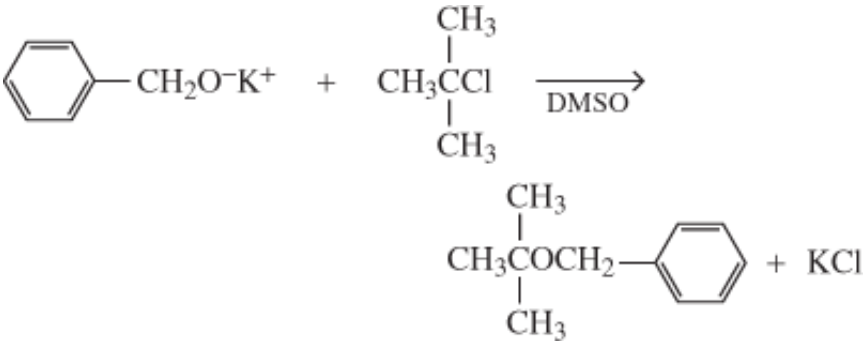
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18.43 The Williamson ether synthesis involves treating a haloalkane with a metal alkoxide. The following two reactions are intended to give benzyl *tert*-butyl ether. One reaction gives the ether in good yield, but the other does not. Which reaction gives the ether? What is the product of the other reaction, and how do you account for its formation?

(a)

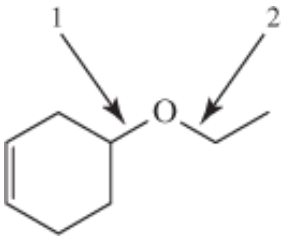


(b)

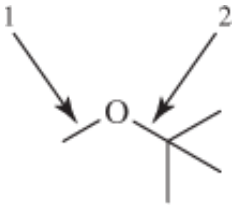


18.44 The following ethers can, in principle, be synthesised by two different combinations of a haloalkane or halocycloalkane with a metal alkoxide. Show one combination that forms ether bond 1 and another that forms ether bond 2. Which combination gives the higher yield of ether?

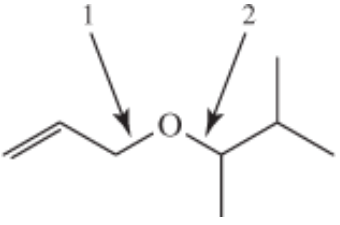
(a)



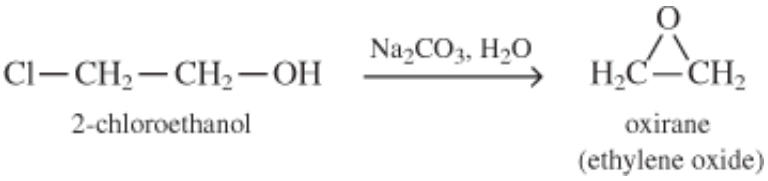
(b)



(c)



18.45 Propose a mechanism for the following reaction.



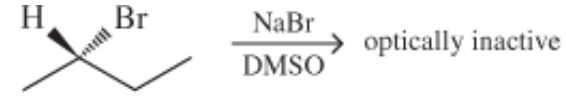
2-chloroethanol

oxirane
(ethylene oxide)

18.46 An —OH group is a poor leaving group, yet substitution occurs readily in the following reaction. Propose a mechanism for this reaction that shows how OH overcomes its limitation of being a poor leaving group.

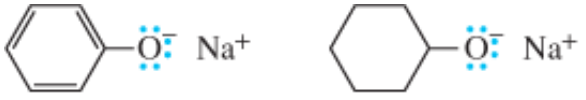


18.47 Explain why (*S*)-2-bromobutane becomes optically inactive when treated with sodium bromide in DMSO.



optically active

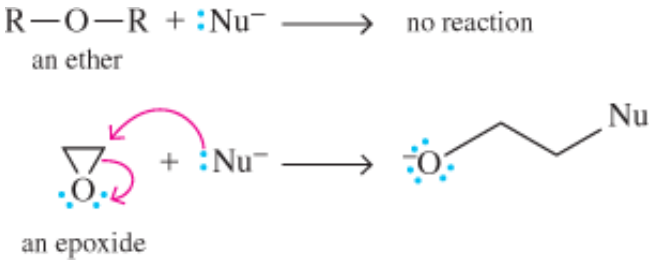
18.48 Explain why phenoxide is a much poorer nucleophile than cyclohexoxide.



sodium phenoxide

sodium cyclohexoxide

18.49 In ethers, each side of the oxygen is essentially an — OR group and so is a poor leaving group. Epoxides are three-membered ring ethers (oxirane in question 18.45 is an example of an epoxide). Explain why an epoxide reacts readily with a nucleophile despite being an ether.

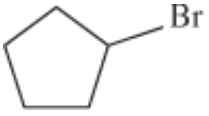


an ether

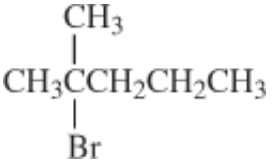
an epoxide

18.50 What alkene(s) and reaction conditions give each of the following haloalkanes in good yield? (*Hint:* Review chapter 8.)

(a)



(b)

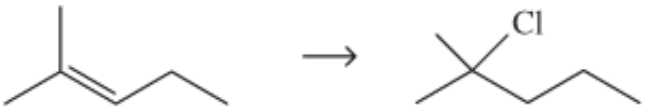


(c)



18.51 Show reagents and conditions that bring about the following conversions.

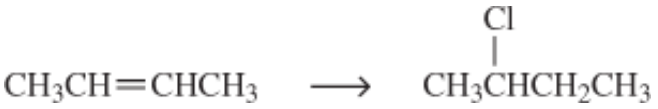
(a)



(b)



(c)



(d)



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KEY TERMS

β-elimination
aprotic solvents
bimolecular reaction
dehydrohalogenation
E1
E2
haloalkanes
haloform
halogenation
nucleophile
nucleophilic substitution
nucleophilicity
aprotic solvents
radical substitution
radical
S_N1
S_N2
solvolysis
steric hindrance
unimolecular reaction
Zaitsev's rule

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CHAPTER

19 Alcohols, Amines and Related Compounds

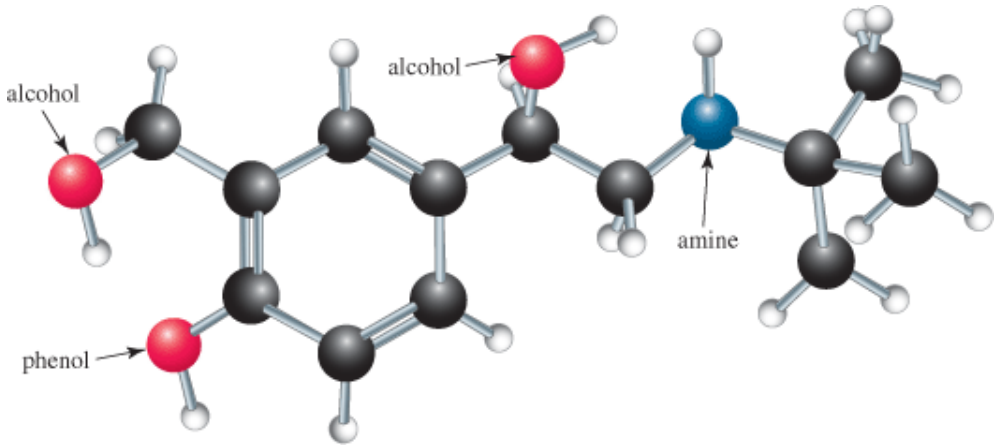
On a per capita basis, Australia and New Zealand have the highest incidence of asthma in the world. The inhaler in the picture delivers puffs of salbutamol (also known as albuterol or, more commonly, as Ventolin®), which is a potent synthetic bronchodilator used in the treatment of asthma. The structure of salbutamol (shown below) is patterned after that of epinephrine (adrenaline) and, like many drugs, salbutamol is a polyfunctional compound (it contains more than one type of functional group). The functional groups present in salbutamol include a primary and secondary alcohol, a phenol and a secondary amine. These functional groups are important in the binding of salbutamol to the receptors (active site) in the lungs which causes smooth muscle relaxation. The binding occurs through hydrogen bonding between the hydroxyl groups, and ion–ion attractions between the protonated amine and a carboxylate group in the active site. The bulky tertiary butyl group helps to reduce side effects by preventing binding at similar shaped receptors that cause smooth muscle contraction.



Alcohols, phenols, ethers and amines are extremely common in nature and these functional groups play important roles in many biological, pharmaceutical and industrial applications. Thiols, sulfur-containing analogues of alcohols, play important roles in biological systems including flavour and odour chemistry. In this chapter, we study the physical and chemical properties of these functional groups. We will learn how they can be prepared from, and transformed into, other functional groups.

KEY TOPICS

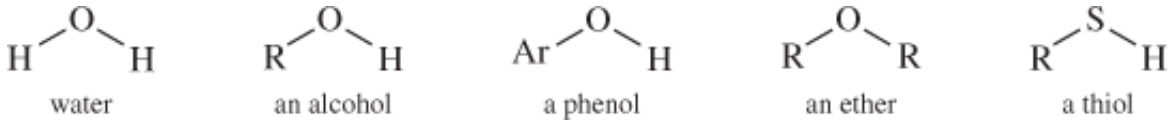
19.1 Alcohols
19.2 Reactions of alcohols
19.3 Phenols
19.4 Ethers
19.5 Thiols
19.6 Amines
19.7 Reactions of amines



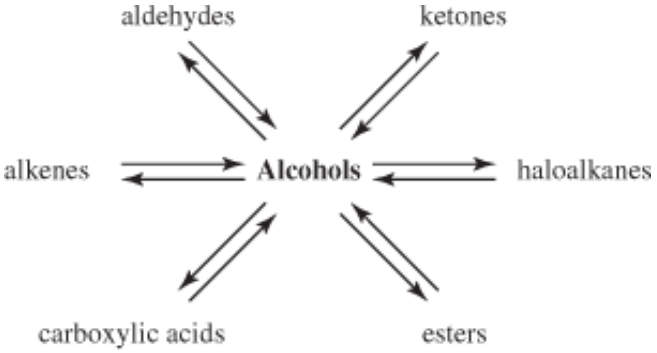
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19.1 Alcohols

Alcohols, phenols and ethers can be thought of as three classes of compounds that are related to water, while thiols are sulfur-containing analogues of alcohols.



Alcohols are particularly important in both laboratory reactions and biochemical transformations of organic compounds. They can be converted into other types of compounds, such as alkenes, haloalkanes, aldehydes, ketones, carboxylic acids and esters. Alcohols can be converted to these compounds, and they can also be prepared from them. Thus, alcohols play a central role in the interconversion of organic functional groups.



The **alcohol** functional group is an —OH **(hydroxyl) group** bonded to an sp^3 hybridised carbon atom. The oxygen atom of an alcohol is also sp^3 hybridised. Two sp^3 hybrid orbitals of oxygen form σ bonds to atoms of carbon and hydrogen. The other two sp^3 hybrid orbitals of oxygen each contains an unshared pair of electrons. Figure 19.1 shows a Lewis structure and a ball-and-stick model of methanol, CH_3OH, the simplest alcohol.

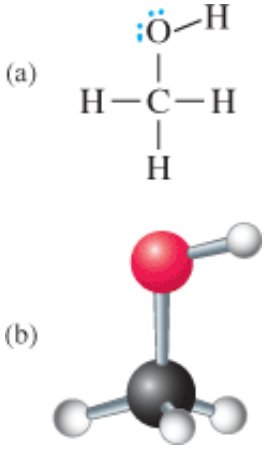
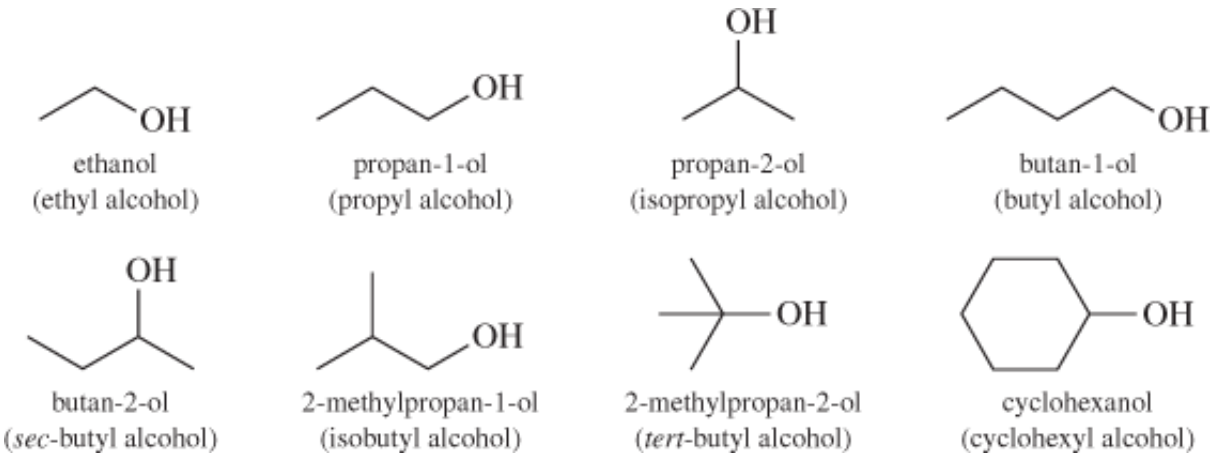


FIGURE 19.1 Methanol, CH_3OH:
(a) Lewis structure and
(b) ball-and-stick model. The bond angles in methanol are very close to the tetrahedral angle.

We explained the basic rules of IUPAC nomenclature in chapter 2. Here, we will briefly describe the process for naming alcohols to refresh your memory. Alcohols are named in the same manner as alkanes, with the following differences:

1. Select, as the parent alkane, the longest chain of carbon atoms that contains the —OH group, and number that chain from the end closest to the —OH group. In numbering the parent chain, the location of the —OH group takes precedence over alkyl groups and halogens.
2. Change the suffix of the parent alkane from *-e* to *-ol* (section 2.3), and use a number to show the location of the —OH group. The ending *-ol* tells us that the compound is an alcohol. For cyclic alcohols, numbering begins at the carbon atom bearing the —OH group.
3. Name and number substituents and list them in alphabetical order.

To derive common names for alcohols, we name the alkyl group bonded to the —OH group and add the word *alcohol*. The following diagram shows the IUPAC names and, in parentheses, the common names of eight low-molar-mass alcohols.



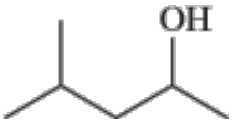
WORKED EXAMPLE 19.1

Naming Alcohols

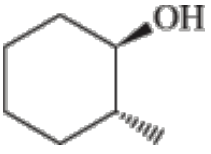
Write the IUPAC name for each of the following alcohols.

(a) $CH_3(CH_2)_6CH_2OH$

(b)



(c)



Analysis

A general strategy for nomenclature questions is to draw the structure (if it is not already in a suitable form), identify the key functional group (in this case the —OH group), and then number the carbon chain starting from the end closest to the functional group. Finally, identify all other substituents. As the compounds in this example are alcohols, the names will all end in-*ol*. Compound (a) is derived from an unbranched alkane so we need to identify

only the alkane and the position of the —OH group. Compound (b) includes a branch on the second last carbon atom, and the —OH group is on the second carbon atom. Compound (c) is a little more complex. It is a cyclic alcohol, so we start numbering from the —OH group. There is also a methyl group on the second carbon atom which is *trans*- to the —OH group. Thus, at a minimum, we need to indicate the relative stereochemistry, the position of the substituent and that it is a cyclic alcohol. To be more precise, we should indicate the absolute stereochemistry of the two stereocentres using the (*R*,*S*) system from section 17.3.

Solution

(a) octan-1-ol

(b) 4-methylpentan-2-ol

(c) *trans*-2-methylcyclohexanol or (1*R*,2*R*)-2-methylcyclohexanol

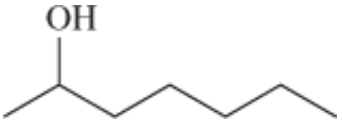
Is our answer reasonable?

The best way to check if your answer is reasonable is to draw a structure from your answer and determine if the structure represents the same molecule as the question.

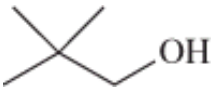
PRACTICE EXERCISE 19.1

Write the IUPAC name for each of the following alcohols.

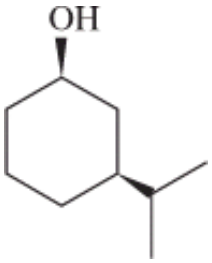
(a)



(b)

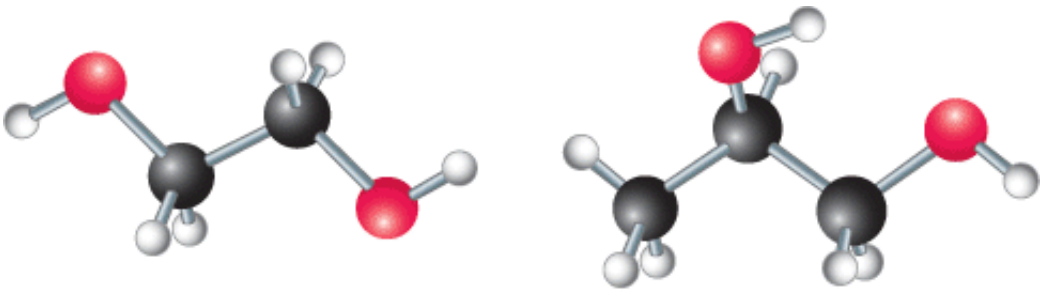


(c)



In the IUPAC system, a compound containing two hydroxyl groups is named as a **diol**, one containing three hydroxyl groups is named as a **triol** and so on. In IUPAC names for diols, triols and so on, the final -*e* of the parent alkane name is retained, for example, ethane-1,2-diol.

As with many organic compounds, common names for certain diols and triols have persisted. Compounds containing two hydroxyl groups on adjacent carbons are often referred to as **glycols**. Ethylene glycol (see figure 19.2) and propylene glycol are synthesised from ethylene (ethene) and propylene (propene) respectively, hence their common names as shown below.

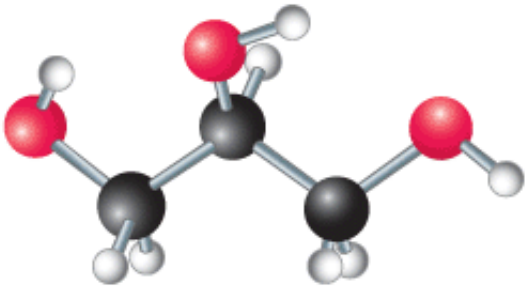


CH_2CH_2
| |
OH OH

ethane-1,2-diol
(ethylene glycol)

CH_3CHCH_2
| |
HO OH

propane-1,2-diol
(propylene glycol)



CH_2CHCH_2
| | |
HO HO OH

propane-1,2,3-triol
(glycerol, glycerin)



FIGURE 19.2 Ethylene glycol is a polar molecule and dissolves readily in water, a polar solvent. (*Note:* Ethylene glycol itself is colourless.)

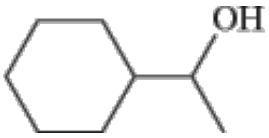
We classify alcohols as primary (1°), secondary (2°) or tertiary (3°), depending on whether the —OH group is on a primary, secondary or tertiary carbon atom.

WORKED EXAMPLE 19.2

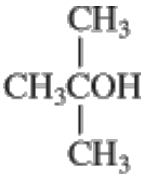
Primary, Secondary and Tertiary Alcohols

Classify each of the following alcohols as primary, secondary or tertiary.

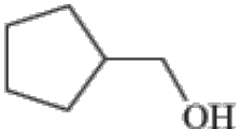
(a)



(b)



(c)



Analysis

To determine whether an alcohol is primary, secondary or tertiary, identify the carbon atom bonded to the —OH group. Now count the number of alkyl groups bonded to this carbon atom. If there is one, the alcohol is primary, if two, secondary, and if three, tertiary. Alternatively, you may wish to consider the number of hydrogen atoms on the carbon atom with the —OH group; two hydrogen atoms = primary, one hydrogen atom = secondary, and no hydrogen atoms = tertiary.

Solution

(a) secondary (2°)

(b) tertiary (3°)

(c) primary (1°)

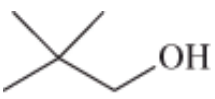
Is our answer reasonable?

As there are two ‘counting’ methods (number of alkyl groups or number of hydrogen atoms), you should double check your answer by using the alternative method.

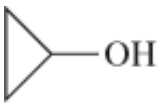
PRACTICE EXERCISE 19.2

Classify each of the following alcohols as primary, secondary or tertiary.

(a)

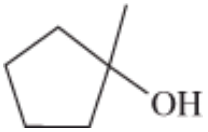


(b)



(c) $CH_2{=}CHCH_2OH$

(d)



Physical Properties

The most important physical property of alcohols is the polarity of their —OH groups. The large difference in electronegativity (figure 5.5, p. 168) between oxygen and carbon (3.5 - 2.5 = 1.0) and between oxygen and hydrogen (3.5 - 2.1 = 1.4), means both the C—O and O—H bonds are polar covalent, and alcohols are polar molecules, as shown for methanol in figure 19.3.

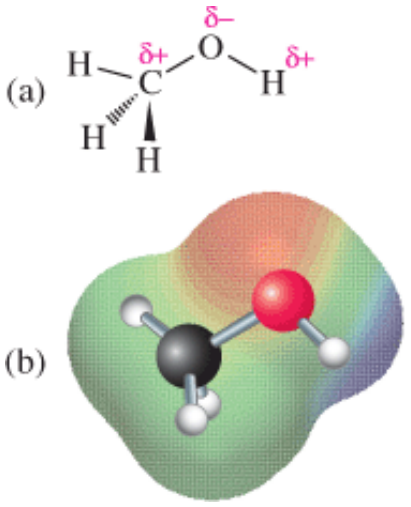


FIGURE 19.3 Polarity of the C—O—H bond in methanol:

(a) There are partial positive charges on carbon and hydrogen and a partial negative charge on oxygen.

(b) An electron density map showing the partial negative charge (in red) around oxygen and a partial positive charge (in blue) around hydrogen of the —OH group.

Table 19.1 lists the boiling points and water solubility for five groups of alcohols and alkanes with the same number of electrons and similar molar mass. Notice that, of the compounds compared in each group, the alcohol has the higher boiling point and is more soluble in water.

TABLE 19.1 Boiling points and solubilities in water of five groups of alcohols and alkanes with the same number of electrons and similar molar mass

Structural formula	Name	Molar mass	Total electrons	Boiling point (°C)	Solubility in water
CH_3OH	methanol	32	18	65	infinite
CH_3CH_3	ethane	30	18	-89	insoluble
CH_3CH_2OH	ethanol	46	26	78	infinite
$CH_3CH_2CH_3$	propane	44	26	-42	insoluble

$CH_3CH_2CH_2OH$	propan-1-ol	60	34	97	infinite
$CH_3CH_2CH_2CH_3$	butane	58	34	0	insoluble
$CH_3CH_2CH_2CH_2OH$	butan-1-ol	74	42	117	8 g/100 g
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	42	36	insoluble
$CH_3CH_2CH_2CH_2CH_2OH$	pentan-1-ol	88	50	138	2.3 g/100 g
$HOCH_2CH_2CH_2CH_2OH$	butane-1,4-diol	90	50	230	infinite
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane	86	50	69	insoluble

The boiling points of all types of compounds, including alcohols, increase with increasing number of electrons because of increased dispersion forces between larger molecules (see chapter 6, pp. 241–2). Compare, for example, the boiling points of ethanol, propan-1-ol, butan-1-ol and pentan-1-ol in table 19.1.

Alcohols have higher boiling points than alkanes with the same or a similar number of electrons, because alcohols are polar and can associate in the liquid state by **hydrogen bonding** as depicted for ethanol in figure 19.4. We first encountered this type of intermolecular attraction in section 6.8.

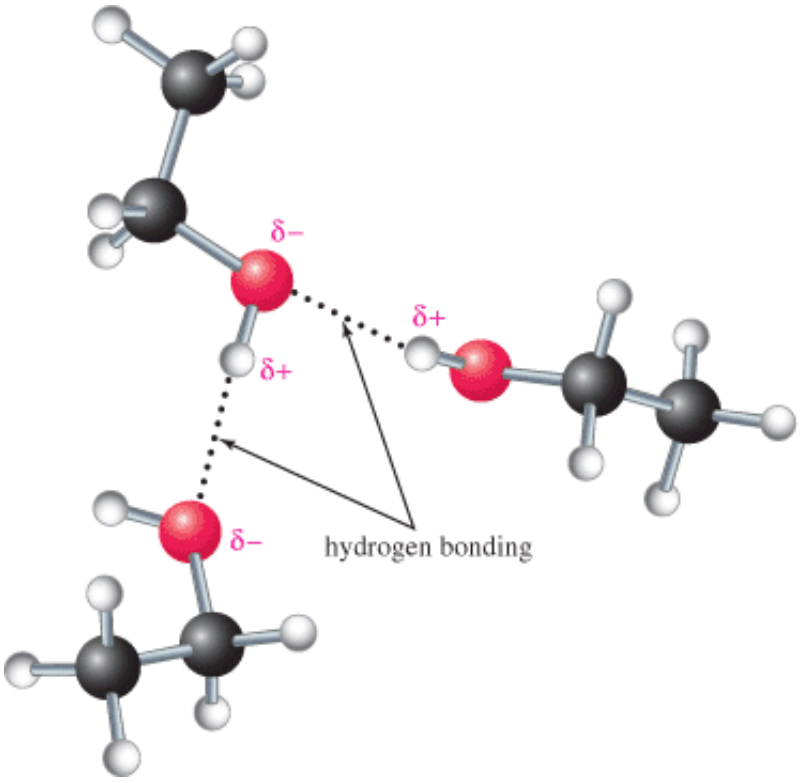


FIGURE 19.4 The association of ethanol molecules in the liquid state. Each —OH group can participate in up to three hydrogen bonds (one through hydrogen and two through oxygen). Only two of these three possible hydrogen bonds per molecule are shown in the figure.

Extra energy is required to separate each alcohol molecule from its neighbours because of hydrogen bonding between alcohol molecules in the liquid state. This results in the relatively high boiling points of alcohols compared with alkanes. Additional hydroxyl groups in a molecule further increase the extent of hydrogen bonding, as can be seen by comparing the boiling points of pentan-1-ol (138 °C) and butane-1,4-diol (230 °C), which have the same number of electrons (and hence the same dispersion forces).

Alcohols are much more soluble in water than alkanes, alkenes and alkynes with a comparable number of electrons. The hydroxyl group in alcohols readily forms hydrogen bonds with water molecules, resulting in the higher solubility of alcohols in water. Methanol, ethanol and propan-1-ol are soluble in water in all proportions. As the number of electrons (and size) increases, the physical properties of alcohols become more like those of hydrocarbons with a similar number of electrons. Alcohols of higher molar mass are much less soluble in water because of the increased size of the hydrocarbon parts of the molecules.

Preparation of Alcohols

Alcohols can be prepared from many functional groups using many different reactions. Some of these reactions are discussed briefly here and in more detail elsewhere in this text. As ethanol is arguably the most important alcohol, we will discuss its manufacture separately before going on to the general synthetic methods available for the preparation of alcohols.

In Australia, ethanol is produced by the fermentation of sugars. There are two main sources of these sugars: sugar cane (figure 19.5) and grains. Sugars from cane and molasses (a by-product of the sugar industry) can be converted directly into ethanol. Grains, however, produce starches, which must first be hydrolysed (broken down) to fermentable sugars, before being used to produce ethanol.



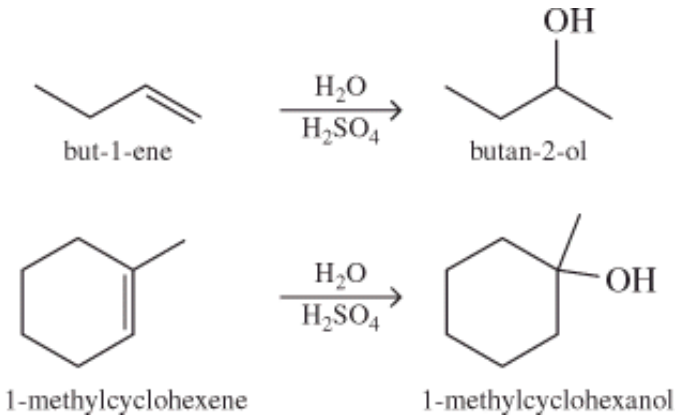
FIGURE 19.5 Sugar cane can be used for ethanol production.

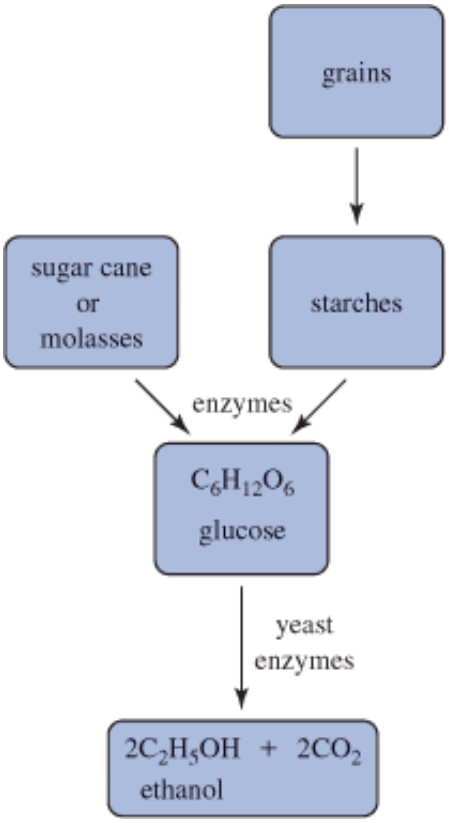
Ethanol is also produced industrially by the vapour phase hydration of ethylene (ethene) in the presence of an acid catalyst.

$$H_2C=CH_2 + H_2O \xrightarrow[\text{catalyst}]{\text{acid}} CH_3CH_2OH$$

Preparation from Alkenes

Alcohols can be prepared by the acid-catalysed hydration of alkenes (see section 16.5). When the alkene is asymmetrically substituted, the addition obeys Markovnikov's rule (the hydrogen atom adds to the carbon atom of the double bond with more hydrogen atoms, thus producing the more stable carbocation intermediate).





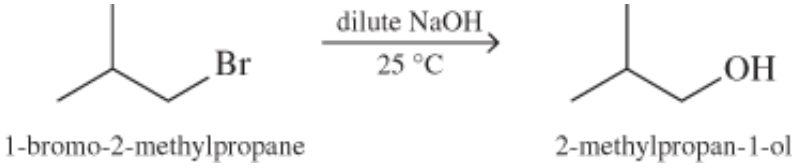
Preparation from Haloalkanes

Alcohols can be prepared from haloalkanes by nucleophilic substitution with a hydroxide ion or water (see section 18.2). Tertiary haloalkanes are readily converted to alcohols by water.

$$\underset{\text{2-bromo-2-methylpropane}}{(CH_3)_3C-Br} + H_2O \rightleftharpoons \underset{\text{2-methylpropan-2-ol}}{(CH_3)_3C-OH} + HBr$$

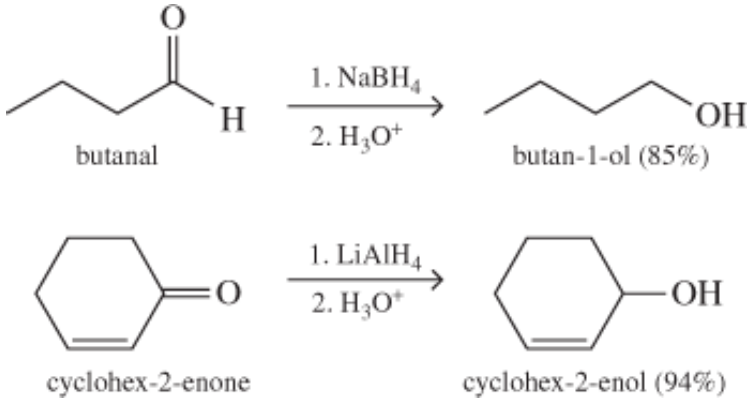
(*tert*–butyl bromide) (*tert*–butyl alcohol)

Secondary and primary alcohols are better prepared by reaction with hydroxide ions.

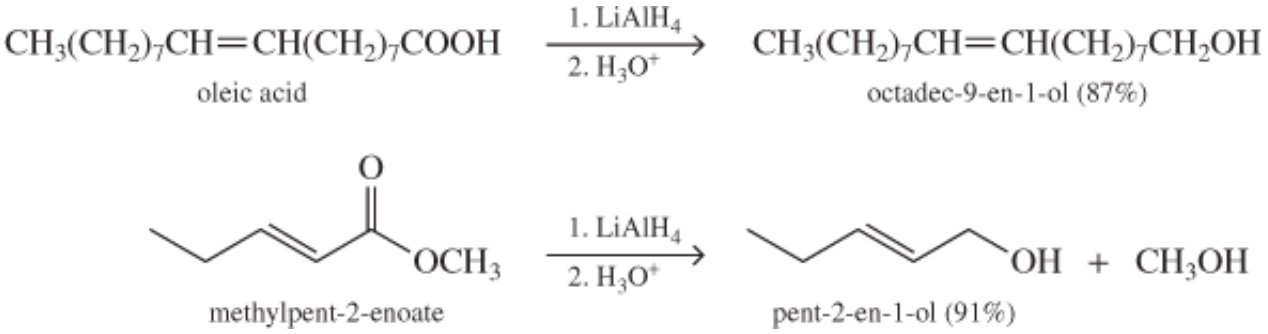


Reduction of Carbonyl Compounds

Alcohols can be prepared by the reduction of carbonyl compounds. Aldehydes are reduced to primary alcohols, and ketones are reduced to secondary alcohols (discussed further in section 21.5). This is most commonly carried out using metal hydride reducing agents such as sodium borohydride, $NaBH_4$, or lithium aluminium hydride, $LiAlH_4$.

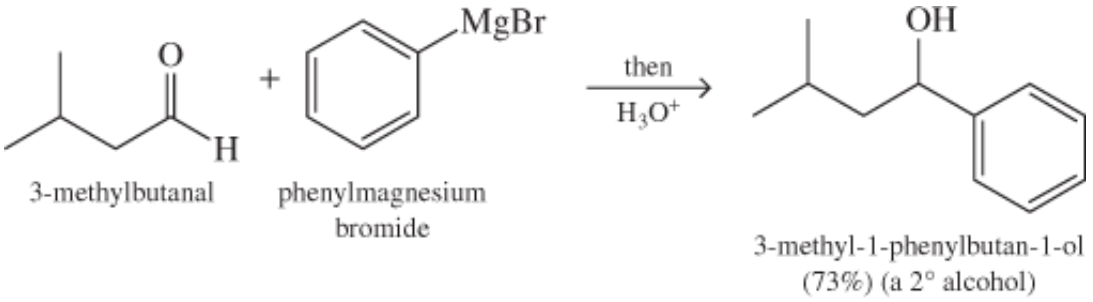


Carboxylic acids and esters can be reduced to form primary alcohols (discussed further in section 23.5). This reduction requires the use of the more powerful reducing agent, $LiAlH_4$.

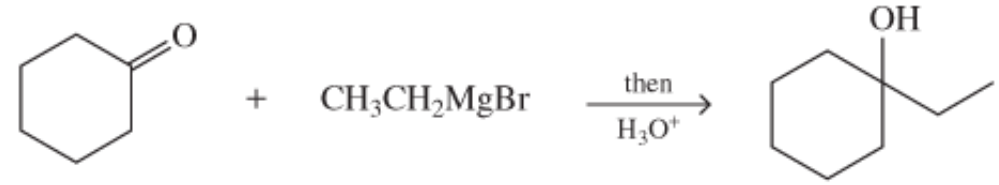


Addition of Grignard Reagents to Carbonyl Compounds

Alcohols can be prepared by the addition of Grignard reagents to carbonyl compounds. Aldehydes react with Grignard reagents to give secondary alcohols (except formaldehyde (methanal), which gives primary alcohols), while ketones give tertiary alcohols (discussed in greater detail in section 21.5).

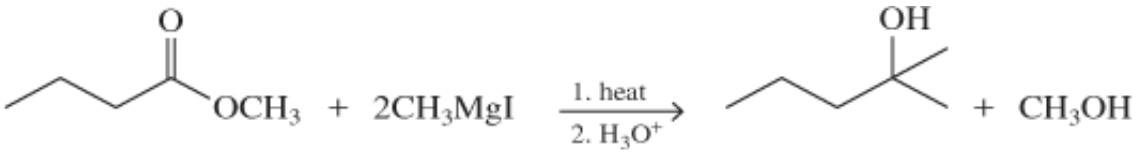


3-methylbutanal + phenylmagnesium bromide → 3-methyl-1-phenylbutan-1-ol (73%) (a 2° alcohol)



cyclohexanone + ethylmagnesium bromide → 1-ethylcyclohexanol (89%) (a 3° alcohol)

Esters can also be converted into tertiary alcohols by reaction with Grignard reagents (discussed further in section 21.5). In this case, 2 equivalents of Grignard reagent add to the ester to give the tertiary alcohol.



methyl butanoate + methylmagnesium iodide → 2-methylpentan-2-ol + CH_3OH

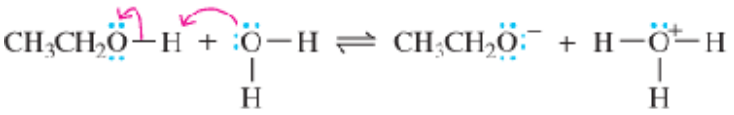
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19.2 Reactions of Alcohols

In this section, we study the acidity and basicity of alcohols, their dehydration to alkenes, their conversion to haloalkanes, and their oxidation to aldehydes, ketones or carboxylic acids.

Acidity of Alcohols

Alcohols have similar acid ionisation constants (pK_a) to water (15.7), which means that aqueous solutions of alcohols have a pH close to that of pure water. The pK_a of ethanol, for example, is 15.9. The reaction below is a simple acid–base reaction in which ethanol is acting as an acid and water is acting as a base.



$$K_a = \frac{[CH_3CH_2O^-][H_3O^+]}{[CH_3CH_2OH]} = 1.3 \times 10^{-16}$$

$$pK_a = 15.9$$

Table 19.2 gives the acid ionisation constants for several low-molar-mass alcohols. Methanol and ethanol are about as acidic as water. Higher-molar-mass, water-soluble alcohols are slightly weaker acids than water (pH of aqueous solutions = 7). (At this point, it would be worthwhile to review the position of equilibrium in acid–base reactions discussed in chapter 11). Note that, although acetic acid is a 'weak acid' compared with acids such as HCl, its K_a is still 10^{10} times greater than that of alcohols.

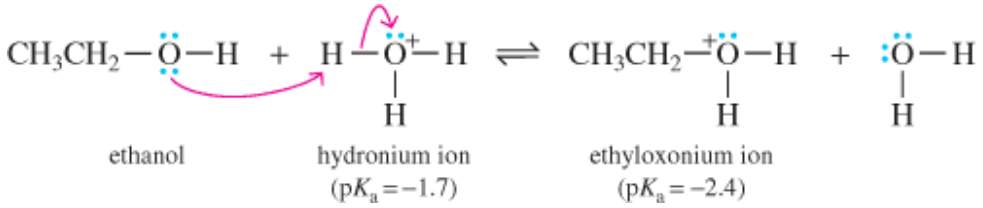
TABLE 19.2 pK_a values for selected alcohols in dilute aqueous solution[(a)].

Compound	Structural formula	pK_a	
hydrogen chloride	HCl	–7	stronger acid
acetic acid	CH_3COOH	4.74	
methanol	CH_3OH	15.5	
water	H_2O	15.7	
ethanol	CH_3CH_2OH	15.9	
propan-2-ol	$(CH_3)_2CHOH$	17	
2-methylpropan-2-ol	$(CH_3)_3COH$	18	weaker acid

(a) Also given for comparison are pK_a values for water, acetic acid and hydrogen chloride.

Basicity of Alcohols

In the presence of a strong acid, the oxygen atom of an alcohol is a weak base and reacts with the acid by proton transfer to form an oxonium ion. The reaction below is a simple acid–base reaction in which ethanol is acting as a base and the hydronium ion is acting as an acid.



ethanol — hydronium ion ($pK_a = -1.7$) — ethyloxonium ion ($pK_a = -2.4$)

Thus, depending on conditions, alcohols can function as both weak acids and weak bases.

Reaction with Active Metals

Like water, alcohols react with Li, Na, K, Mg and other active metals to liberate hydrogen gas, although, in the case of alcohols, metal alkoxides rather than hydroxides are formed. In the following oxidation–reduction reaction, Na is oxidised to Na^+ and H^+ is reduced to H_2 (figure 19.6).

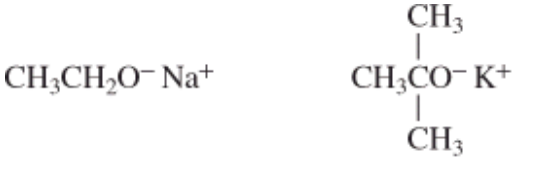
$$2CH_3OH + 2Na \rightarrow \underset{\text{sodium methoxide}}{2CH_3O^-Na^+} + H_2$$



FIGURE 19.6 Methanol reacts with sodium metal to produce hydrogen gas.

To name a metal alkoxide, write the name of the cation followed by the name of the anion. The name of an alkoxide ion is derived from a prefix showing the number of carbon atoms and their arrangement (e.g. *meth-*, *eth-*, *isoprop-*, *tert-but-*) followed by the suffix *-oxide*. Alkoxides can also be named as alkanolates by adding the suffix *-ate* to the alcohol name (e.g. methanolate, ethanolate).

Alkoxide ions are generally stronger bases than the hydroxide ion. In addition to sodium meth-oxide, the following metal salts of alcohols are commonly used in organic reactions that require a strong base in a nonaqueous solvent: sodium ethoxide in ethanol, and potassium *tert*-butoxide in 2-methylpropan-2-ol (*tert*-butyl alcohol).



sodium ethoxide potassium *tert*-butoxide

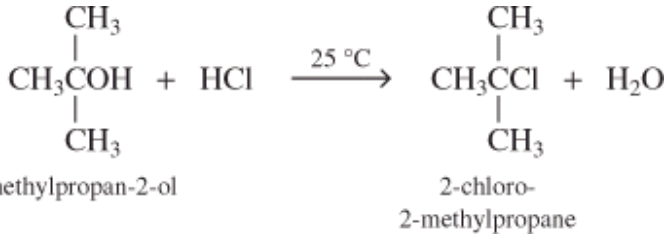
As we saw in chapter 18, alkoxide ions can also be used as nucleophiles in substi tution reactions.

Conversion to Haloalkanes

The conversion of an alcohol to a haloalkane involves substituting a halogen for the —OH group at a saturated carbon atom. The most common reagents for this conversion are the hydrohalic acids (halogen acids), thionyl chloride and phosphorus halides.

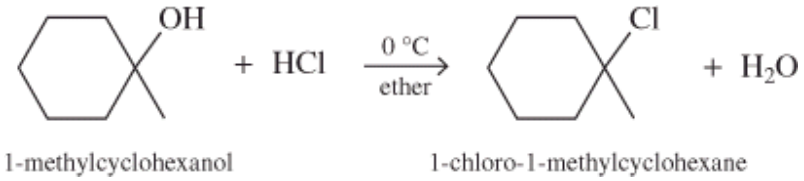
Reaction with Hydrohalic Acids (HCl, HBr and HI)

Water-soluble tertiary alcohols react very rapidly with HCl, HBr and HI. Mixing a tertiary alcohol with concentrated hydrochloric acid for a few minutes at room temperature converts the alcohol to a water-insoluble chloroalkane that separates from the aqueous layer.



Low-molar-mass, water-soluble primary and secondary alcohols do not react under these conditions.

Water-insoluble tertiary alcohols are converted to tertiary halides by bubbling gaseous HX through a solution of the alcohol dissolved in diethyl ether or tetrahydrofuran (THF).



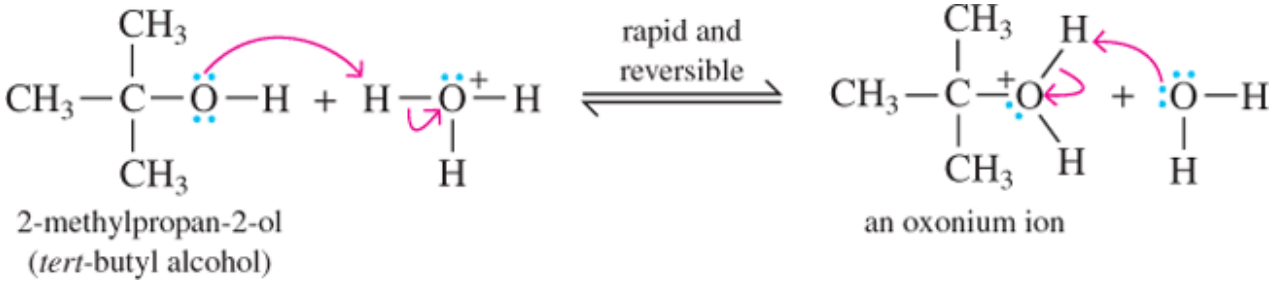
Water-insoluble primary and secondary alcohols react only slowly under these conditions.

Primary and secondary alcohols are converted to bromoalkanes and iodoalkanes by treatment with concentrated hydrobromic and hydroiodic acids. The conditions required to convert a primarly alcohol to a bromoalkane are very harsh and cannot be used in the presence of most other functional groups. For example, boiling butan-1-ol with concentrated HBr gives 1-bromobutane.

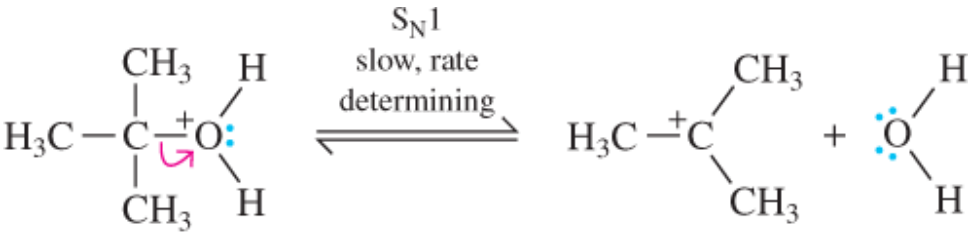


From observations of the relative ease of reaction of alcohols with HX (3° > 2° > 1°), it was proposed that the conversion of tertiary and secondary alcohols to haloalkanes by concentrated HX occurs by an S_Nl mechanism (see section 18.2 for further discussion of nucleophilic substitution mechanisms) and involves the formation of a carbocation intermediate. This was later confirmed by appropriate kinetics experiments. The reaction is believed to occur through the three steps shown below.

Step 1: Rapid and reversible proton transfer from the acid to the —OH group gives an oxonium ion (a simple acid–base reaction). This proton transfer converts the leaving group from OH^-, a poor leaving group, to H_2O, a better leaving group.



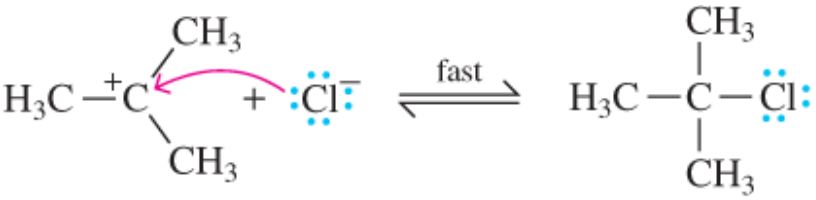
Step 2: Loss of water from the oxonium ion gives a 3° carbocation intermediate (or a 2° carbocation intermediate if we started with a 2° alcohol).



oxonium ion — 3° carbocation

When we say that a reaction is slow, we are *not* suggesting that individual bonds are broken/ formed slowly. The *number* of molecules that undergo the described transformation in a given period of time determines the rate of the reaction (see section 15.1 for more details).

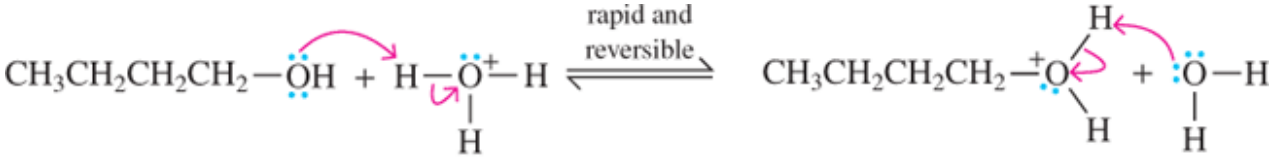
Step 3: Reaction of the 3° carbocation intermediate (an electrophile) with a chloride ion (a nucleophile) gives the haloalkane product.



2-chloro-2-methylpropane
(*tert*-butyl chloride)

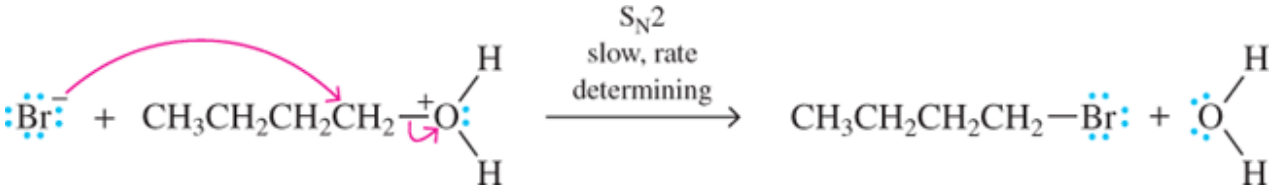
Primary alcohols react with HX by an S_N2 mechanism. In the rate-determining step, the halide ion displaces H_2O from the carbon atom bearing the oxonium ion. The displacement of H_2O and the formation of the C—X bond are simultaneous.

Step 1: Rapid and reversible proton transfer to the —OH group (a simple acid–base reaction) converts the leaving group from OH^- to H_2O, which is a better leaving group.



an oxonium ion

Step 2: The nucleophilic displacement of H_2O by Br^- then gives the bromoalkane.



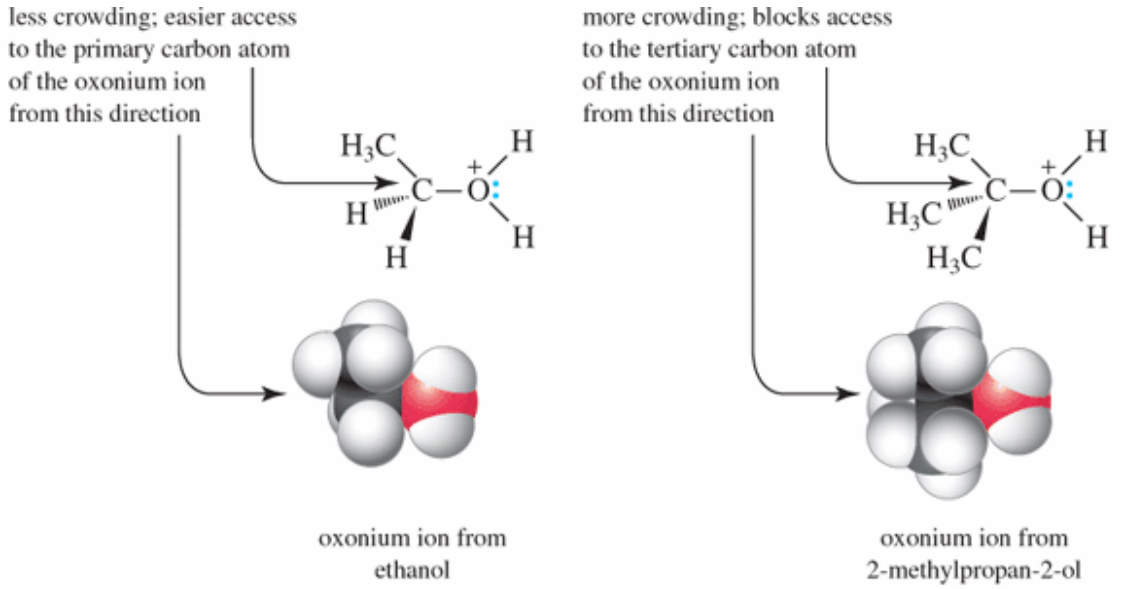
(Theoretically this step is reversible, but in practice the reverse reaction is so slow that we generally consider it as nonreversible.)

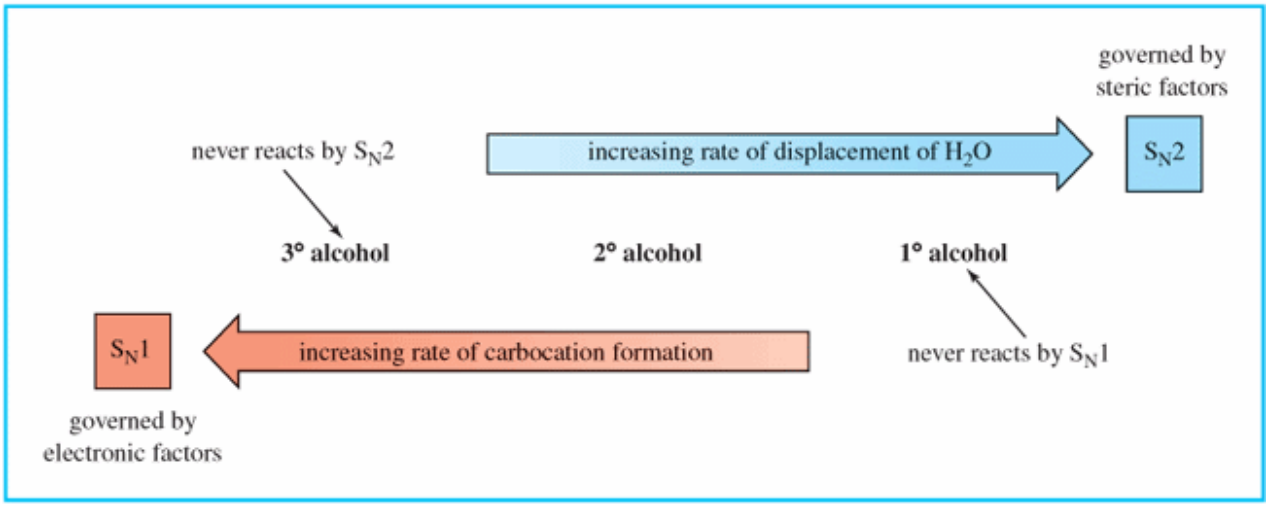
Why do tertiary alcohols react with HX by formation of carbocation intermediates (S_N1), whereas primary alcohols react by direct displacement of the $—OH_2^+$ group (the protonated — OH group) (S_N2)? The answer is a combination of the same two factors involved in nucleophilic substitution reactions of haloalkanes (section 18.2):

1. *Electronic factors:* Tertiary carbocations are the most stable and most readily formed, whereas primary carbocations are the least stable and hardest to form. Therefore, tertiary alcohols are most likely to react by carbocation formation, secondary alcohols are intermediate and primary alcohols rarely, if ever, react by

carbocation formation.

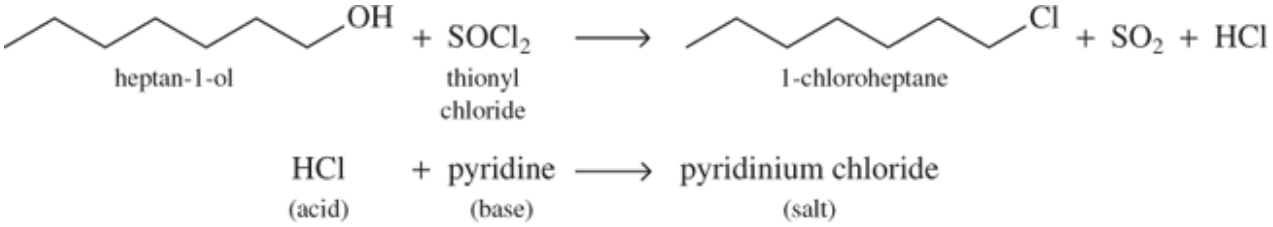
2. *Steric factors:* To form a new carbon–halogen bond by an S_N2 mechanism, the halide ion must approach the carbon atom bearing the leaving group from the side directly opposite that group and begin to form a new covalent bond. If we compare the carbon atom attached to the oxygen atom of an oxonium ion generated from a primary alcohol with one generated from a tertiary alcohol, we see that the approach is considerably easier in the case of the primary alcohol. For a primary alcohol, the approach from the side opposite the carbon atom bearing the oxonium ion is screened by two hydrogen atoms and one alkyl group, whereas, in tertiary alcohols, this type of approach is screened by three alkyl groups.





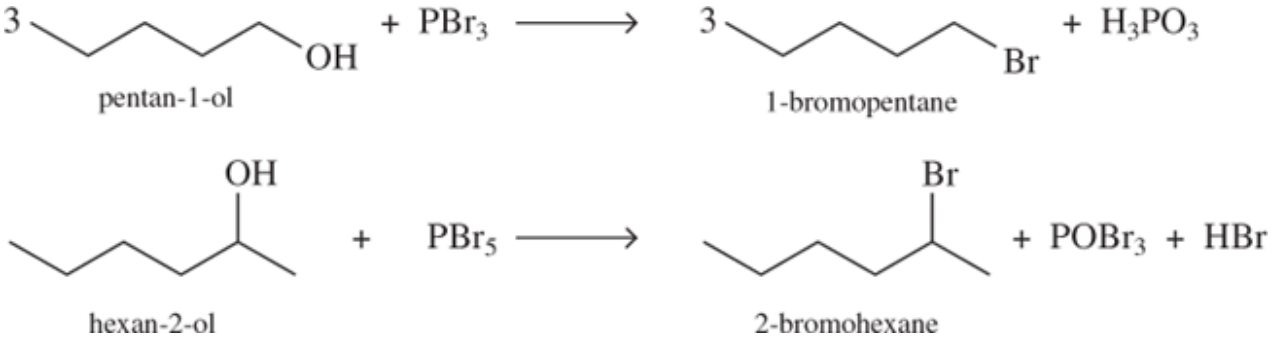
Reaction with Thionyl Chloride, $SOCl_2$

The most widely used reagent for the conversion of primary and secondary alcohols to alkyl chlorides is thionyl chloride, $SOCl_2$. The by-products of this nucleophilic substitution reaction are HCl and SO_2, both given off as gases. Often, an organic base such as pyridine is added to neutralise the HCl by-product.



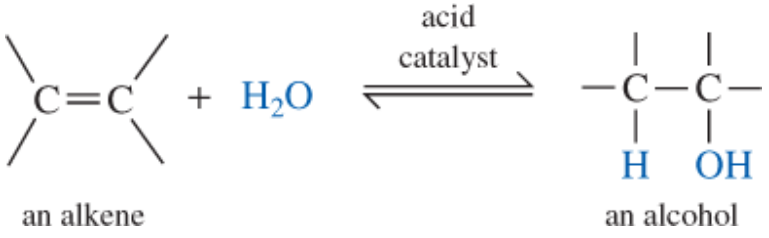
Reaction with Phosphorus Halides

Alcohols can also be converted into haloalkanes by reaction with phosphorus halides (PX_3 or PX_5, where X = Cl or Br). These are particularly useful for the formation of alkyl bromides. The reaction by-products are water soluble so they are easily separated from the haloalkane as haloalkanes are not normally soluble in water. Note that 3 equivalents of alcohol can react with 1 equivalent of phosphorus tribromide.



Acid-catalysed Dehydration to Alkenes

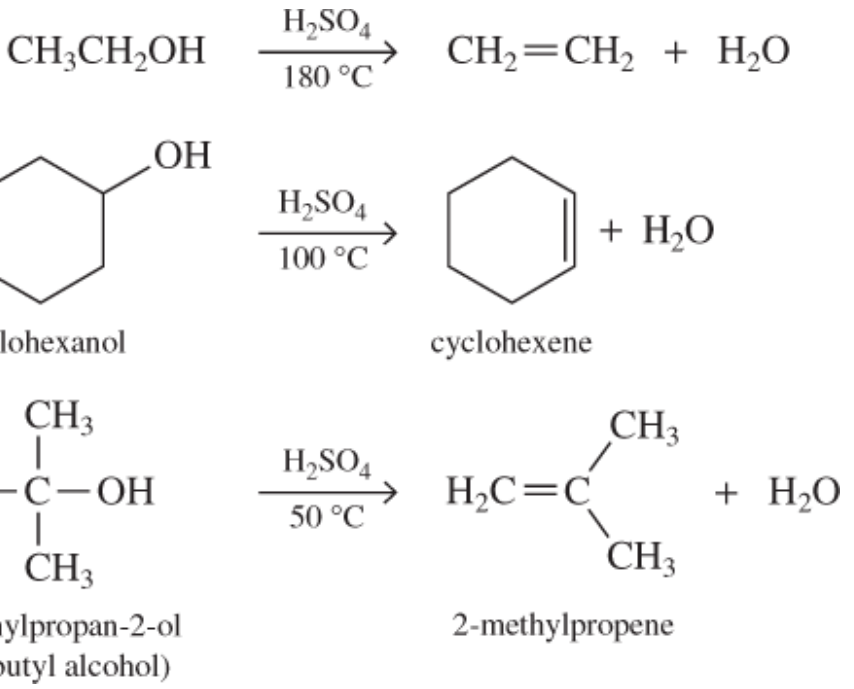
An alcohol can be converted to an alkene by **dehydration**, that is, by the elimination of a molecule of water from adjacent carbon atoms. In section 16.5, we discussed the acid-catalysed hydration of alkenes to give alcohols. In this section, we will discuss the acid-catalysed dehydration of alcohols to give alkenes. In fact, hydration–dehydration reactions are reversible. Alkene hydration and alcohol dehydration are competing reactions, and the following equilibrium exists:



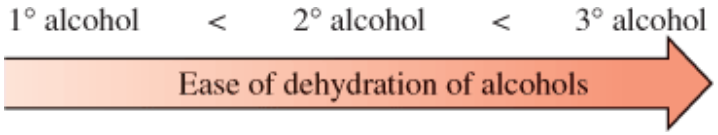
How, then, do we control which product will predominate? Recall that Le Châtelier's principle (section 9.4, p. 364) states that a system in equilibrium will respond to a stress in the equilibrium by counteracting that stress. This response allows us to control these two reactions to give the desired product. Large amounts of water (achieved with the use of dilute aqueous acid) favour alcohol formation, whereas a scarcity of water (achieved using

concentrated acid) or experi-mental conditions that remove water (for example, heating the reaction mixture above 100 °C) favour alkene formation. Thus, depending on the experimental conditions, it is possible to use the hydration–dehydration equilibrium to selectively prepare either alcohols or alkenes in high yields.

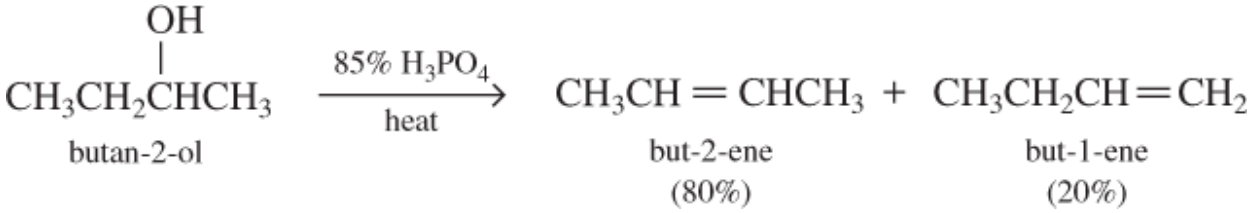
In the laboratory, the dehydration of an alcohol is most often carried out by heating it with either 85% phosphoric acid or concentrated sulfuric acid (typically 98%). Primary alcohols are the most difficult to dehydrate and generally require heating in concentrated sulfuric acid at temperatures as high as 180 °C. Secondary alcohols undergo acid-catalysed dehydration at somewhat lower temperatures. The acid-catalysed dehydration of tertiary alcohols often requires temperatures only slightly above room temperature.



Thus, the ease of acid-catalysed dehydration of alcohols occurs in the order:



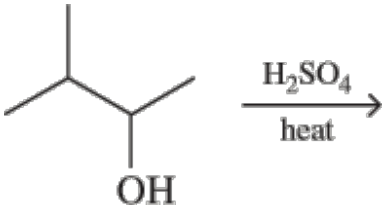
When isomeric alkenes are obtained in the acid-catalysed dehydration of an alcohol, the more stable alkene (the one with the greater number of substituents on the double bond generally pre-dominates; that is, the acid-catalysed dehydration of alcohols follows Zaitsev's rule (section 18.3).



WORKED EXAMPLE 19.3

Acid-catalysed Dehydration

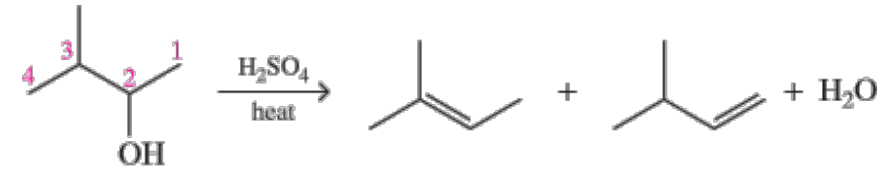
Draw structural formulae for the alkenes that form upon acid-catalysed dehydration of the alcohol on the right, and predict which alkene is the major product.



Analysis

Identify the carbon atom bearing the —OH group, which is C(2) in this example. In a dehydration reaction, a hydrogen ion is removed from one of the carbon atoms neighbouring this carbon atom, C(1) or C(3) in this case. The double bond is formed between the carbon atom with the —OH group and the carbon atom that loses the hydrogen ion, in this example, between C(2) and C(3), or C(2) and C(1). To predict the major product, use Zaitsev's rule.

Solution



3-methylbutan-2-ol — 2-methylbut-2-ene (major product) — 3-methylbut-1-ene

With three alkyl groups (three methyl groups) on the double bond, 2-methylbut-2-ene is the major product and is formed by elimination between C(2) and C(3). With only one alkyl group (an isopropyl group) on the double bond, 3-methylbut-1-ene is the minor product and is formed by elimination between C(2) and C(1).

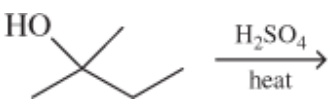
Is our answer reasonable?

You should check that, in each of the alkenes, the carbon atom that was bonded to the —OH group is now one of the carbon atoms in the double bond.

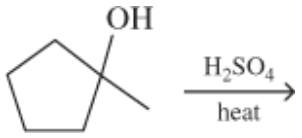
PRACTICE EXERCISE 19.3

Draw structural formulae for the alkenes that form upon acid-catalysed dehydration of the following alcohols, and predict which alkene is the major product.

(a)

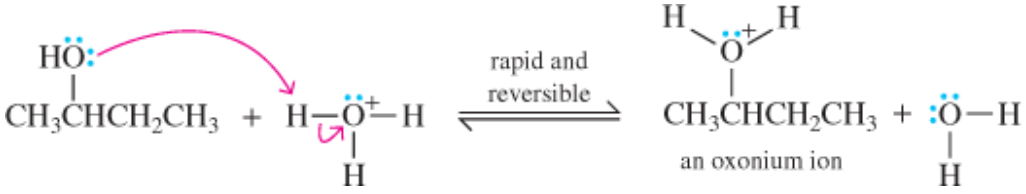


(b)

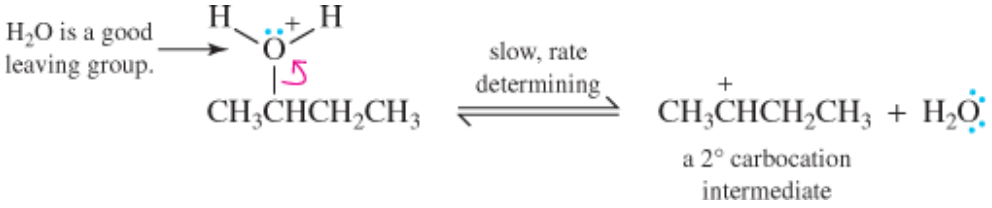


From the relative ease of dehydration of alcohols (3° > 2° > 1°), chemists proposed a three-step mechanism for the acid-catalysed dehydration of secondary and tertiary alcohols. This mechanism involves the formation of a carbocation intermediate in the rate-determining step and is therefore an E1 mechanism.

Step 1: Proton transfer from H_3O^+ to the —OH group of the alcohol gives an oxonium ion (a simple acid–base reaction). This converts OH-, a poor leaving group, into H_2O, a better leaving group.

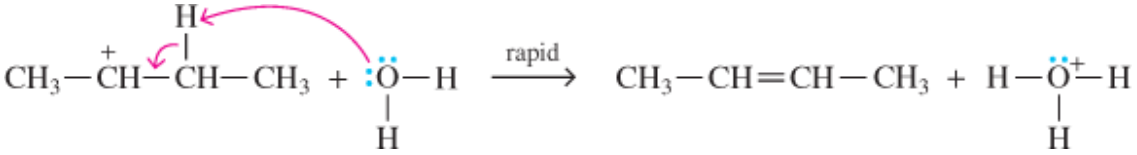


Step 2: Breaking of the C—O bond gives a 2° carbocation intermediate (or a 3° carbocation intermediate if we started with a 3° alcohol) and H_2O.



You should note that the two steps above are the same as those for the acid-catalysed conversion of secondary and tertiary alcohols into haloalkanes (p. 817).

Step 3: Proton transfer to H_2O from the carbon atom adjacent to the positively charged carbon atom gives the alkene and regenerates the catalyst. The σ electrons of a C—H bond become the φ electrons of the carbon–carbon double bond.

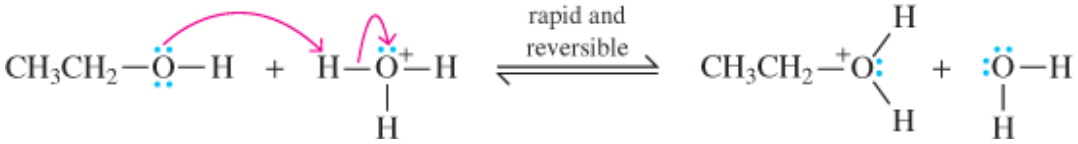


Note that but-2-ene, the major product as predicted by Zaitsev's rule, is obtained as a mixture of *cis* and *trans* isomers. Removal of a proton from the methyl group adjacent to the positively charged carbon atom will produce but-1-ene.

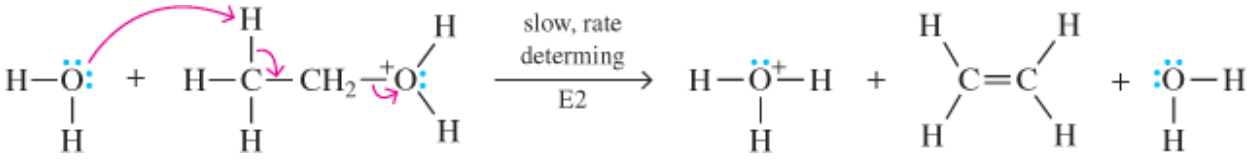
Because the rate-determining step in the acid-catalysed dehydration of secondary and tertiary alcohols is the formation of a carbocation intermediate, the relative ease of dehydration of these alcohols parallels the ease of formation of carbocations.

Primary alcohols do not readily dehydrate, but, when they do, it is believed that they react by the following two-step E2 mechanism, in which step 2 is the rate-determining step.

Step 1: Proton transfer from H_3O^+ to the —OH group of the alcohol gives an oxonium ion (a simple acid–base reaction).

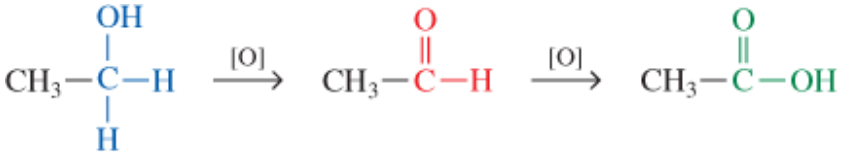


Step 2: Simultaneous proton transfer to the solvent and loss of H_2O gives the alkene.

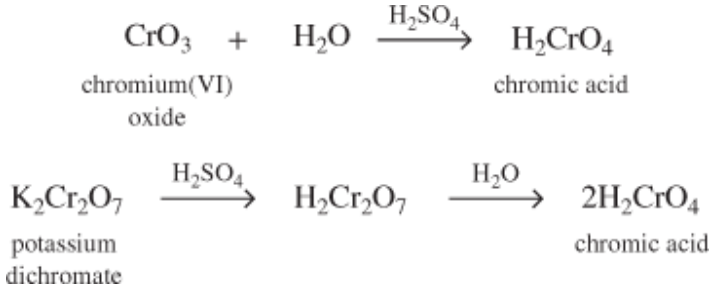


Oxidation of primary and secondary alcohols

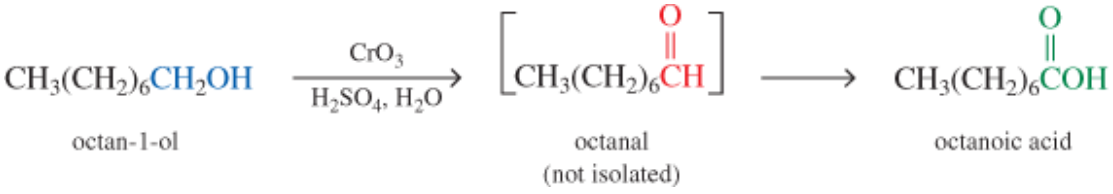
The oxidation of alcohols is another example of oxidation–reduction (redox) chemistry, as discussed in chapter 12 (see sections 12.1 and 12.2). Oxidation of a primary alcohol gives an aldehyde or a carboxylic acid, depending on the experimental conditions. Secondary alcohols are oxidised to ketones. Tertiary alcohols are not easily oxidised. The following is a series of transformations in which a primary alcohol is oxidised first to an aldehyde and then to a carboxylic acid. The fact that each transformation involves oxidation is indicated by the symbol [O] over the reaction arrow.



There are many oxidising agents available for the oxidation of alcohols. A small selection of these reagents includes potassium permanganate, sodium hypochlorite (bleach) and nitric acid. However, the reagent most commonly used in the laboratory for the oxidation of a primary alcohol to a carboxylic acid, and a secondary alcohol to a ketone, is chromic acid, H_2CrO_4. Chromic acid is prepared by dissolving either chromium(VI) oxide or potassium dichromate in aqueous sulfuric acid.



The oxidation of octan-1-ol by chromic acid in aqueous sulfuric acid gives octanoic acid in high yield. These experimental conditions are more than sufficient to oxidise the intermediate aldehyde to a carboxylic acid.

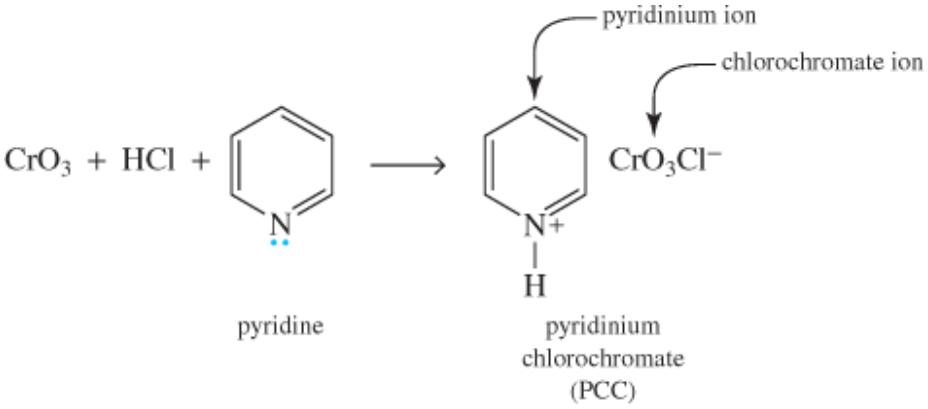


Let us consider the two half-equations for the reaction above (for revision, see section 12.2) and the balanced

equation. This allows us to determine the number of equivalents of oxidising agent required. For convenience, we will use the molecular formulae for octan-1-ol and octanoic acid:

$$C_8H_{18}O + H_2O \rightarrow C_8H_{16}O_2 + 4H^+ + 4e^- \quad \text{(oxidation)}$$
$$H_2CrO_4 + 6H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad \text{(reduction)}$$
$$3C_8H_{18}O + 4H_2CrO_4 + 12H^+ \rightarrow 3C_8H_{16}O_2 + 4Cr^{3+} + 13H_2O \quad \text{(overall reaction)}$$

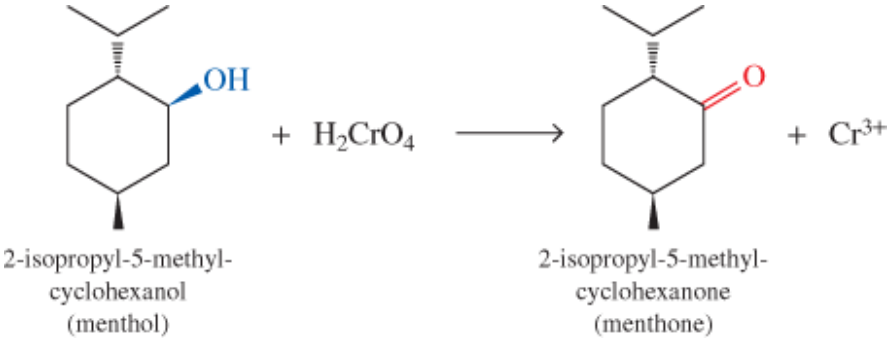
To prepare aldehydes by oxidising primary alcohols, the mild oxidising agent, **pyridinium chlorochromate (PCC)**, is commonly used. This is prepared by dissolving CrO_3 in aqueous HCl and adding pyridine to precipitate the PCC as an orange solid as shown below. (*Note:* The oxidation state of chromium is still +6.) PCC oxidations are carried out in aprotic solvents, most commonly dichloromethane, CH_2Cl_2.



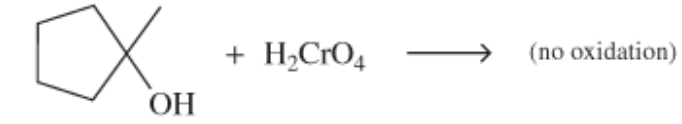
This reagent is selective for the oxidation of primary alcohols to aldehydes and also has little effect on carbon–carbon double bonds or other easily oxidised functional groups. In the following example, geraniol, a molecule produced by honey bees, is oxidised to geranial, a lemon-scented molecule used in perfumes, without affecting either carbon–carbon double bond.



Secondary alcohols are oxidised to ketones by both chromic acid and PCC.



Tertiary alcohols are resistant to oxidation because the carbon atom bearing the —OH group is bonded to three carbon atoms and therefore cannot form a carbon–oxygen double bond.



1-methylcyclopentanol

Note that the essential feature of the oxidation of an alcohol is the presence of at least one hydrogen atom on the carbon atom bearing the —OH group. Tertiary alcohols lack such a hydrogen, so they are not oxidised.

WORKED EXAMPLE 19.4

PCC Oxidations

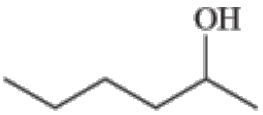
Draw the product of the treatment of each of the following alcohols with PCC.

(a)



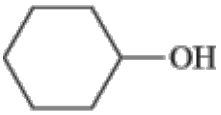
hexan-1-ol

(b)



hexan-2-ol

(c)



cyclohexanol

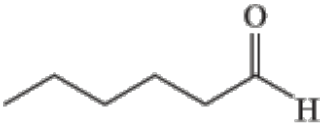
Analysis

As the oxidising agent is PCC, primary alcohols will be oxidised to aldehydes and secondary alcohols to ketones. Identify the carbon atom bearing the —OH group; the carbonyl group is formed at this position.

Solution

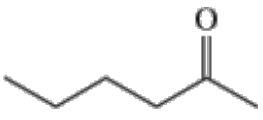
The primary alcohol hexan-1-ol is oxidised to hexanal. The secondary alcohol hexan-2-ol is oxidised to hexan-2-one. Cyclohexanol, a secondary alcohol, is oxidised to cyclohexanone.

(a)



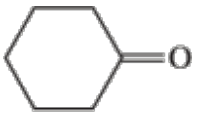
hexanal

(b)



hexan-2-one

(c)



cyclohexanone

Is our answer reasonable?

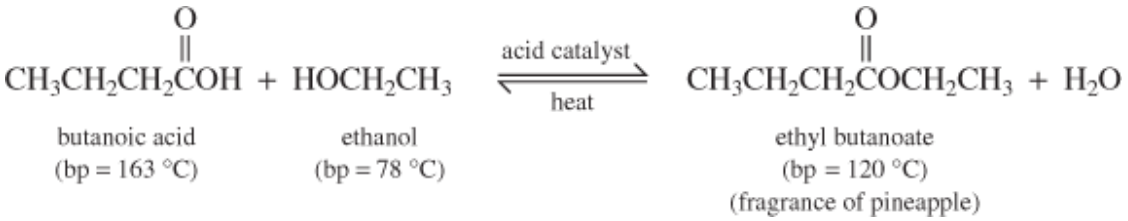
Check that an aldehyde has been formed from a primary alcohol, and a ketone has been formed from a secondary alcohol. Check also that the position of the carbonyl group is correct (particularly important for ketones).

PRACTICE EXERCISE 19.4

What is the product obtained on treating each of the alcohols in worked example 19.4 with chromic acid?

Ester Formation

An important reaction of alcohols is the formation of esters by condensation with carboxylic acids, acid chlorides or anhydrides. The chemistry will be introduced briefly here and discussed in greater detail in chapter 23.



Alcohols can also form esters with inorganic acids such as nitric acid, phosphoric acid, sulfuric and sulfonic acids (RSO_3H). Nitroglycerin is an example of an ester formed between glycerol and three mole equivalents of nitric acid. DNA and RNA (see chapter 25) are polymers in which the backbone consists of alternating units of phosphoric acid and a monosaccharide bonded together through ester linkages between the alcohol groups of the monosaccharide and the phosphoric acid mol ecules. Figure 19.7 shows some examples of esters formed between alcohols and inorganic acids.

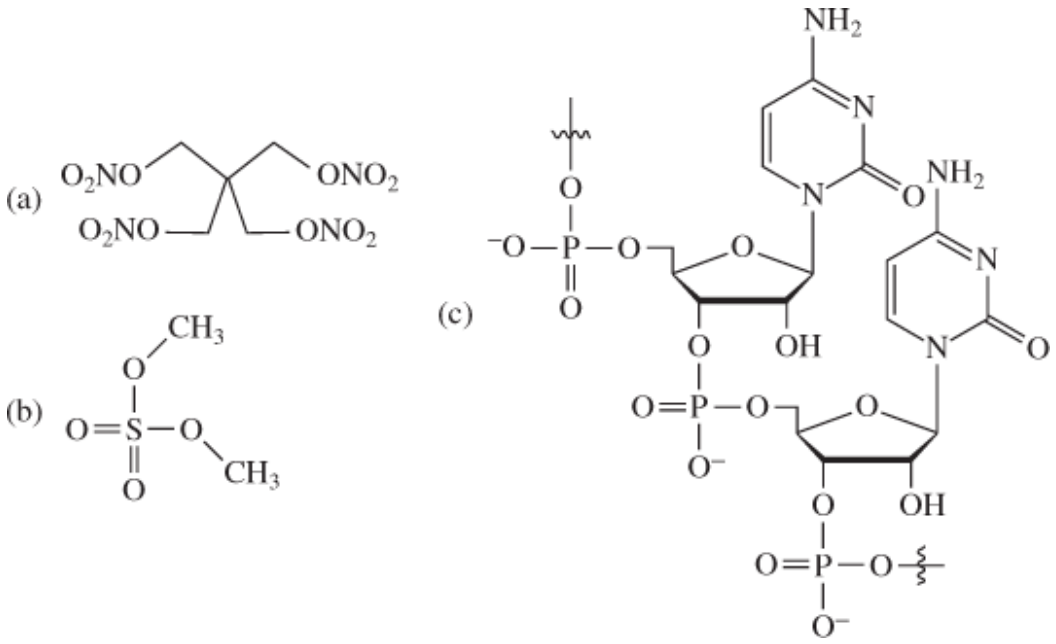


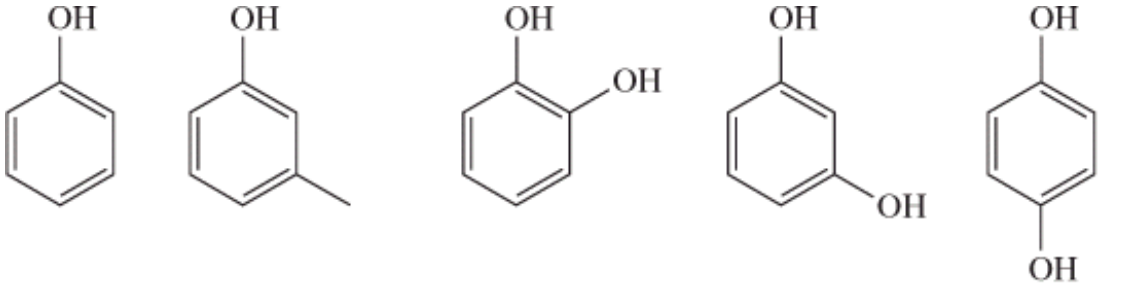
FIGURE 19.7 Examples of esters of inorganic acids:
(a) pentaerythritol tetranitrate (an explosive),
(b) dimethyl sulfate (an industrial methylating agent) and **(c)** a fragment of RNA.

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19.3 Phenols

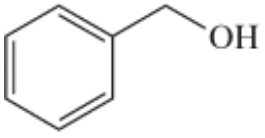
Phenols are compounds with one or more hydroxyl groups bonded directly to an aromatic ring. In the previous section we discussed the chemistry of alcohols (ROH) and here we will introduce the chemistry of phenols (ArOH). Although these functional groups are similar (they both form esters and ethers), they have some important differences, particularly their acidity.

We name substituted phenols either as derivatives of phenol or by common names as shown below.



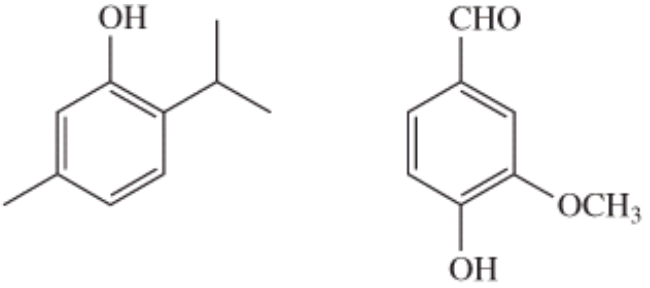
phenol | 3-methylphenol (*m*-cresol) | benzene-1,2-diol (catechol) | benzene-1,3-diol (resorcinol) | benzene-1,4-diol (hydroquinone)

Note that benzyl alcohol (phenylmethanol) is *not* a phenol because the hydroxyl group is not connected directly to the aromatic ring. It is the direct connection of the hydroxyl group to an aromatic ring that gives rise to the different chemical properties of phenols; these will be discussed below.



benzyl alcohol

Phenols are widely distributed in nature. Phenol itself and the isomeric cresols (*o*-, *m*- and *p*-cresol) are found in coal tar (the liquid distilled from coal in the production of coke). The phenol derivatives thymol and vanillin are important constituents of thyme and vanilla beans (figure 19.8), respectively.



2-isopropyl-5-methylphenol (thymol) | 4-hydroxy-3-methoxy-benzaldehyde (vanillin)



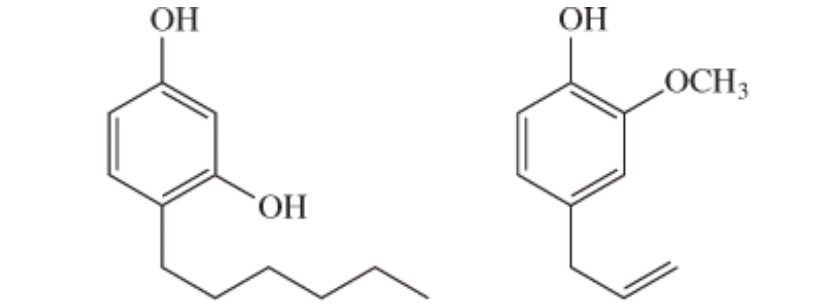


FIGURE 19.8 Vanillin is a constituent of vanilla beans.

Phenol, or carbolic acid, as it was once called, is a solid with a low melting point and is only slightly soluble in water. In sufficiently high concentrations, it is corrosive to all kinds of cells, because it has a high permeability across the cell membrane and disrupts biochemical processes within the cell. In dilute solutions, phenol has some antiseptic properties and was introduced into the practice of surgery by Joseph Lister, who demonstrated his technique of aseptic surgery at the University of Glasgow School of Medicine in 1865. Nowadays, phenol has been replaced by antiseptics that are more powerful and have fewer undesirable side effects. Among these is hexylresorcinol, which is widely used in nonprescription prepara tions as a mild antiseptic and disinfectant. Eugenol, which can be isolated from the flower buds of *Eugenia aromatica* (clove), is used as a dental antiseptic and analgesic. Capsaicin is the pungent component of various chillies and is also the active ingredient in oleoresin capsicum spray (commonly known as pepper spray, figure 19.9).



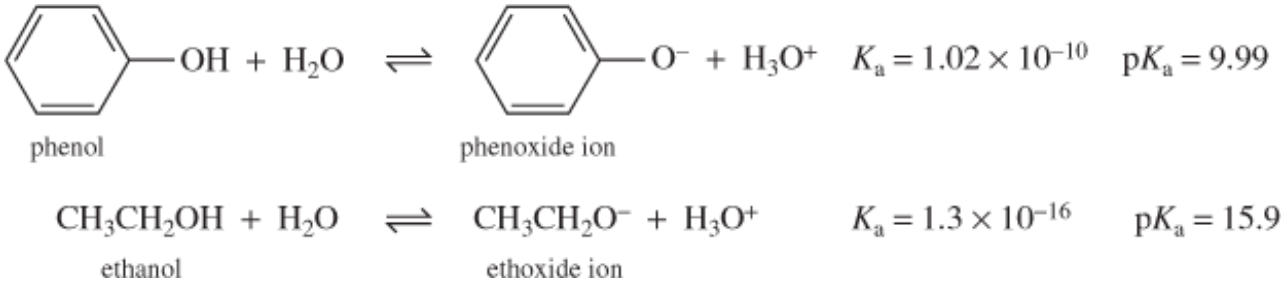
FIGURE 19.9 Capsicum spray contains the phenol derivative capsaicin.





Acidity of phenols

Phenols and alcohols both contain an —OH group. We group phenols as a separate class of compounds, however, because their chemical properties are quite different from those of alcohols. One of the most important differences is that phenols are significantly more acidic than alcohols. Indeed, the acidity constant for phenol is 10^6 times larger than that of ethanol.



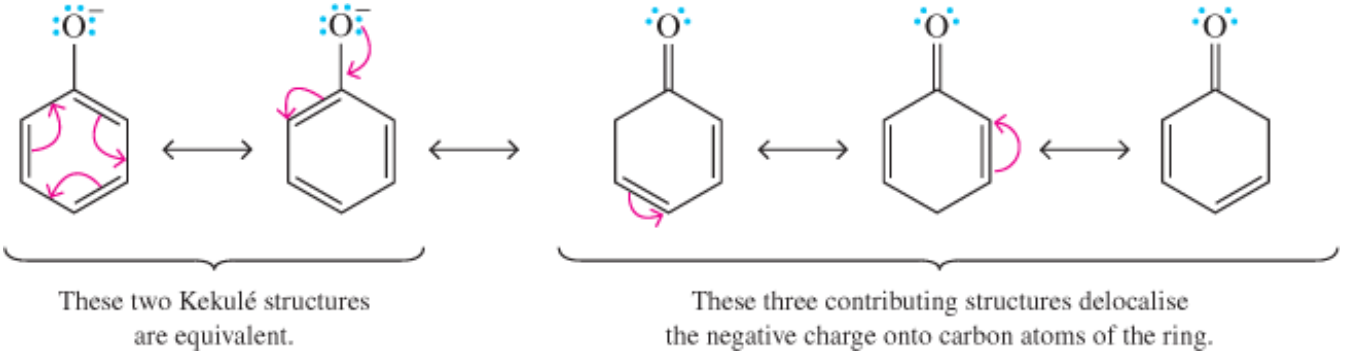
Another way to compare the relative acid strengths of ethanol and phenol is to look at the hydronium ion concentration and pH of a 0.1 m aqueous solution of each (table 19.3). For comparison, the $[H_3O^+]$ and pH of 0.1 m HCl are also included.

TABLE 19.3 Relative acidities of 0.1 M solutions of ethanol, phenol and HCl

Acid ionisation equation	$[H_3O^+]$	pH
$CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+$	1.0×10^{-7}	7.0
$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$	3.3×10^{-6}	5.4
$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$	0.1	1.0

In aqueous solution, alcohols are neutral substances, and the hydronium ion concentration of 0.1 M ethanol is the same as that of pure water. A 0.1 M solution of phenol is slightly acidic and has a pH of 5.4. By contrast, 0.1 M HCl, a strong acid (completely ionised in aqueous solution), has a pH of 1.0.

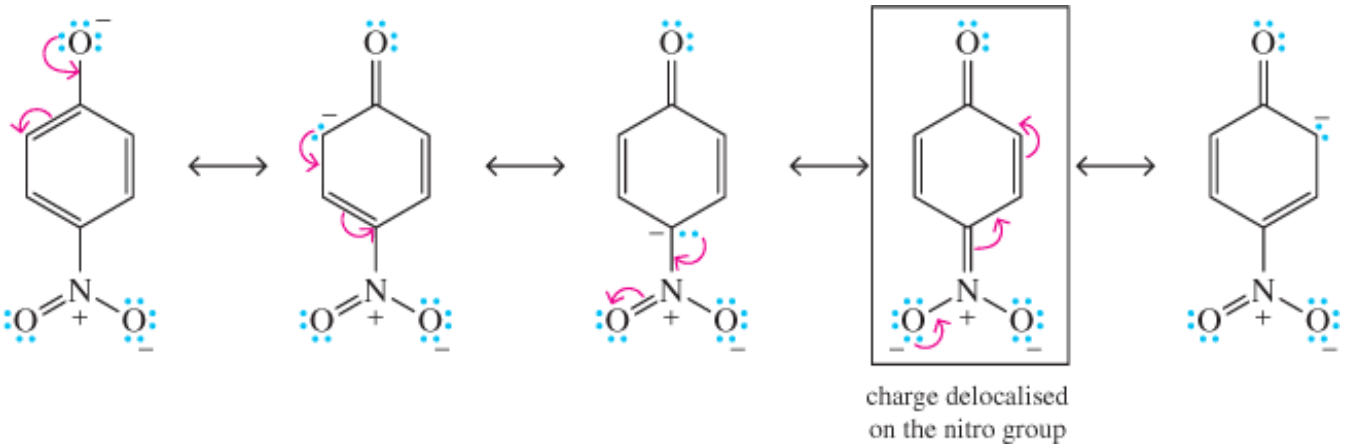
The greater acidity of phenols compared with alcohols results from the greater stability of the phenoxide ion compared with an alkoxide ion. The negative charge on the phenoxide ion is delocalised by resonance. The two contributing structures below left for the phenoxide ion place the negative charge on oxygen, while the three on the right place the negative charge on the *ortho* and *para* positions of the ring. Thus, in the resonance hybrid, the negative charge of the phenoxide ion is delocalised over four atoms, which stabilises the phenoxide ion relative to an alkoxide ion, for which no delocalisation is possible.



Note that, although the resonance model helps us understand why phenol is a stronger acid than ethanol, it does not provide any quantitative means of predicting just how much stronger an acid it might be. To find out how much stronger one acid is than another, we must determine their pK_a values experimentally and compare them.

Ring substituents have marked effects on the acidities of phenols through a combination of inductive and

resonance effects. Electron-withdrawing groups such as chloro, cyano and nitro withdraw electron density from the aromatic ring, weaken the O—H bond and stabilise the phenoxide ion. The diagram at the top of the next page shows the resonance forms for the 4-nitrophenoxide ion. You will notice that there is an extra resonance form (only one of the Kekulé forms has been shown) for this ion where the charge has been delocalised on an oxygen atom of the nitro group. This delocalisation on the oxygen atom increases the stability of the phenoxide ion and makes 4-nitrophenol a stronger acid than phenol.



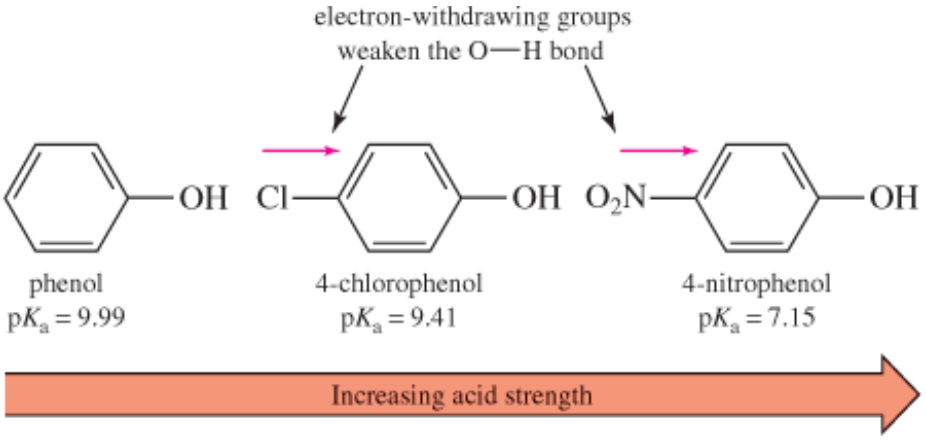
Conversely, electron-donating groups like amino, alkoxy and alkyl groups increase the electron density of the aromatic ring and destabilise the phenoxide ion. Table 19.4 lists the pK_a values for some phenols.

TABLE 19.4 The pK_a values for some phenols. The pK_{a1} value for acetic acid is given for comparison

Name	pK_a
2,4,6-trinitrophenol	0.42
acetic acid	4.76
4-nitrophenol	7.15
4-chlorophenol	9.41
phenol	9.99
4-methoxyphenol	10.21
4-methylphenol	10.26

stronger acid

weaker acid



WORKED EXAMPLE 19.5

Acidity

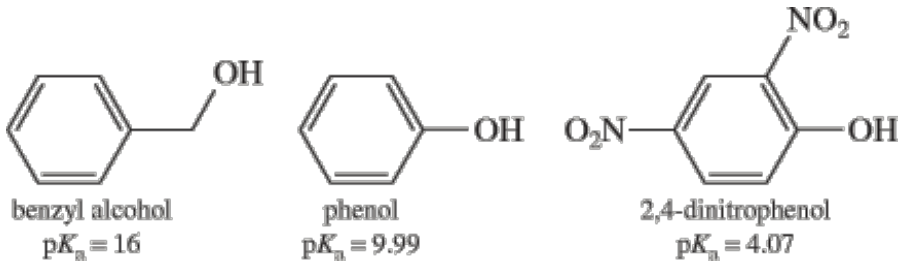
Arrange these compounds in order of increasing acidity: 2,4-dinitrophenol, phenol and benzyl alcohol.

Analysis

As alcohols are significantly less acidic than phenols, these should be listed first. Of the phenols, determine whether the substituents are electron withdrawing or electron donating. Electron-withdrawing groups increase the acidity of the phenol, while electron-donating groups decrease the acidity.

Solution

Benzyl alcohol, a primary alcohol, has a pK_a of approximately 16. The pK_a of phenol is 9.99. Nitro groups are electron withdrawing and increase the acidity of the phenolic —OH group. In order of increasing acidity, these compounds are:



benzyl alcohol pK_a = 16 | phenol pK_a = 9.99 | 2,4-dinitrophenol pK_a = 4.07

Is our answer reasonable?

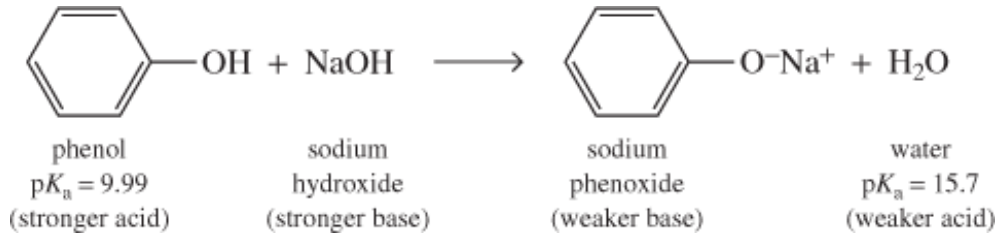
Check that your answer has the compounds in the order of: alcohols < phenols with electron-donating groups < phenol < phenols with electron withdrawing groups.

PRACTICE EXERCISE 19.5

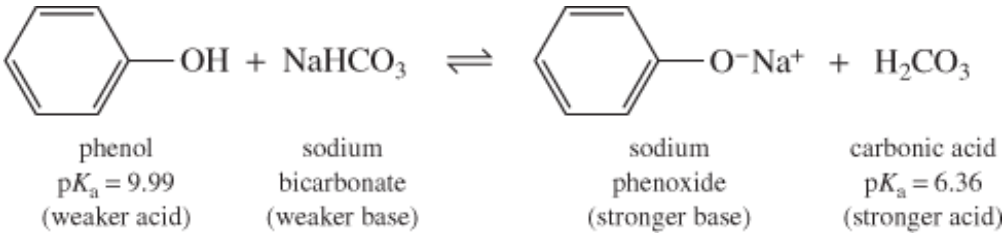
Arrange these compounds in order of increasing acidity: 2,4-dichlorophenol, phenol and cyclohexanol.

Acid–base Reactions of Phenols

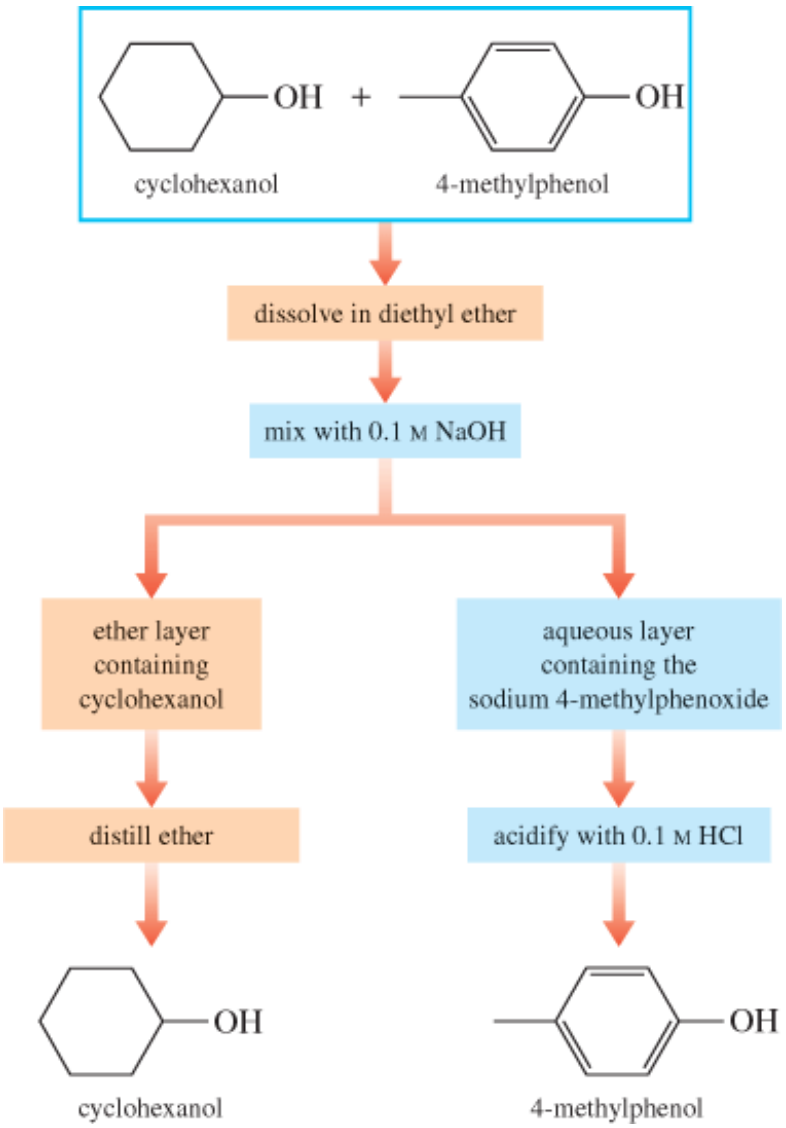
Phenols are weak acids and react with strong bases, such as NaOH, to form water-soluble salts.



Most phenols do not react with weaker bases, such as sodium bicarbonate, and do not dissolve in aqueous sodium bicarbonate. Carbonic acid is a stronger acid than most phenols and, consequently, the equilibrium for the reaction of phenols with bicarbonate ions lies far to the left (see chapter 11).

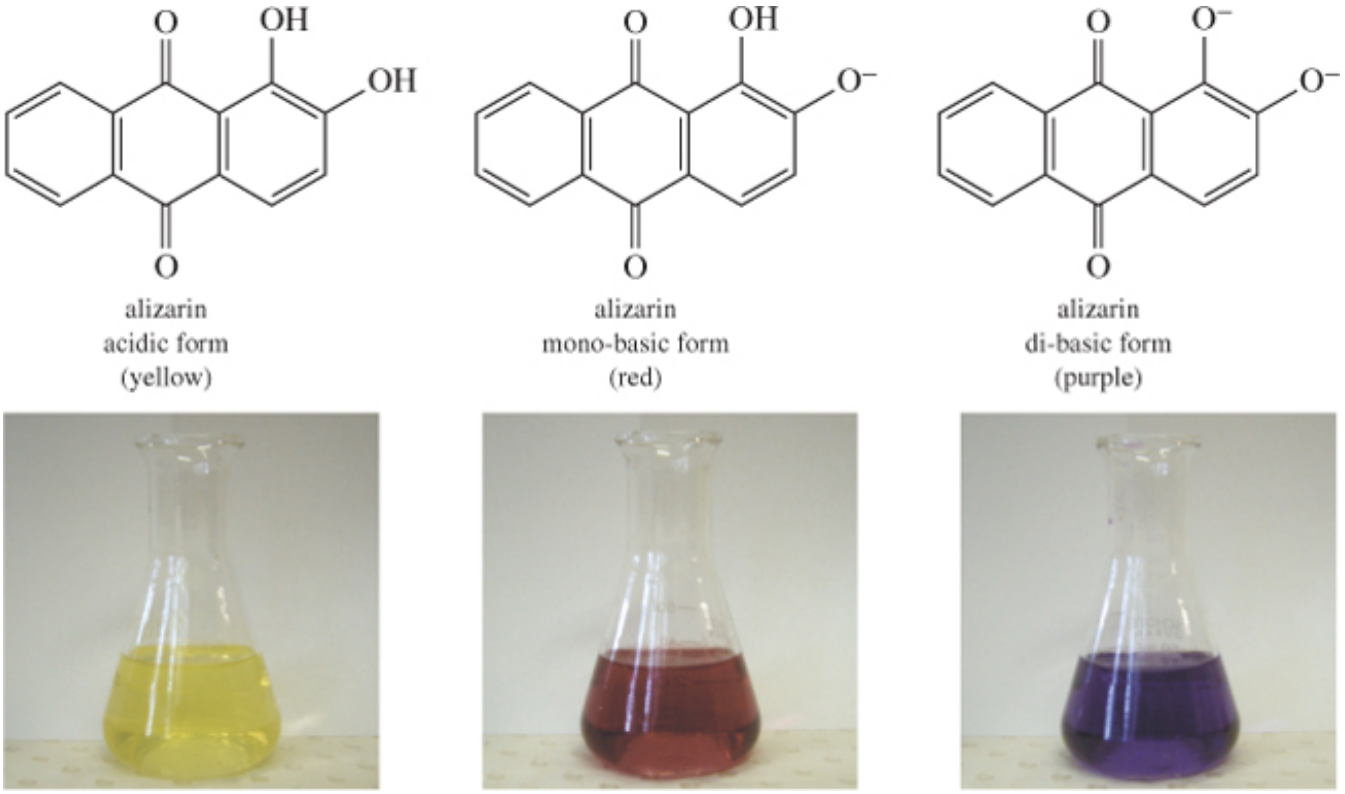


The fact that phenols are weakly acidic, whereas alcohols are neutral, provides a convenient way to separate phenols from water-insoluble alcohols. Suppose that we want to separate 4-methylphenol from cyclohexanol. Each is only slightly soluble in water; therefore, they cannot be separated on the basis of their water solubility. They can be separated, however, on the basis of their difference in acidity. First, the mixture of the two is dissolved in diethyl ether or some other water-immiscible solvent. Next, the ether solution is placed in a separating funnel and shaken with dilute aqueous NaOH. Under these conditions, 4-methylphenol reacts with NaOH to give sodium 4-methylphenoxide, a water-soluble salt. The upper layer in the separating funnel, diethyl ether (density = 0.74 g mL^{-1}), now contains only dissolved cyclohexanol. The lower aqueous layer contains dissolved sodium 4-methylphenoxide. The layers are separated, and distillation of the ether (bp = 35 °C) leaves pure cyclohexanol (bp = 161 °C). Acidification of the aqueous phase with 0.1 M HCl or another strong acid converts sodium 4-methylphenoxide to 4-methylphenol, which is sparingly soluble in water and can be extracted with ether and recovered in pure form. The flowchart on the right summarises these experimental steps.

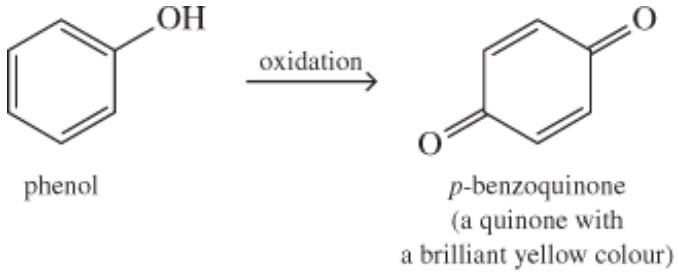


Oxidation of Phenols

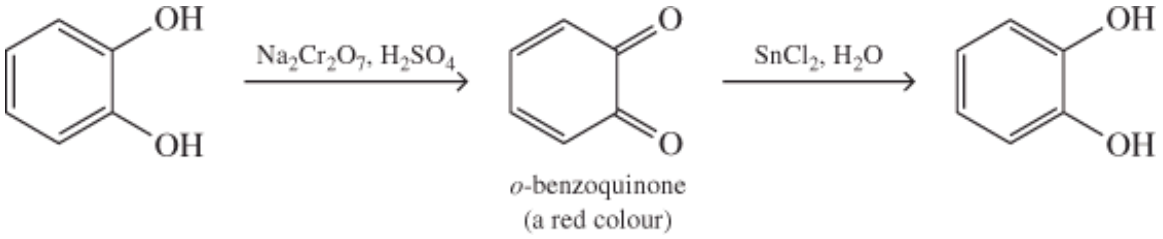
Phenols are readily oxidised to give quinones. Quinones are intensely coloured compounds ranging from red through to violet. The pink tinge found in old bottles of phenol is due to trace amounts of quinones. The pH indicator alizarin is a quinone. It has two acidic hydrogens, so it can be used for two different pH regions. It is yellow at pH < 5.5, red at pH 6.8–11 and purple at pH > 12.



The oxidation of phenols is quite different from the oxidation of alcohols (see section 19.2) because they do not have a hydrogen atom on the carbon atom bearing the hydroxyl group. The parent compound, phenol, is easily oxidised and gives rise to cyclohexa-2,5-dien-1,4-dione (*p*-benzoquinone).

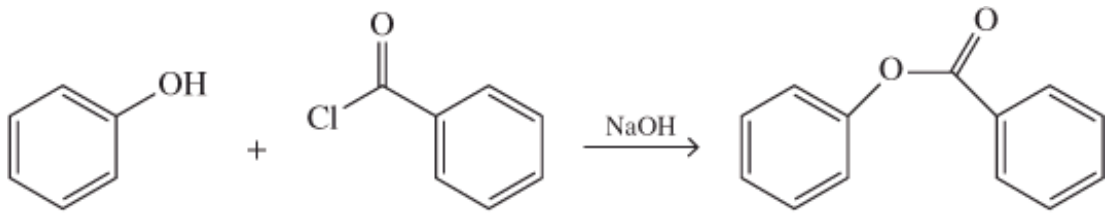


The oxidation of 1,2- and 1,4-dihydroxybenzene also occurs readily and gives the corresponding *o*- and *p*-benzoquinone. The benzoquinone can also be easily reduced to the original dihydroxybenzene by treatment with a mild reducing agent.



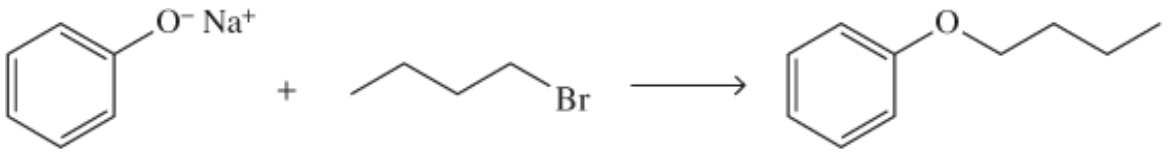
Ester and Ether Formation

Phenols can form esters by reaction with acid chlorides or acid anhydrides. However, unlike the alcohols (see section 19.2), esters cannot be prepared by treatment of phenols with carboxylic acids as phenols are generally too unreactive. This lack of reactivity is due in part to the delocalisation of the electrons on the oxygen atom of the phenol, making it less nucleophilic.



phenol benzoyl chloride phenyl benzoate (76%)

Since phenols are quite acidic, they are readily deprotonated to give phenoxide ions. These ions are good nucleophiles and will displace halogens from haloalkanes (see section 18.2) to produce ethers.



sodium phenoxide butyl bromide butyl phenyl ether (80%)

You may have noticed that many of the reactions of phenols are similar to those of alcohols. Careful inspection will reveal that phenols and alcohols react in the same way when the reaction involves breaking the O—H bond (reactions with bases, oxidation, and ether and ester formation). Phenols do not readily undergo reactions that require breaking the C—O bond (reaction with HX to form aryl halides or dehydration).

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19.4 Ethers

In the previous sections we studied compounds related to water in which a hydrogen atom was replaced by an alkyl group (alcohols) or an aryl group (phenols). In this section we will investigate 'relatives' of water where both hydrogen atoms have been replaced by either alkyl or aryl groups — ethers. The functional group of an **ether** is an atom of oxygen bonded to two carbon atoms that are not bonded to **heteroatoms** (e.g. O, N, S, halogen). Figure 19.10 shows a Lewis structure and ball-and-stick model of dimethyl ether, CH_3OCH_3, the simplest ether. In dimethyl ether, two sp^3 hybrid orbitals of oxygen form σ bonds to carbon atoms. The other two sp^3 hybrid orbitals of oxygen each contain an unshared pair of electrons.

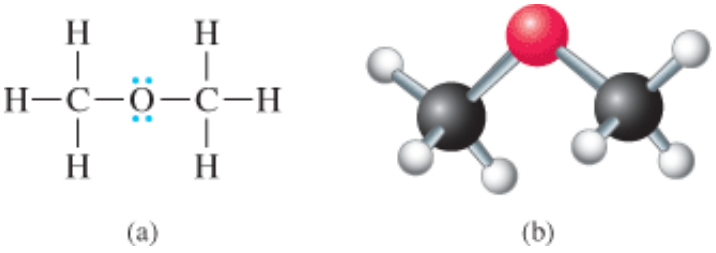
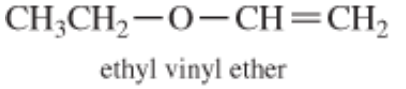
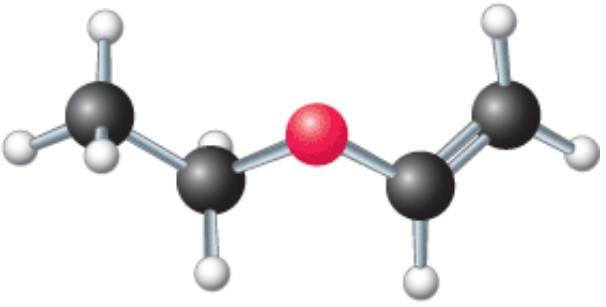


FIGURE 19.10 Dimethyl ether, CH_3OCH_3:
(a) Lewis structure and
(b) ball-and-stick model.

In ethyl vinyl ether, the ether oxygen atom is bonded to one sp^3 hybridised carbon atom and one sp^2 hybridised carbon atom.



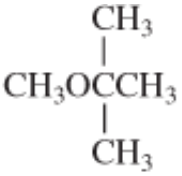
ethyl vinyl ether



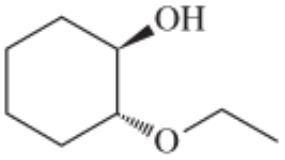
Ethers are named in the IUPAC system by selecting the longest carbon chain as the parent alkane and naming the —OR group bonded to it as an **alkoxy** (*alkyl* + *oxygen*) group. Common names are derived by listing the alkyl groups bonded to oxygen in alphabetical order and adding the word *ether*.



ethoxyethane
(diethyl ether)



2-methoxy-2-methylpropane
(methyl *tert*-butyl ether, MTBE)



trans-2-ethoxycyclohexanol

Chemists almost invariably use common names for low-molar-mass ethers. For example, although ethoxyethane is the IUPAC name for $CH_3CH_2OCH_2CH_3$, it is rarely called that, but instead is called diethyl ether, ethyl ether, or, even more commonly, simply ether.

Cyclic ethers are heterocyclic compounds in which the ether oxygen atom is one of the atoms in a ring.

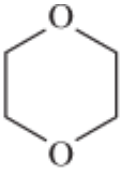
These ethers are generally known by their common names.



ethylene oxide



tetrahydrofuran (THF)



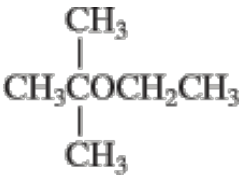
1,4-dioxane

WORKED EXAMPLE 19.6

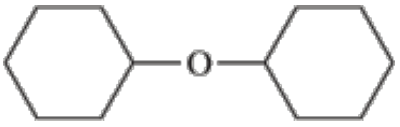
Naming Ethers

Write the IUPAC and common names for each of the following ethers.

(a)



(b)



Analysis

To name ethers, you should first identify the ether oxygen atom and then identify the two alkyl groups attached to this oxygen atom. In the IUPAC system, the larger of the two groups (if they are different) is the parent alkane and the other is the alkoxy group. Using the common nomenclature, the alkyl groups are listed alphabetically followed by the word 'ether'.

Solution

(a) 2-ethoxy-2-methylpropane. Its common name is *tert*-butyl ethyl ether.

(b) cyclohexoxycyclohexane. Its common name is dicyclohexyl ether.

Is our answer reasonable?

To check that your names are sensible, draw structures that correspond to your answers and compare these with the structures provided in the question.

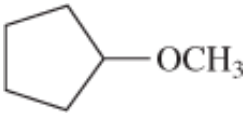
PRACTICE EXERCISE 19.6

Write the IUPAC and common names for each of the following ethers.

(a)



(b)



Physical Properties

Ethers are moderately polar compounds in which the oxygen atom has a partial negative charge, and each carbon atom bonded to it has a partial positive charge (figure 19.11). Because of steric hindrance, however, only weak forces of attraction exist between ether molecules in the pure liquid. Consequently, boiling points of ethers are much lower than those of alcohols with a similar number of electrons (table 19.5) and are closer to hydrocarbons of comparable number of electrons (table 19.1).

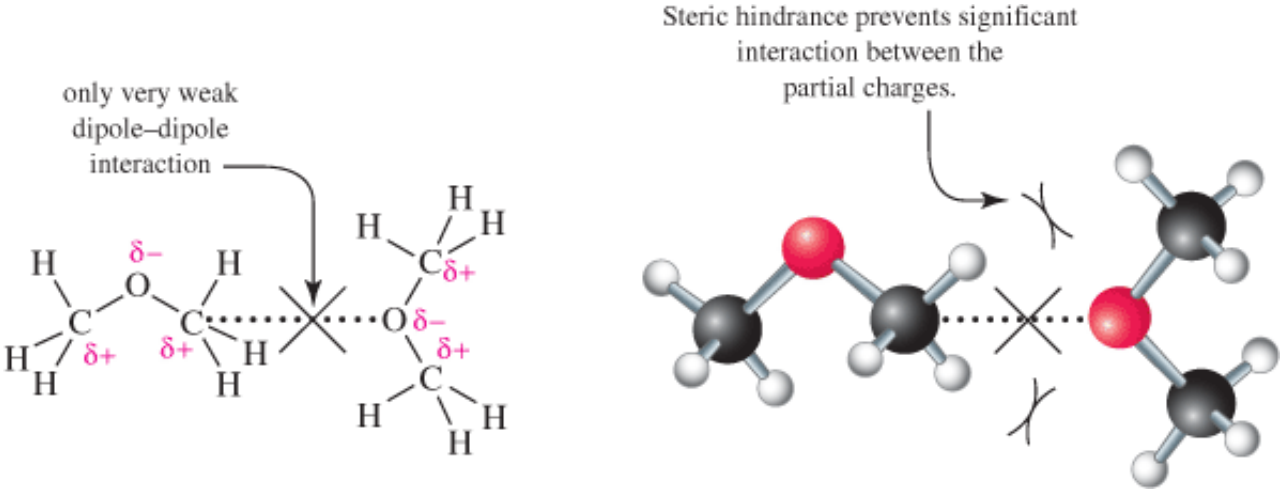


FIGURE 19.11 Ethers are polar molecules, but, because of steric hindrance, only weak attractive interactions exist between their molecules in the pure liquid.

TABLE 19.5 Boiling points and solubilities in water of some alcohols and ethers of comparable number of electrons

Structural formula	Name	Total electrons	Boiling point (°C)	Solubility in water
CH_3CH_2OH	ethanol	26	78	infinite
CH_3OCH_3	dimethyl ether	26	–24	7.8 g/100 g
$CH_3CH_2CH_2CH_2OH$	butan-1-ol	42	117	7.4 g/100 g
$CH_3CH_2OCH_2CH_3$	diethyl ether	42	35	8 g/100 g
$CH_3CH_2CH_2CH_2CH_2OH$	pentan-1-ol	50	138	2.3 g/100 g
$CH_3CH_2CH_2CH_2OCH_3$	butyl methyl ether	50	71	slight
$CH_3OCH_2CH_2OCH_3$	1,2-dimethoxyethane	50	84	infinite

Because the oxygen atom of an ether carries a partial negative charge, ethers form hydrogen bonds with water (figure 19.12) and are more soluble in water than hydrocarbons with a similar number of electrons and shape (compare data in tables 19.1 and 19.5).

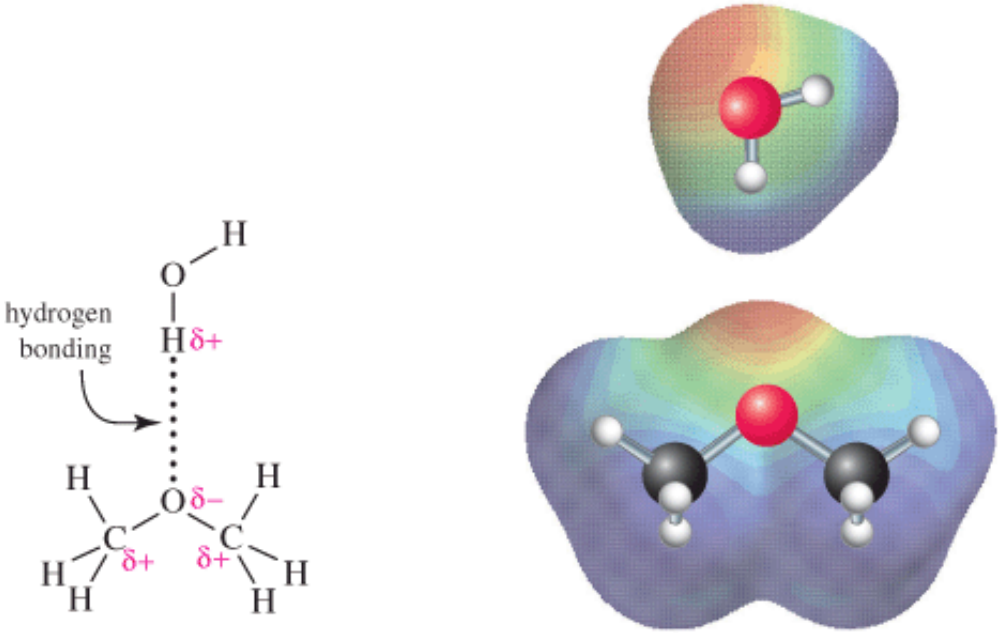


FIGURE 19.12 Dimethyl ether in water. The partially negative oxygen atom of the ether is the hydrogen bond acceptor, and a partially positive hydrogen atom of a water molecule is the hydrogen bond donor. Ethers are hydrogen bond acceptors only; they are not hydrogen bond donors.

The effect of hydrogen bonding is illustrated dramatically by comparing the boiling points of ethanol (78 °C) and its constitutional isomer dimethyl ether (-24 °C). The difference in boiling points between these two compounds is due to the polar O—H group in the alcohol, which is capable of forming intermolecular hydrogen bonds. This hydrogen bonding increases the attractive force between molecules of ethanol; thus, ethanol has a higher boiling point (and water solubility) than dimethyl ether.

CH_3CH_2OH	CH_3OCH_3
ethanol	dimethyl ether
bp = 78°C	bp = −24°C

WORKED EXAMPLE 19.7

Solubility

Arrange the following compounds in order of increasing solubility in water.

$CH_3OCH_2CH_2OCH_3$	$CH_3CH_2OCH_2CH_3$	$CH_3CH_2CH_2CH_2CH_3$
1,2-dimethoxyethane	diethyl ether	hexane

Analysis

As water is a polar solvent we expect polar compounds to have a greater solubility in water than nonpolar compounds. Both diethyl ether and 1,2-dimethoxyethane are polar compounds due to the presence of polar C—O—C groups, and each interacts with water as a hydrogen bond acceptor. Hexane is a nonpolar hydrocarbon and, therefore, we expect it to have the lowest solubility in water. Generally, compounds with more polar groups are more soluble in

water.

Solution

$CH_3CH_2CH_2CH_2CH_2CH_3$ insoluble $CH_3CH_2OCH_2CH_3$ 8g/100g water $CH_3OCH_2CH_2OCH_3$ soluble in all proportions

Is our answer reasonable?

Check the number of polar groups in each compound. Are your compounds listed in order of lowest number of polar groups to highest number of polar groups?

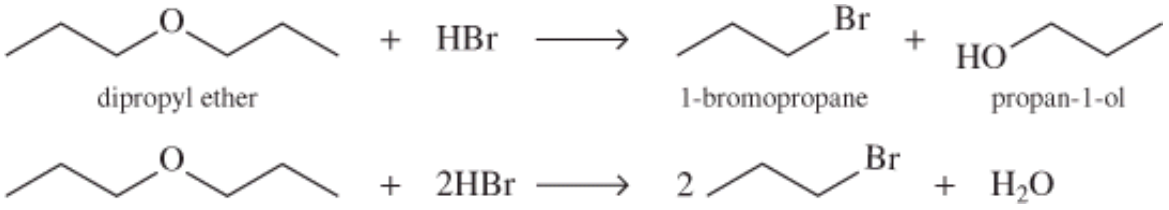
PRACTICE EXERCISE 19.7

Arrange the following compounds in order of increasing boiling point.

$CH_3OCH_2CH_2OCH_3$ $HOCH_2CH_2OH$ $CH_3OCH_2CH_2OH$

Reactions of Ethers

Ethers, R—O—R, resemble hydrocarbons in their resistance to chemical reactions. They do not react readily with oxidising agents (e.g. potassium dichromate or potassium permanganate) or reducing agents (e.g. sodium borohydride or lithium aluminium hydride). They are not affected by most acids or bases at moderate temperatures. However, they can be cleaved with concentrated hydrobromic or hydroiodic acid to give the corresponding haloalkane and alcohol. If an excess of HX is used, the alcohol can react further to give a haloalkane and water (see section 19.2).



This reaction is another example of a nucleophilic substitution and is similar to the reaction of alcohols with HX. The first step involves the protonation of the ether oxygen to form an oxonium ion (R_2OH^+).

Because of their good solvent properties and general inertness to chemical reaction, ethers are excellent solvents in which to carry out many organic reactions.

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19.5 Thiols

The sulfur analogue of an alcohol is called a **thiol** (thi- from the Greek: *theion*, sulfur) or, in the older literature, a **mercaptan**, which literally means 'mercury capturing'. Since sulfur and oxygen belong to the same group of the periodic table, they share similar chemical properties. Thiols form thioesters, thioethers and thioacetals in the same way alcohols form esters, ethers and acetals (see chapter 21). The functional group of a thiol is an —SH (sulfhydryl) group.

Figure 19.13 shows a Lewis structure and a ball-and-stick model of methanethiol, CH_3SH, the simplest thiol. The electronegativities of carbon and sulfur in methanethiol are virtually identical (2.55 and 2.58 respectively), while sulfur is slightly more electronegative than hydrogen (2.58 versus 2.20). The electron density model shows some slight partial positive charge on hydrogen atom of the S—H group and some slight partial negative charge on the sulfur atom.

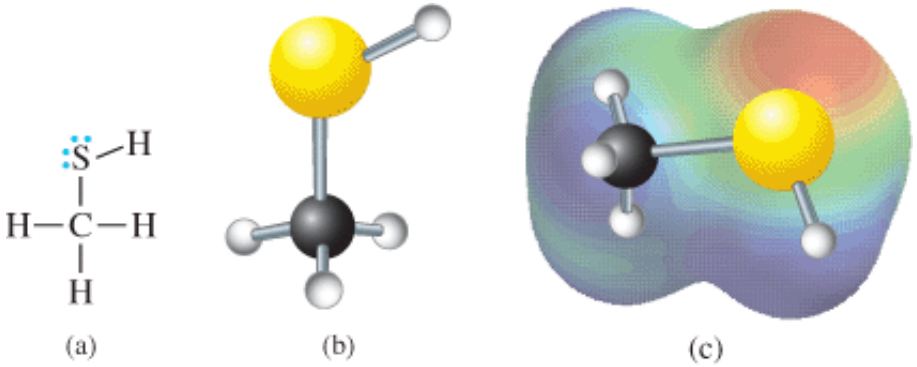
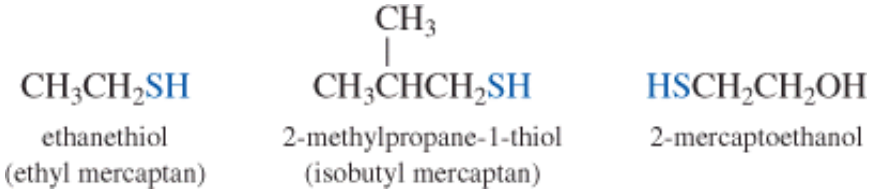
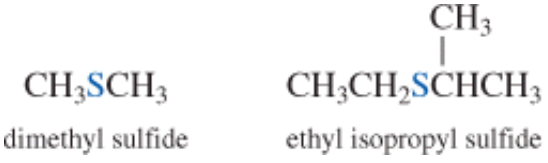


FIGURE 19.13 Methanethiol, CH_3SH:
(a) Lewis structure,
(b) ball-and-stick model and
(c) electron density model.

In the IUPAC system, thiols are named in the same way as alcohols, except that the ending *-thiol* is added to the name of the parent alkane. Common names for simple thiols are derived by naming the alkyl group bonded to the —SH group and adding the word *mercaptan*. In compounds containing other functional groups, the presence of an —SH group is indicated by the prefix *mercapto-*.



Sulfur analogues of ethers are named by using the word *sulfide* to show the presence of the —S— group. The following are common names of two sulfides.

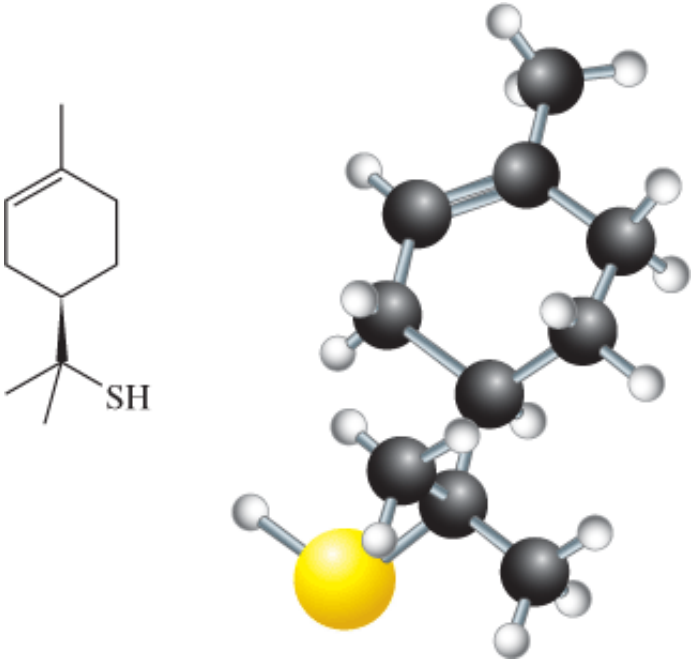


The most outstanding property of low-molar-mass thiols is their strong, often unpleasant odour, such as those from rotten eggs and sewage. However, not all thiols have an unpleasant odour; for example, grapefruits, mushrooms, onions, garlic and coffee (figure 19.14) all contain sulfur compounds.



FIGURE 19.14 All of these foods contain sulfur compounds.

The aroma of grapefruit is primarily due to a thiol, commonly known as grapefruit mercaptan. The structural formula and a ball-and-stick model of grapefruit mercaptan are shown below. Only the *R*-enantiomer has the characteristic odour.



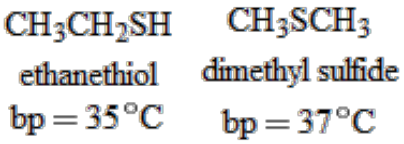
Physical Properties

Because of the small difference in electronegativity between sulfur and hydrogen (2.5 - 2.1 = 0.4), we classify the S—H bond as nonpolar covalent. Because of this lack of polarity, thiols show little intermolecular association by hydrogen bonding. Consequently, they have lower boiling points and are less soluble in water and other polar solvents than alcohols of similar molar mass. Table 19.6 gives the boiling points of three low-molar-mass thiols. For comparison, the table also gives the boiling points of alcohols with the same number of carbon atoms.

TABLE 19.6 Boiling points of three thiols and three alcohols with the same number of carbon atoms

Thiol	Boiling point (°C)	Alcohol	Boiling point (°C)
methanethiol	6	methanol	65
ethanethiol	35	ethanol	78
butane-1-thiol	98	butan-1-ol	117

Earlier, we illustrated the importance of hydrogen bonding in alcohols by comparing the boiling points of ethanol (78 °C) and its constitutional isomer dimethyl ether (-24 °C). By comparison, the boiling point of ethanethiol is 35 °C, and that of its constitutional isomer dimethyl sulfide is 37 °C.



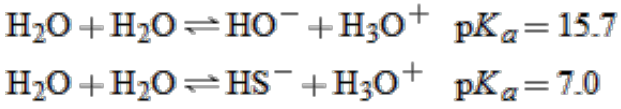
The fact that the boiling points of these constitutional isomers are almost identical indicates that little or no hydrogen bonding occurs between thiol molecules.

Reactions of Thiols

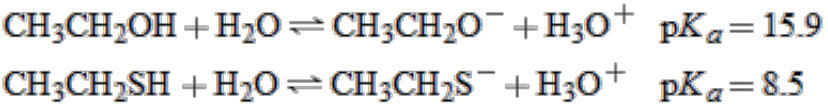
In this section, we discuss the acidity of thiols, and their reaction with strong bases and with molecular oxygen.

Acidity

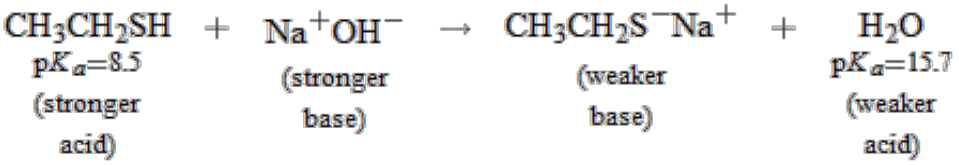
Hydrogen sulfide is a stronger acid than water.



Similarly, thiols are stronger acids than alcohols. Compare, for example, the pK_a of ethanol and the pK_a of ethanethiol in dilute aqueous solution.

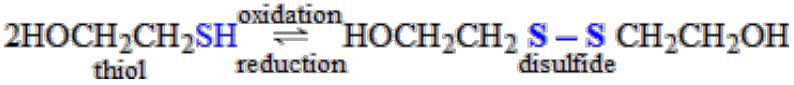


Thiols are sufficiently strong acids that, when dissolved in aqueous sodium hydroxide, they are converted completely to alkylsulfide salts.



Oxidation to Disulfides

Many of the chemical properties of thiols occur because the sulfur atom of a thiol is easily oxidised to several higher oxidation states. The most common reaction of thiols in biological systems is their oxidation to disulfides, the functional group of which is a **disulfide** (—S—S—) bond. Thiols are readily oxidised to disulfides by molecular oxygen. In fact, they are so susceptible to oxidation that they must be protected from contact with air during storage. Disulfides, in turn, are easily reduced to thiols by several reagents. This easy interconversion between thiols and disulfides is very important in protein chemistry, as we will see in chapter 24.



We derive common names of simple disulfides by listing the names of the groups bonded to sulfur and adding the word *disulfide,* for example, $CH_3S—SCH_3$ is named dimethyldisulfide.

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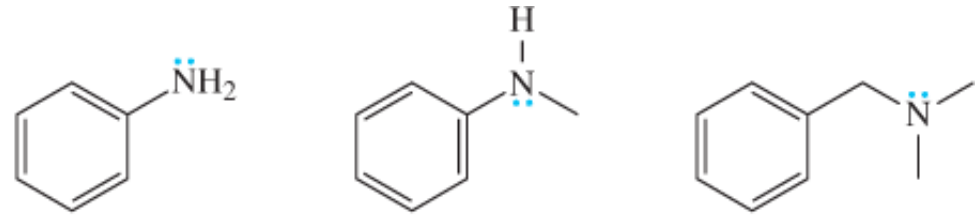
19.6 Amines

Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl or aryl groups. Amines are classified as primary (1°), secondary (2°) or tertiary (3°), depending on the number of hydrogen atoms of ammonia that are replaced. Note that 1°, 2° and 3° refer to the degree of substitution on the *nitrogen* atom, not the carbon atom bearing the nitrogen atom (unlike haloalkanes and alcohols — see section 19.1).



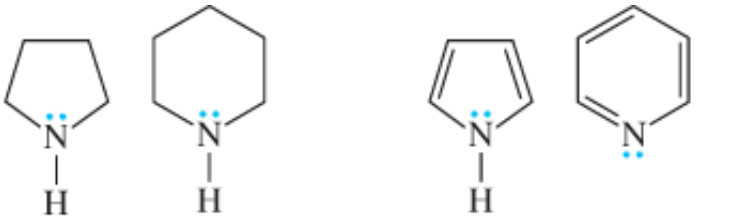
ammonia | methylamine (a 1° amine) | dimethylamine (a 2° amine) | trimethylamine (a 3° amine)

Amines are further divided into aliphatic amines and aromatic amines. In an **aliphatic amine**, all the carbon atoms bonded directly to the nitrogen atom are derived from alkyl groups; in an **aromatic amine**, one or more of the groups bonded directly to the nitrogen atom are aryl groups. Note that the third example below (benzyldimethylamine) is not classed as an aromatic amine because the nitrogen atom is not bonded directly onto the aromatic ring.



aniline (a 1° aromatic amine) | *N*-methylaniline (a 2° aromatic amine) | benzyldimethylamine (a 3° aliphatic amine)

An amine in which the nitrogen atom is part of a ring is classified as a **heterocyclic amine**. When the nitrogen atom is part of an aromatic ring (section 16.7, p. 726), the amine is classified as a **heterocyclic aromatic amine**. The following are structural formulae for two heterocyclic aliphatic amines and two heterocyclic aromatic amines.



pyrrolidine, piperidine (heterocyclic aliphatic amines) | pyrrole, pyridine (heterocyclic aromatic amines)

WORKED EXAMPLE 19.8

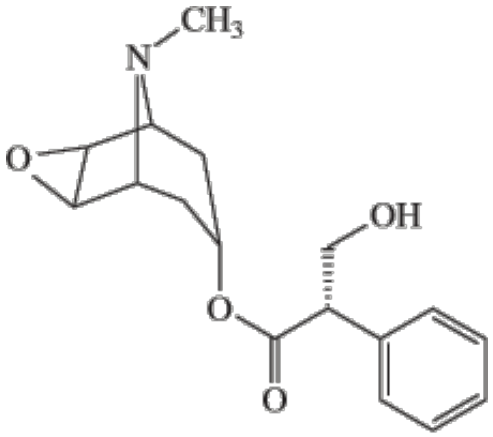
Classifying Amines

Alkaloids are basic nitrogen-containing compounds found in plants. Many alkaloids have physio logical activity when administered to humans.

Examples of alkaloids that are physiologically active in humans include scopolamine, nicotine and cocaine. Scopolamine (also known as hyoscine) is obtained from the leaves of the Australian *Duboisia* tree and is classified as an anticholinergic (it blocks the action of acetylcholine). The hydrobromide salt is used in the prevention of motion sickness. In small doses, nicotine is an addictive stimulant. In larger doses, it causes depression, nausea and vomiting. In still larger doses, it is a deadly poison. Solutions of nicotine in water are used as insecticides. Cocaine is a central nervous system stimulant obtained from the leaves of the coca plant.

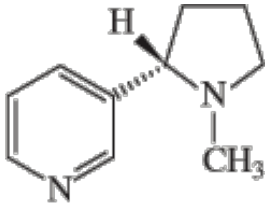
Classify each amino group in the following alkaloids according to type (primary, secondary, tertiary, heterocyclic, aliphatic or aromatic).

(a)



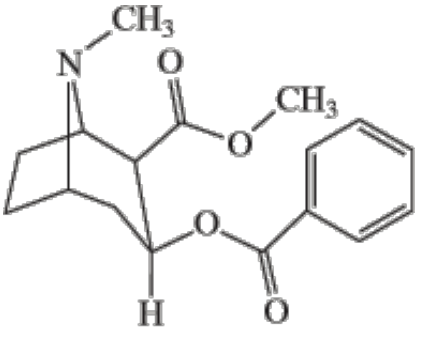
scopolamine

(b)



(*S*)-nicotine

(c)



cocaine

Analysis

First identify the nitrogen atom in the compound. Now, check the following.

i. Ensure that the nitrogen atom is part of an amine. (There are other functional groups where the nitrogen atom is not bound to alkyl or aryl groups. These are called amide, nitrile and nitro groups.)

ii. If the nitrogen atom is part of a ring, the compound is heterocyclic.

iii. If the nitrogen atom is bonded directly to an aromatic ring, or part of an aromatic ring, then the compound is an aromatic amine.

Then count the number of groups bonded to the nitrogen atom to determine if it is primary, secondary or tertiary.

Solution

(a) a tertiary heterocyclic aliphatic amine

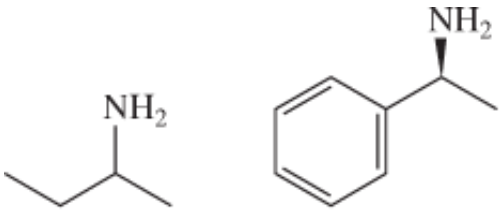
(b) one tertiary heterocyclic aliphatic amine and one heterocyclic aromatic amine

(c) a tertiary heterocyclic aliphatic amine

PRACTICE EXERCISE 19.8

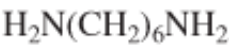
Identify all carbon stereocentres in scopolamine, nicotine and cocaine.

Systematic names for aliphatic amines are derived just as they are for alcohols. The suffix *-e* of the parent alkane is dropped and is replaced by *-amine*; that is, they are named alkanamines.



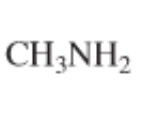
butan-2-amine

(*S*)-1-phenylethanamine

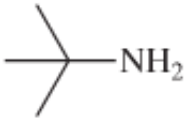


hexane-1,6-diamine

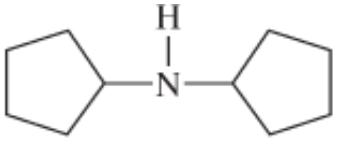
Common names for most aliphatic amines are derived by listing the alkyl groups bonded to nitrogen in alphabetical order in one word ending in the suffix *-amine*; that is, they are named as **alkylamines**.



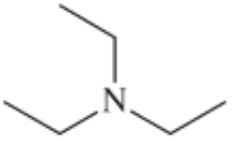
methylamine



tert-butylamine



dicyclopentylamine



triethylamine

WORKED EXAMPLE 19.9

Naming Amines

Write the IUPAC name for each of the following amines.

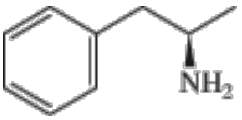
(a)



(b)



(c)



Analysis

First, you need to identify the longest chain as this will be the parent amine. The suffix *-e* of the parent alkane is then dropped and replaced by *-amine* to give an alkanamine. If there is more than one amino group, then use *-diamine*, *-triamine* etc. remembering to indicate the position of the amino groups. Next you should identify any substituents. These are listed in alphabetical order, with numbers indicating the position of the substituent.

Solution

(a) hexan-1-amine

(b) butane-1,4-diamine (This is also commonly known as putrescine because it smells putrid.)

(c) The systematic name of this compound is (*R*)-1-phenylpropan-2-amine. Its common name is amphetamine. The dextrorotatory isomer of amphetamine (shown here) is a central nervous system stimulant and is manufactured and sold under several trade names. The salt with sulfuric acid is marketed as Dexedrine® sulfate.

Is our answer reasonable?

To check that your names are correct, draw structures that correspond to your answers and compare these with the structures provided in the question.

PRACTICE EXERCISE 19.9

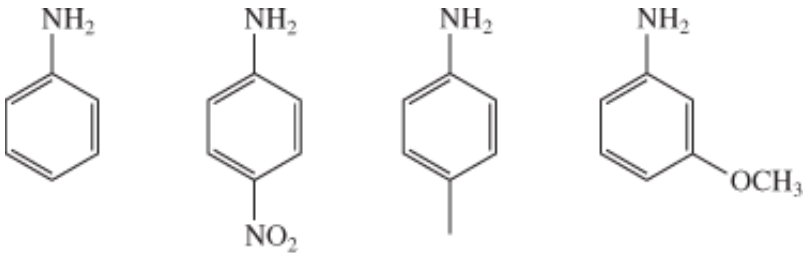
Write a structural formula for each of the following amines.

(a) 2-methylpropan-1-amine

(b) cyclohexanamine

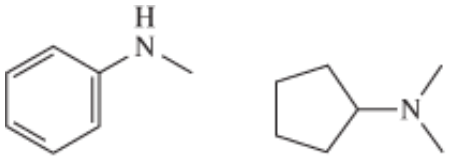
(c) (*R*)-butan-2-amine

IUPAC nomenclature retains the common name **aniline** for $C_6H_5NH_2$, the simplest aromatic amine. Its simple derivatives are named with the prefixes *o*-, *m*- and *p*-, or numbers to locate substituents. Several derivatives of aniline have common names that are still widely used. Among these are toluidine, for a methyl-substituted aniline, and anisidine, for a methoxy-substituted aniline.



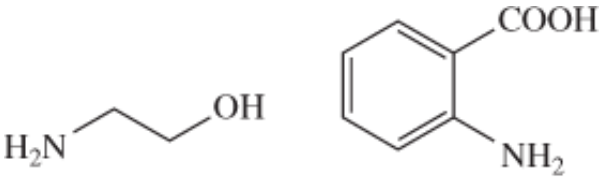
aniline | 4-nitroaniline (*p*-nitroaniline) | 4-methylaniline (*p*-toluidine) | 3-methoxyaniline (*m*-anisidine)

Secondary and tertiary amines are commonly named as *N*-substituted primary amines. For asymmetrical amines, the largest group is taken as the parent amine, then the smaller group or groups bonded to nitrogen are named, and their location is indicated by the prefix *N* (specifying that they are attached to nitrogen).



N-methylaniline | *N*,*N*-dimethylcyclopentanamine

Among the various functional groups discussed in this text, the —NH_2 group has one of the lowest nomenclature priorities (the priority list is provided in table 20.1). The following compounds each contains a functional group of higher precedence than the amino group, and, accordingly, the —NH_2 group is indicated by the prefix *amino*-.



2-aminoethanol (ethanolamine) | 2-aminobenzoic acid (anthranilic acid)

Physical Properties

Amines are polar compounds, and both primary and secondary amines form intermolecular hydrogen bonds (figure 19.15).

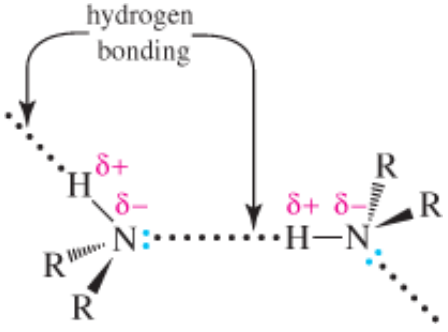


FIGURE 19.15 Intermolecular association of 1° and 2° amines by hydrogen bonding. Nitrogen is approximately tetrahedral in shape, with the axis of the hydrogen bond along the fourth axis of the tetrahedron.

An N—H…N hydrogen bond is weaker than an O—H…O hydrogen bond, because the difference in electronegativity between nitrogen and hydrogen (3.0 - 2.1 = 0.9) is less than that between oxygen and hydrogen (3.5 - 2.1 = 1.4). We can illustrate the effect of intermolecular hydrogen bonding by comparing the boiling points of methylamine and methanol as shown in the table below.

	CH_3NH_2	CH_3OH
number of electrons	18	18
boiling point (°C)	-6.3	65.0

Both compounds are polar molecules and interact in the pure liquid by hydrogen bonding. Methanol has the higher boiling point because hydrogen bonding between its molecules is stronger than that between molecules of methylamine.

All classes of amines form hydrogen bonds with water and are more soluble in water than hydrocarbons of a comparable number of electrons. Most low-molar-mass amines are completely soluble in water (table 19.7). Higher-molar-mass amines are only moderately soluble or insoluble.

TABLE 19.7 Physical properties of selected amines

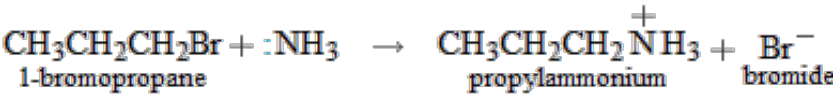
Name	Structural formula	Melting point (°C)	Boiling point (°C)	Solubility in water
ammonia	NH_3	–78	–33	very soluble
Primary amines				
methylamine	CH_3NH_2	–95	–6	very soluble
ethylamine	$CH_3CH_2NH_2$	–81	17	very soluble
propylamine	$CH_3CH_2CH_2NH_2$	–83	48	very soluble
cyclohexylamine	$C_6H_{11}NH_2$	–17	135	slightly soluble
Secondary amines				
diethylamine	$(CH_3CH_2)_2NH$	–48	56	very soluble
Tertiary amines				
triethylamine	$(CH_3CH_2)_3N$	–114	89	slightly soluble
Aromatic amines				
aniline	$C_6H_5NH_2$	–6	184	slightly soluble
Heterocyclic aromatic amines				
pyridine	C_5H_5N	–42	116	very soluble

Preparation of Amines

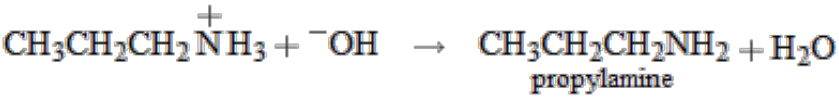
Amines can be prepared by a variety of methods, from a range of starting materials. Some of the more common methods will be discussed here.

Preparation from Haloalkanes

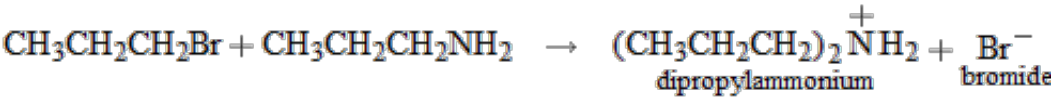
Amines can be prepared from haloalkanes by nucleophilic substitution reactions (see section 18.2). Given that ammonia is a good nucleophile, it can be used to prepare amines from haloalkanes.



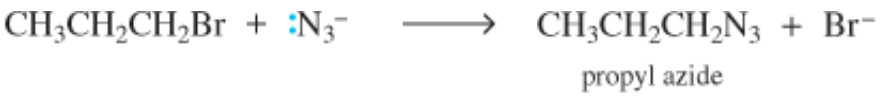
Note that the charge is balanced (both sides have zero net charge). The alkyl ammonium salt is readily converted to the amine by reaction with a stronger base than the amine (e.g. NaOH).

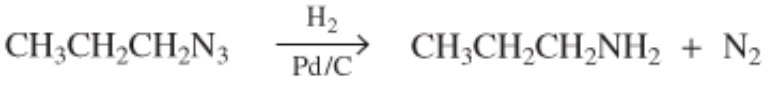


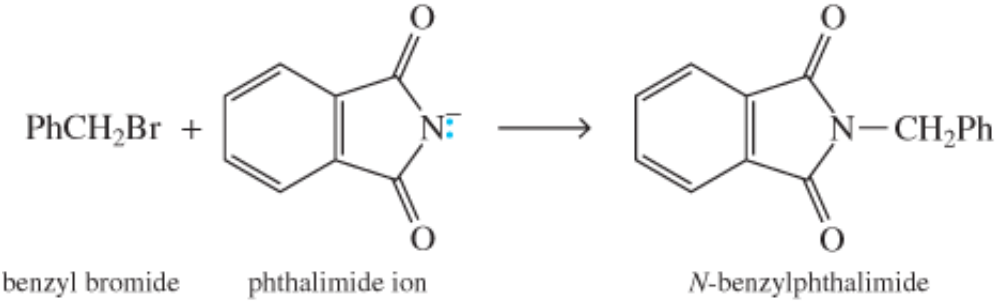
A problem with using ammonia to prepare primary amines is that these amines are also nucleophilic species and can react in the same way as ammonia to produce secondary amines. Similarly, secondary amines can react to give tertiary amines. Consequently, mixtures of 1°, 2° and 3° amines are usually obtained.

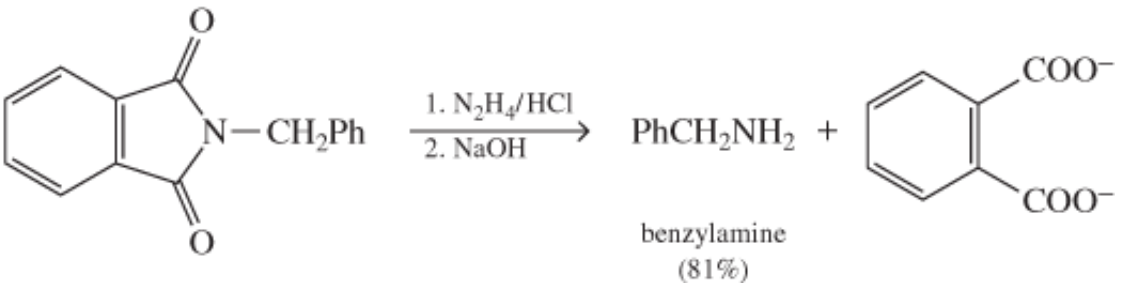


Primary amines can be prepared, in a two-step process, by using the azide ion (N_3^-) or phthalimide ion (use of the latter is known as the Gabriel synthesis) as nucleophiles. Using these processes, secondary and tertiary amines are not produced.



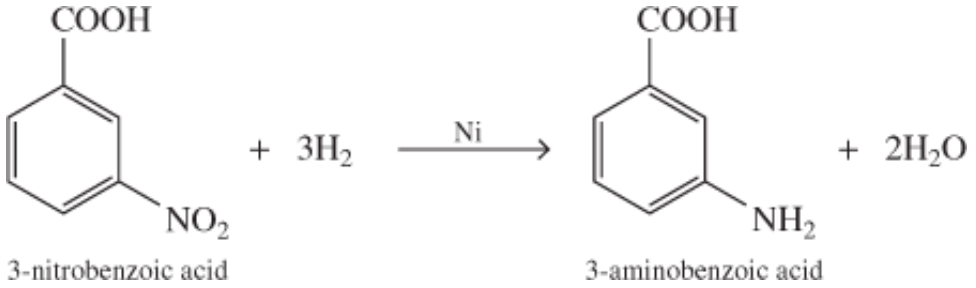






Synthesis of Arylamines: Reduction of the —NO_2 Group

As we have already seen (section 16.8), the nitration of an aromatic ring introduces a —NO_2 group. A particular value of nitration is the fact that the resulting nitro group can be reduced to a primary amino group, —NH_2, by hydrogenation in the presence of a transition metal catalyst such as nickel, palladium or platinum.



3-nitrobenzoic acid 3-aminobenzoic acid

Chemistry

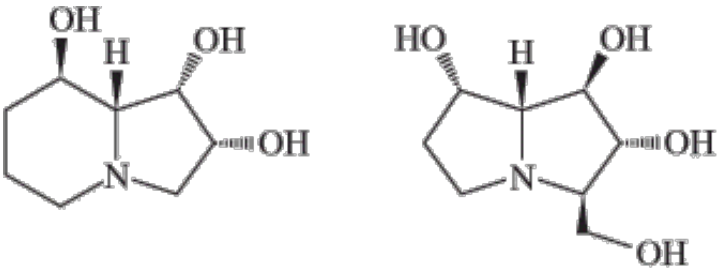
Chemistry Research

Synthesising polyhydroxyalkaloids

The development of new strategies and reactions for the synthesis of compounds is an important field of chemistry research. This research provides us with access to a wide range of compounds that can be used in a variety of applications, including medicine, agriculture, industry and the environment. Natural products (compounds obtained from plants or animals) are often chosen as synthetic targets to demonstrate the utility of the new strategies or reactions. These new strategies often allow the synthesis of analogues or isomers of compounds with only minor modification to the synthetic process, thus providing scientists with a range of similar compounds that can be used to better understand the effect of structure on reactivity in given processes (usually biological processes).

The research team led by Professor Stephen Pyne at the University of Wollongong has developed new strategies for the synthesis of polyhydroxyalkaloids. Of particular interest are swainsonine and australine, which have been isolated from Australian plants and have significant biological activity (i.e. they affect biological processes in living things).

As a result of investigations to identify the toxic component responsible for ‘Swainsona’ poisoning, Murdoch University researchers isolated swainsonine from the Australian Darling pea (*Swainsona canescens*, figure 19.16). It is the first inhibitor of glycoprotein-processing enzymes (glycoproteins are compounds containing carbohydrates bonded to proteins and are involved in many cellular processes) to be selected for clinical testing as an anticancer drug; however, clinical trials have been hampered by its high cost. Australine was isolated from the seeds of the Australian tree *Castanospermum australe (*figure 19.17) and is also an inhibitor of glycoprocessing enzymes.



swainsonine australine



FIGURE 19.16 Australian Darling pea *(Swainsona canescens)*.



FIGURE 19.17 *Castanospermum australe*.

The strategies used by Pyne's group in the synthesis of these alkaloids can be summarised into three key steps:

1. reaction of a primary amine with an epoxide (Epoxides are highly strained cyclic ethers in which the oxygen atom is part of a three-membered ring.)
2. the formation of a cycloalkene
3. the oxidation of the alkene group to form a vicinal diol. (The —OH groups are on adjacent carbon atoms.)

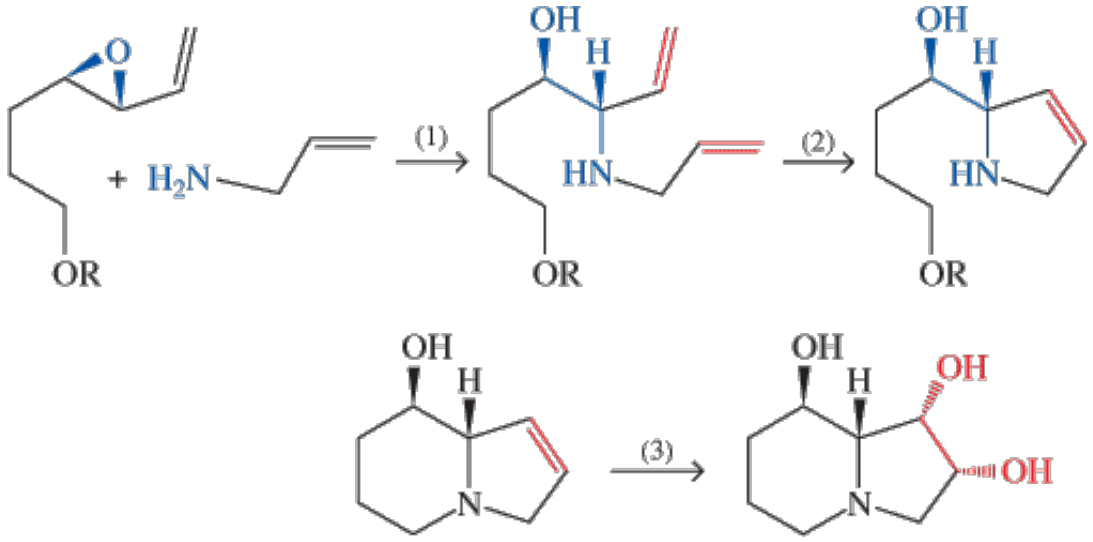
These reactions are illustrated below using the particular steps in the synthesis of swainsonine.

The first key step involves the cleavage of an ether. Although ethers are generally fairly unreactive, epoxides are an exception due to the high ring strain associated with the three-

membered ring. Consequently the opening of the epoxide by reaction with an amine occurs quite readily.

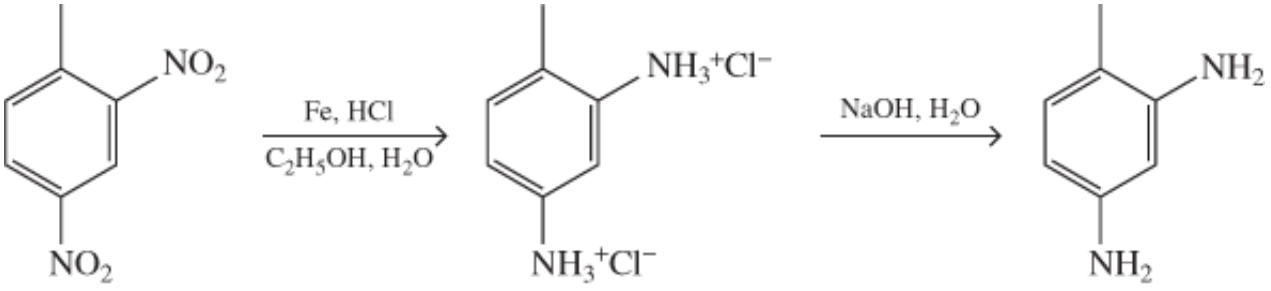
In the second key step, known as a 'ring closing metathesis', two alkene groups react to produce a cyclic alkene (with loss of ethene). The developer of this reaction, Robert Grubbs, was awarded the 2005 Nobel Prize in chemistry for his contributions to metathesis reactions.

The final key step is the conversion of an alkene to a diol with control of the stereochemistry (known as asymmetric dihydroxylation). The developer of this chemistry, Barry Sharpless, was awarded a Nobel Prize in 2001 for the development of asymmetric oxidation reactions.



This method has the potential disadvantage that other susceptible groups, such as a carbon–carbon double bond, and the carbonyl group of an aldehyde or ketone, may also be reduced. Note that neither the —COOH nor the aromatic ring is reduced under these conditions.

Alternatively, a nitro group can be reduced to a primary amino group by a metal in acid.



2,4-dinitrotoluene

2,4-diaminotoluene

The most commonly used metal reducing agents are iron, zinc or tin in dilute HCl. When reduced by this method, the amine is obtained as a salt, which is then treated with a strong base to liberate the free amine.

Other Methods for the Preparation of Amines

There are many other methods available for the preparation of amines. Some of these, discussed in more detail later, include the reductive amination of aldehydes and ketones (section 21.5), and the reduction

or hydrolysis of amides (section 23.5).

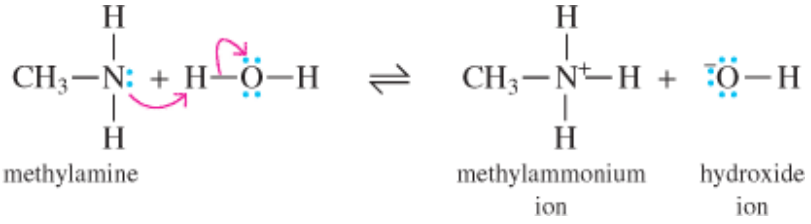
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19.7 Reactions of Amines

The reactions of amines are governed by the unshared pair of electrons on the nitrogen atom. Because of these unshared electrons, amines are both basic and nucleophilic. Consequently, amines react readily with acids to form salts and also react with electrophilic species like haloalkanes, acyl halides and many others.

Basicity of Amines

Like ammonia, all amines are weak bases, and aqueous solutions of amines are basic. The following acid–base reaction between an amine and water is written using curved arrows to emphasise that, in this proton-transfer reaction, the unshared pair of electrons on nitrogen forms a new covalent bond with hydrogen and displaces the hydroxide ion.



The value of K_b, the base ionisation constant, for methylamine is 4.37 × 1 0^{-4} (pK_b = 3.36).

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 4.37 \times 10^{-4}$$

It is also common to discuss the basicity of amines by referring to the acidity constant of the corresponding conjugate acid, as illustrated for the ionisation of the methylammonium ion below.

$$CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$$

$$K_a = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]} = 2.29 \times 10^{-11}$$

$$pK_a = 10.64$$

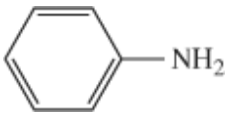
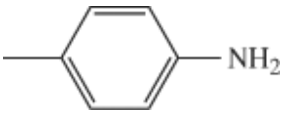
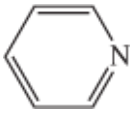
Values of pK_a and pK_b for any acid–conjugate base pair are related by the equation:

$$pK_a + pK_b = 14.00 \quad (\text{at } 25\,^\circ\text{C})$$

Values of pK_a and pK_b for selected amines are given in table 19.8 on the next page. You may wish to review chapter 11 for further discussion of acid–base equilibria.

TABLE 19.8 Base strengths (pK_b) of selected amines and acid strengths (pK_a) of their conjugate acids at 25 °C[(a)]

Amine	Structure	pK_b	pK_a
ammonia	NH_3	4.74	9.26
Primary amines			
ethylamine	$CH_3CH_2NH_2$	3.19	10.81
cyclohexylamine	$C_6H_{11}NH_2$	3.34	10.66
Secondary amines			
diethylamine	$(CH_3CH_2)_2NH$	3.02	10.98
Tertiary amines			
triethylamine	$(CH_3CH_2)_3N$	3.25	10.75
Aromatic amines			

aniline		9.36	4.64
4-methylaniline		8.92	5.08
4-nitroaniline		13.0	1.0
Heterocyclic aromatic amines			
pyridine		8.82	5.18

(a) For each amine, $pK_a + pK_b = 14.00$ at 25 °C.

WORKED EXAMPLE 19.10

Predicting Equilibrium

Predict the position of equilibrium for the acid–base reaction below.

$$CH_3NH_3 + CH_3COOH \rightleftharpoons CH_3NH_3^+ + CH_3COO^-$$

Analysis

Use the approach we developed earlier to predict the position of equilibrium in acid–base reactions. Equilibrium favours the reaction between the stronger acid and stronger base to form the weaker acid and weaker base.

Solution

Equilibrium favours the formation of methylammonium ions and acetate ions.

$$\underset{\text{(stronger base)}}{CH_3NH_2} + \underset{\substack{pK_a = 4.76 \\ \text{(stronger acid)}}}{CH_3COOH} \rightleftharpoons \underset{\substack{pK_a = 10.64 \\ \text{(weaker acid)}}}{CH_3NH_3^+} + \underset{\text{(weaker base)}}{CH_3COO^-}$$

PRACTICE EXERCISE 19.10

Predict the position of equilibrium for the following acid–base reaction.

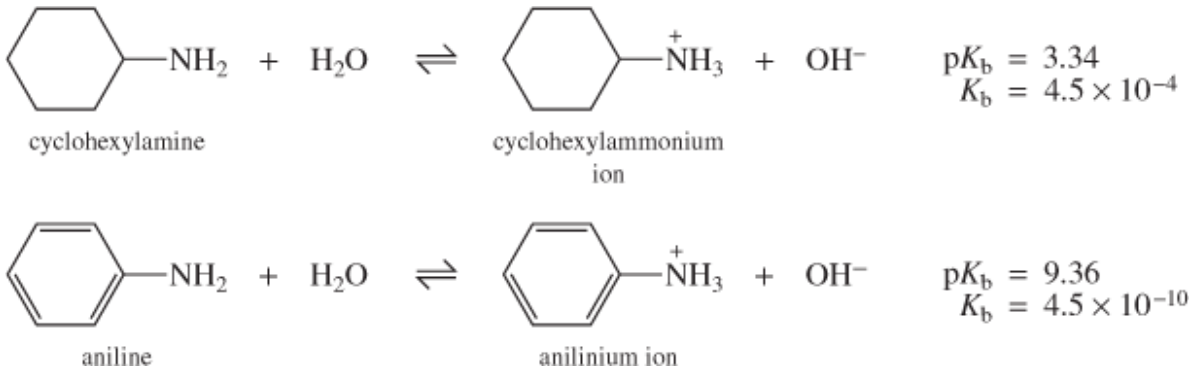
$$CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$$

From the information in table 19.8, we can make the following generalisations about the acid– base properties of the various classes of amines:

1. All aliphatic amines have about the same base strength, with pK_b values from 3.0 to 4.0, and are slightly

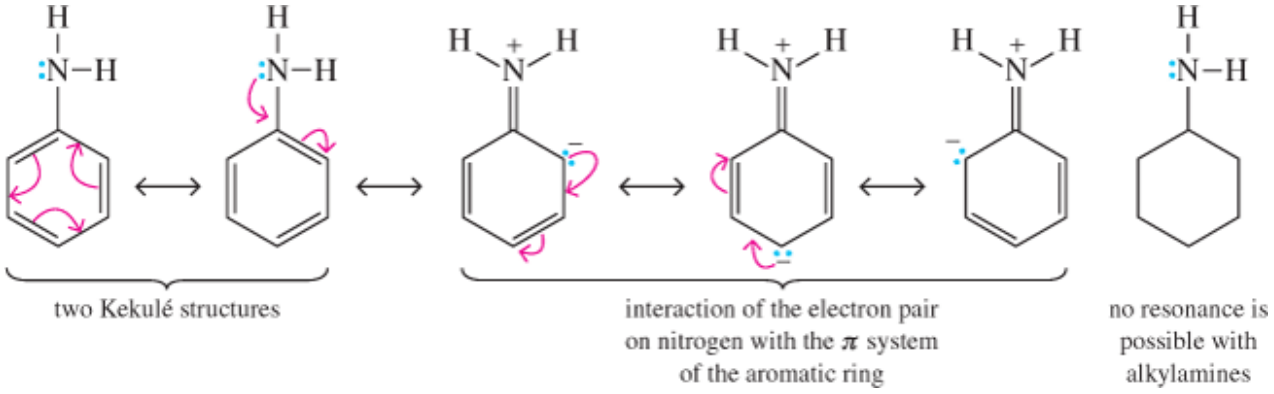
stronger bases than ammonia.

2. Aromatic amines are considerably weaker bases than aliphatic amines. Compare, for example, the values of pK_b for aniline and cyclohexylamine shown below.

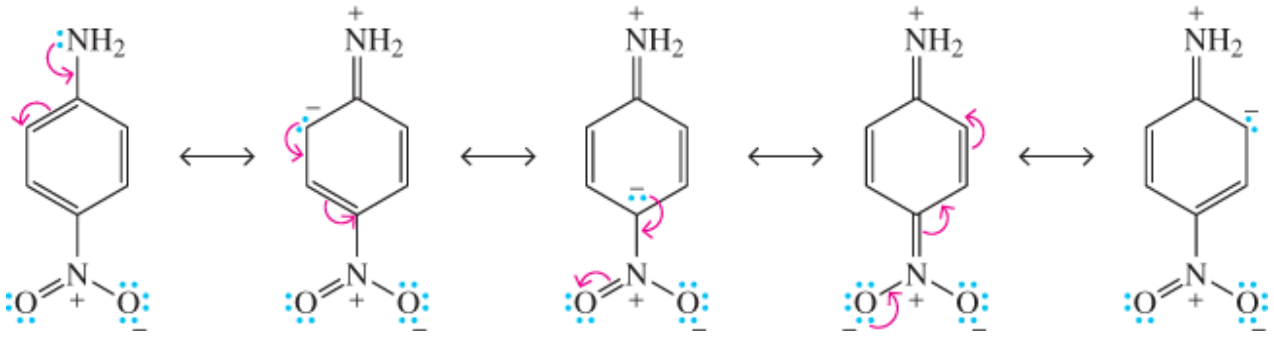


The basicity constant for aniline is smaller (the larger the value of pK_b, the weaker is the base) than that for cyclohexylamine by a factor of 10^6.

Aromatic amines are weaker bases than aliphatic amines because of the resonance interaction of the unshared pair of electrons on nitrogen with the π electron system of the aromatic ring. This resonance interaction is also the reason that phenols are more acidic than alcohols (compare the resonance diagram below with that for phenoxide ion on p. 826). This resonance reduces the electron density on the nitrogen atom (or oxygen atom in the case of phenols) making it a poorer proton acceptor (or a better proton donor in the case of phenols) than the non-aromatic analogues. Because no resonance interaction is possible for an alkylamine, the electron pair on its nitrogen atom is more available for reaction with an acid.



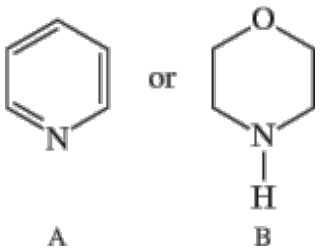
3. Electron-withdrawing groups such as halogens, and nitro and carbonyl groups decrease the basicity of substituted aromatic amines by further decreasing the availability of the electron pair on nitrogen. The diagram below shows the resonance forms for 4-nitroaniline showing how the nitro group reduces the basicity. You will notice that there are four resonance forms in which the nitrogen atom of the amino group does not have a nonbonding pair of electrons (in the case above for aniline there are three). This electron-withdrawing effect of the nitro group has been discussed previously with respect to increasing the acidity of phenols (see section 19.3). In both cases, the nitro group is withdrawing electrons from the heteroatom (nitrogen in anilines, or oxygen in phenols).



Strength of Bases

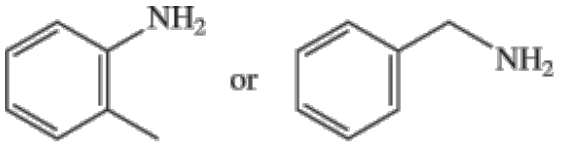
Select the stronger base in each of the following pairs of amines.

(a)



A B

(b)



C D

Analysis

In worked example 19.8, we classified amines as primary, secondary, tertiary, heterocyclic, aliphatic or aromatic. From table 19.8 we deduce that aliphatic amines are stronger bases than aromatic amines. Therefore, once you have classified the amines you should be able to determine which is the stronger base.

Solution

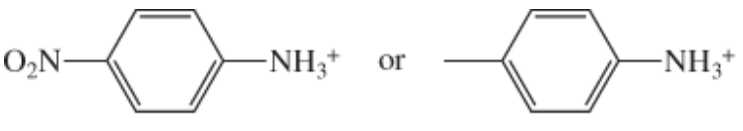
(a) Morpholine (B) is the stronger base ($pK_b = 5.79$). It has a basicity comparable to that of secondary aliphatic amines. Pyridine (A), a heterocyclic aromatic amine ($pK_b = 8.82$), is considerably less basic than aliphatic amines.

(b) Benzylamine (D), a primary aliphatic amine, is the stronger base ($pK_b = 3–4$). The aromatic amine, *o*-toluidine (C), is the weaker base ($pK_b = 9–10$).

PRACTICE EXERCISE 19.11

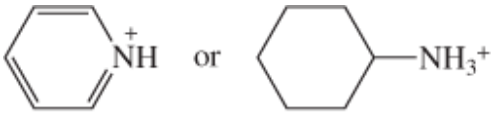
Select the stronger acid from each of the following pairs of ions.

(a)



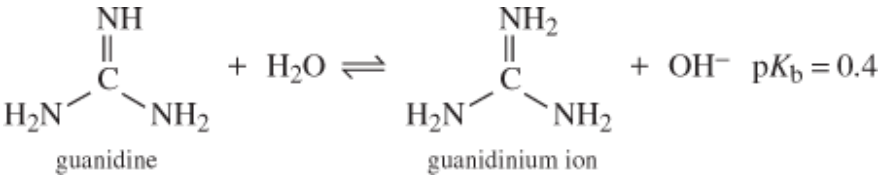
A B

(b)



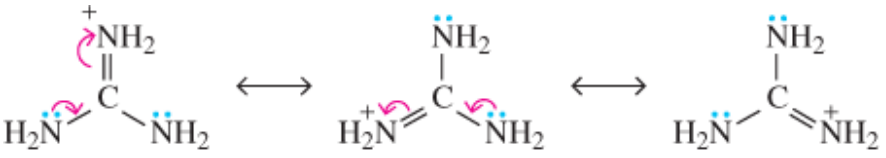
C D

Guanidine, with a pK_b value of 0.4, is one of the strongest bases among neutral compounds.



guanidine guanidinium ion

The remarkable basicity of guanidine is attributed to the fact that the positive charge on the guanidinium ion is delocalised equally over the three nitrogen atoms, as shown by the three equivalent contributing structures below.

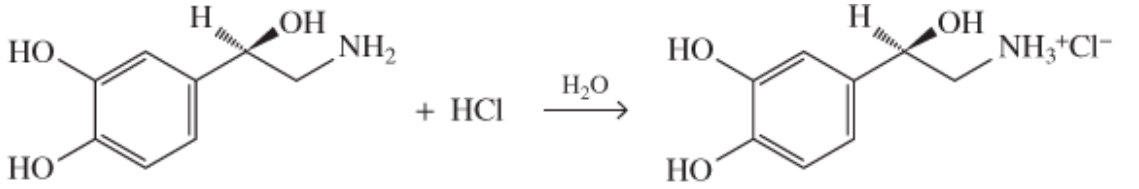


three equivalent contributing structures

Hence, the guanidinium ion is a highly stable cation. The presence of a guanidine group in the amino acid arginine accounts for the basicity of its side chain (section 24.2).

Reaction with Acids

Amines, whether soluble or insoluble in water, react quantitatively with strong acids to form water-soluble salts, as illustrated below by the reaction of (*R*)-norepinephrine (noradrenaline) with aqueous HCl to form a hydrochloride salt.



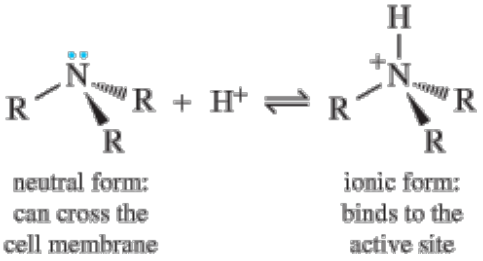
(*R*)-norepinephrine
(only slightly soluble in water)

(*R*)-norepinephrine hydrochloride
(a water-soluble salt)

chemical Connections

Basicity and Drug Activity

Alkaloids are nitrogen-containing compounds of plant or animal origin with significant pharmacological properties. Many drugs also contain at least one nitrogen atom. Why is the nitrogen atom important for pharmacological activity? You will notice that the nitrogen atoms in the compounds mentioned here, along with some others mentioned previously (for example sulbutamol and those in worked example 19.8) are all present as amino groups. Because amines are weak bases at physiological pH (˜7.4), they are present as an equilibrium mixture of the protonated (ionic) and nonprotonated (neutral) forms; at this pH, the ionic form predominates. The equilibrium concentrations of the two forms depend on the pK_a value of the ionic form and the pH of the environment. It is the ionic form that binds to the active site; the positively charged ammonium ion binds to a negatively charged carboxylate ion. Although the ionic form is required to bind to the active site, it is incapable of crossing the nonpolar environment of the cell membranes. So how does the drug reach the target?

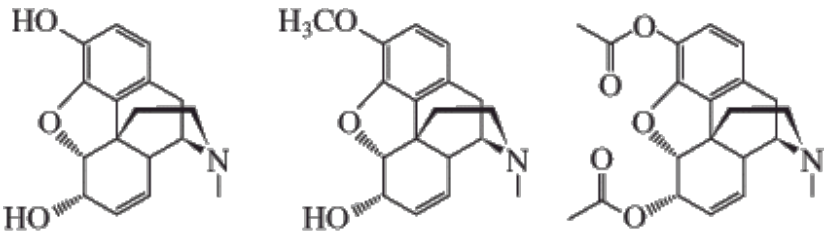


The answer lies in the equilibrium between the ionic and neutral forms of the drug. The neutral form crosses the membrane and, once on the other side, re-establishes equilibrium, producing some of the ionic form that binds to the receptor. On the other side of the membrane, the ionic form that could not cross the membrane also re-establishes equilibrium by forming more of the neutral form that can cross the membrane. In this way, the drug can cross the membrane in the neutral form and interact with the active site as the ionic form. The rate at which this process occurs depends on the equilibrium concentrations of the two forms.

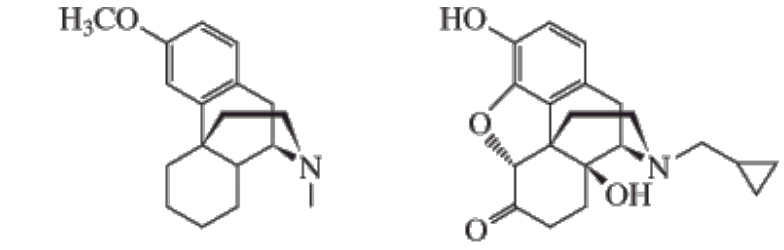
Morphine and codeine (a monomethyl ether of morphine) are opioid analgesics obtained from unripe seed pods of the opium poppy, *Papaver somniferum* (figure 19.18), and have been known for centuries. Heroin is not naturally occurring but is synthesised by treating morphine with 2 mole equivalents of acetic anhydride.



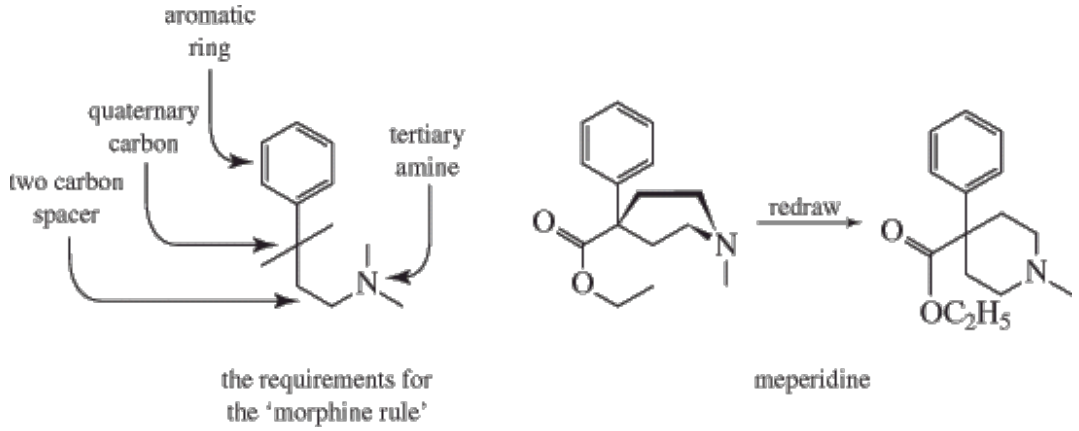
FIGURE 19.18 The opium poppy, *Papaver somniferum*, is the source of morphine and codeine.



Even though morphine is one of modern medicine's most effective painkillers, it has two serious side effects; it is addictive, and it depresses the respiratory control centre of the central nervous system. Large doses of morphine (or heroin) can lead to death by respiratory failure. For these reasons, chemists have sought to produce painkillers without these serious disadvantages. One strategy in this ongoing research has been to synthesise compounds related in structure to morphine in the hope that they would be equally effective analgesics, but with diminished side effects. The following are structural formulae for two such compounds that have proven clinically useful.



Levomethorphan is a potent analgesic. Interestingly, its dextrorotatory enantiomer, dextromethorphan, has no analgesic activity. It does, however, show approximately the same cough-suppressing activity as morphine and is used extensively in cough remedies. Although naltrexone has a similar structure to that of morphine, it counters morphine's (and heroin's) effect and has been used to combat heroin addiction.



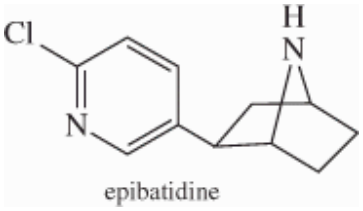
It has been discovered that there can be even further simplification in the structure of morphine-like analgesics; the 'morphine rule' describes the minimum requirements for opiate-like effects. The rule states that, for a compound to exhibit opiate-like effects, it should contain (1) an aromatic ring, (2) a quaternary carbon atom attached to the ring and (3) a tertiary amine two carbon atoms from the quaternary carbon atom, and (4) one of the groups on the tertiary amine must be small (e.g. a methyl group). One such simplification is represented by meperidine, the hydrochloride salt of which is the widely used analgesic Demerol®. It was hoped that meperidine and related synthetic drugs would be free of many of the morphine-like undesirable side effects. It is now clear, however, that they are not.

In 1992, the alkaloid epibatidine was isolated from the skin of the Ecuadorian poison frog, *Epipedobates*

tricolor (figure 19.19).



FIGURE 19.19 *Epipedobates tricolor*, the Ecuadorian poison frog.

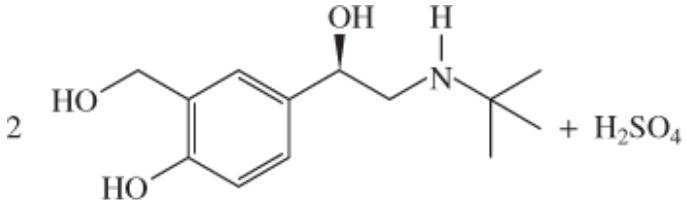


epibatidine

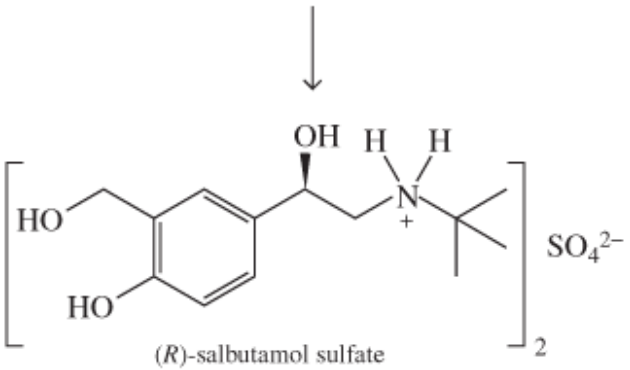
Epibatidine has several times the analgesic potency of morphine and is the first chlorine-containing, nonopioid (nonmorphine-like in structure) analgesic ever isolated from a natural source. It is hoped that this simple alkaloid will be a lead compound in the development of a new family of painkillers. It is currently marketed as its tartrate salt for use in biomedical research.

Norepinephrine is a neurotransmitter and a stress hormone secreted by the medulla of the adrenal gland. It plays an important part in attention and focus. People with ADD/ADHD (attention deficit hyperactivity disorder) are prescribed drugs that help increase the levels of norepinephrine in the brain.

Drug companies have taken advantage of the reaction of amines with strong acids to improve the solubility of many drugs, including codeine and salbutamol. In the treatment of asthma, salbutamol is sold as the sulfate salt for increased water solubility in the lungs.



(*R*)-salbutamol
(slightly soluble in water)



(*R*)-salbutamol sulfate
(soluble in water)

The basicity of amines and the solubility of amine salts in water can be used to separate amines from water-insoluble, nonbasic compounds. Figure 19.20 is a flowchart for the separation of aniline from anisole. Note that aniline is recovered from its salt by treatment with NaOH.

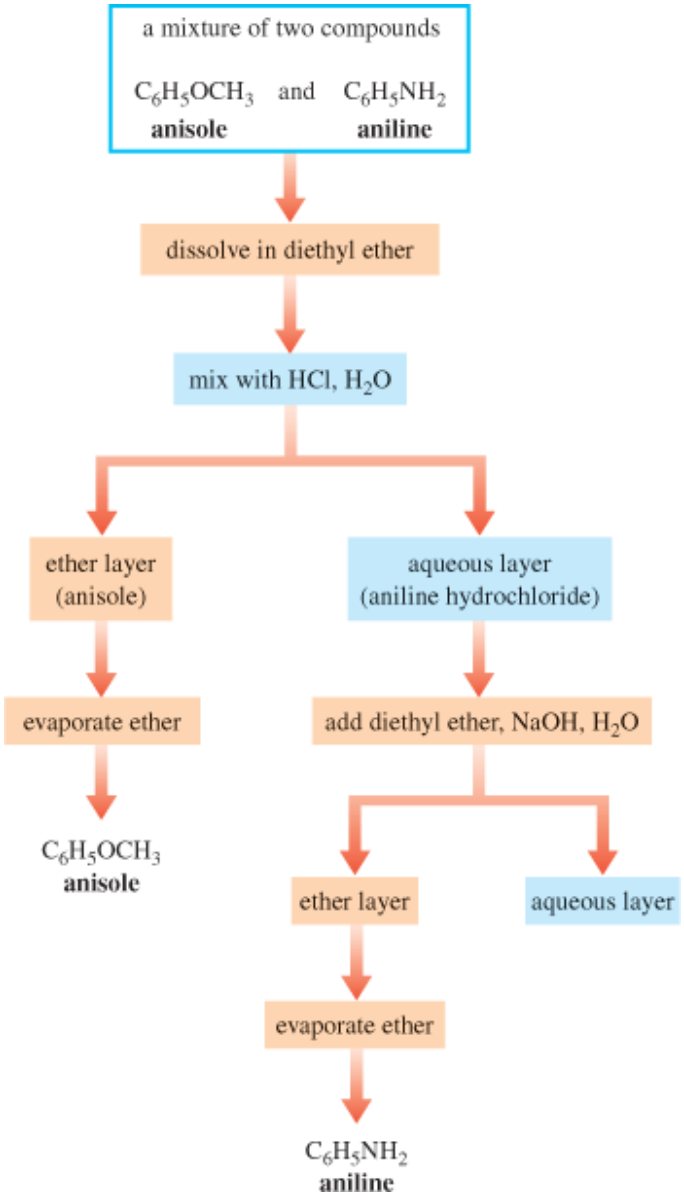
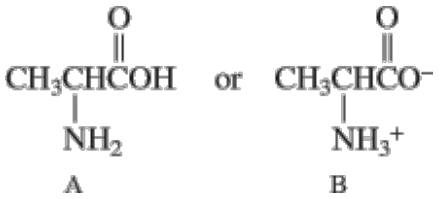


FIGURE 19.20 Separation and purification of an amine and a neutral compound.

WORKED EXAMPLE 19.12

Amino Acid — Alanine

The following are two structural formulae for alanine, 2-aminopropanoic acid, one of the building blocks of proteins (chapter 24).



A or B

Is alanine better represented by structural formula A or B?

Analysis

This question is similar to worked example 19.10 except that the amine and the carboxylic acid are on the same molecule. Structural formula A contains both an amino group (a base) and a carboxyl group (an acid), while structure B contains the ammonium group (the conjugate acid) and the carboxylate group (the conjugate base).

Solution

Proton transfer from the stronger acid (—COOH) to the stronger base (—NH_2) gives an internal salt; therefore, B is the better representation of alanine. Within the field of amino acid chemistry, the internal salt represented by B is called a **zwitterion** (chapter 24).

PRACTICE EXERCISE 19.12

As shown in worked example 19.12, alanine is better represented as a zwitterion. Suppose that the zwitterion is dissolved in water.

(a) In what way would you expect the structure of alanine in aqueous solution to change if concentrated HCl were added to adjust the pH of the solution to 2.0?

(b) In what way would you expect the structure of alanine in aqueous solution to change if concentrated NaOH were added to bring the pH of the solution to 12.0?

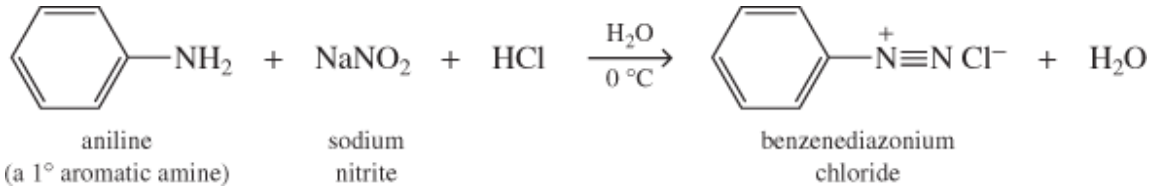
Reaction of Primary Aromatic Amines with Nitrous Acid

Nitrous acid, HNO_2, is an unstable compound that is prepared by adding sulfuric or hydrochloric acid to an aqueous solution of sodium nitrite, $NaNO_2$. Nitrous acid is a weak acid and ionises according to the following equation.

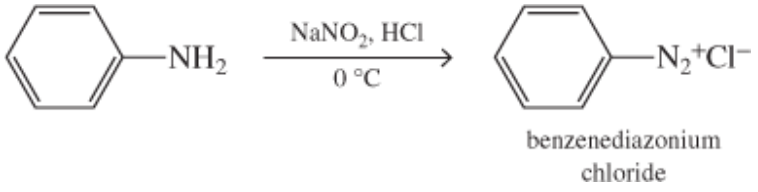
$$\underset{\text{nitrous acid}}{HNO_2} + H_2O \rightleftharpoons H_3O^+ + NO_2^- \qquad K_a = 4.26 \times 10^{-4} \qquad pK_a = 3.57$$

Nitrous acid reacts with amines in different ways, depending on whether the amine is primary, secondary or tertiary, and whether it is aliphatic or aromatic. We concentrate on the reaction of nitrous acid with primary aromatic amines, because this reaction is useful in organic synthesis.

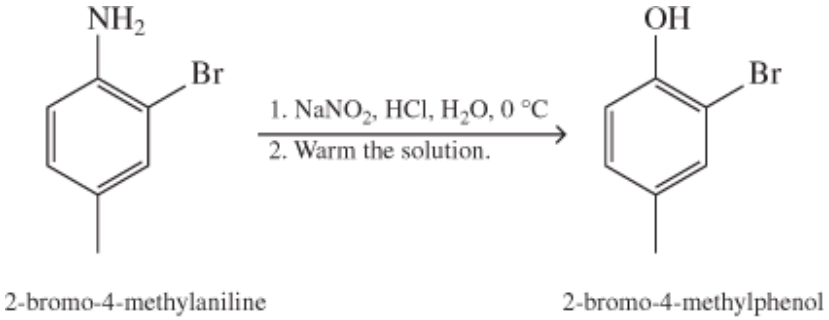
Treatment of a primary aromatic amine, for example aniline, with nitrous acid gives a relatively stable diazonium salt.



We can also write the equation for this reaction in the following more abbreviated form.



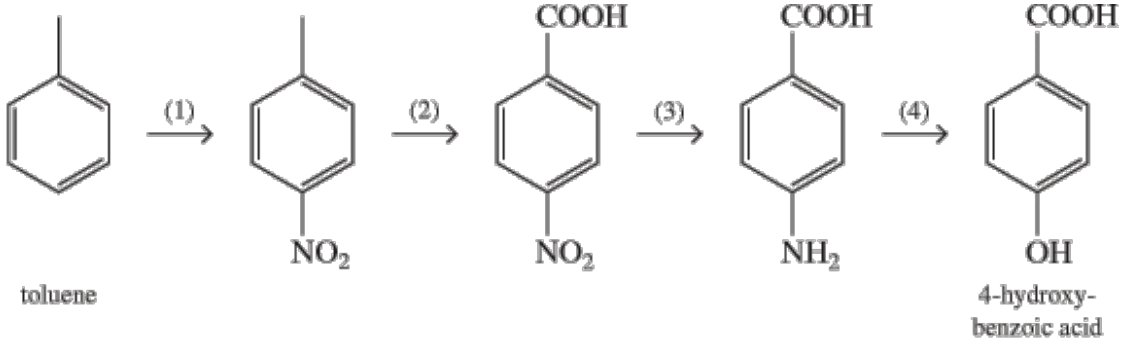
Primary aliphatic amines also give diazonium salts, but these are unstable and decompose immediately to give a complex mixture of products. When we warm an aqueous solution of an aromatic diazonium salt, the $—N_2^+$ group is replaced by an —OH group. This reaction is one of the few methods we have for the synthesis of phenols. It enables us to convert an aromatic amine to a phenol by first forming the aromatic diazonium salt and then heating the solution. In this manner, we can convert 2-bromo-4-methylaniline to 2-bromo-4-methylphenol.



WORKED EXAMPLE 19.13

Conversion of Toluene to 4-hydroxybenzoic Acid

Show the reagents that will bring about each step in this conversion of toluene to 4-hydroxybenzoic acid.



Analysis

In this question you need to identify, in each step, the change in going from the starting material to the product.

Step 1: This is an electrophilic aromatic substitution reaction (section 16.8), specifically a nitration

reaction.

Step 2: This is an oxidation of the benzylic carbon atom (section 23.4).

Step 3: This is a reduction of the nitro group *(section* 19.6*)*.

Step 4: This is a conversion of a primary aromatic amine to a phenol *(section* 19.7*)*.

Solution

Step 1: Treatment with nitric acid/sulfuric acid, followed by separation of the *ortho* and *para* isomers.

Step 2: Treatment with chromic acid or potassium permanganate.

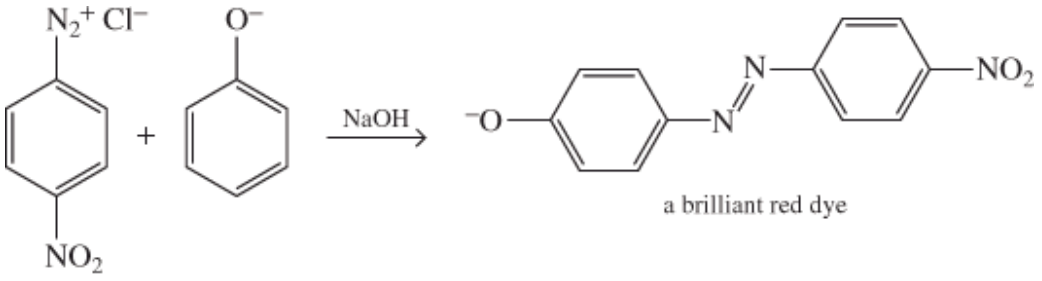
Step 3: Treatment with H_2 in the presence of a transition metal catalyst *or* using Fe, Sn or Zn in the presence of aqueous HCl, followed by neutralisation of the hydrochloride salt.

Step 4: Treatment with $NaNO_2$/HCl to form the diazonium ion salt and then warming the solution.

PRACTICE EXERCISE 19.13

Show how you can use the set of steps from worked example 19.13, but in a different order, to convert toluene to 3-hydroxybenzoic acid.

Diazonium salts can also undergo coupling reactions with phenols and anilines to give **azo compounds** (Ar—N═N—Ar). These compounds are brightly coloured and are commonly used as dyes. This coupling is another example of an electrophilic aromatic substitution reaction (see section 16.8), where the electrophile is the diazonium salt. The addition of the diazonium salt derived from 4-nitroaniline to a basic solution of phenol instantly gives a brilliant red dye (figure 19.21).



a brilliant red dye

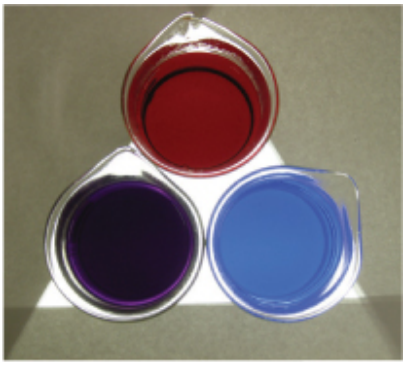
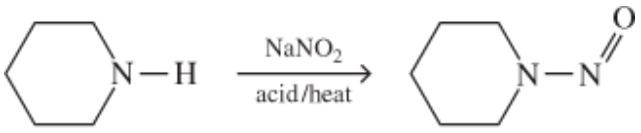


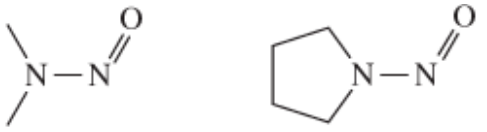
FIGURE 19.21 Azo dyes produced by the addition of 4-nitrobenzenediazonium chloride to phenol (red), 1-naphthol (blue) and 2-naphthol (purple).

The reaction of secondary amines with nitrous acid produces *N*-nitrosamines.



piperidine — *N*-nitrosopiperidine

Nitrosamines are important because many are known to be carcinogens in animals, and they have been found in cooked foods that have been preserved with sodium nitrite. Sodium nitrite is added to meats to inhibit the growth of *Clostridium botulinum*, which causes botulism, a deadly form of food poisoning.

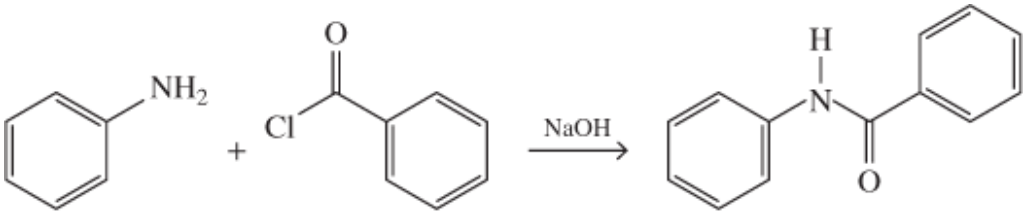


N-nitrosodimethylamine (found in tobacco smoke, beer and hot dogs)

N-nitrosopyrrolidine (formed when bacon cured with sodium nitrite is fried)

Amide formation

An important reaction of amines is the formation of amides by condensation with acid chlorides or carboxylic anhydrides. The chemistry will be discussed in greater detail in chapter 23 (carboxylic acids) and chapter 24 (amino acids and proteins).



aniline — benzoyl chloride — *N*-phenylbenzamide (benzanilide) (75%)

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SUMMARY

Alcohols

The alcohol functional group is an —OH (hydroxyl) group bonded to an sp^3 hybridised carbon atom. Alcohols are classified as primary, secondary or tertiary, depending on whether the —OH group is bonded to a primary, secondary or tertiary carbon atom. IUPAC names for alcohols are formed by changing the suffix of the parent alkane from *-e* to *-ol*. Common names for alcohols are derived by naming the alkyl group bonded to the —OH group and adding the word 'alcohol'.

Alcohols are polar compounds with the oxygen atom bearing a partial negative charge and both the carbon atom and hydrogen atom bonded to it bearing partial positive charges. Because of inter-molecular hydrogen bonding, the boiling points of alcohols are higher than those of hydrocarbons with a similar number of electrons. Because of increased dispersion forces, the boiling points of alcohols increase with increasing number of electrons (molar mass). Alcohols interact with water by hydrogen bonding and therefore are more soluble in water than hydrocarbons with a similar number of electrons.

Reactions of alcohols

Since alcohols have a reactivity similar to water, they can be readily deprotonated to form alkoxides, or protonated to form oxonium ions. They are readily converted into alkenes, haloalkanes, aldehydes, ketones, carboxylic acids and esters. They can also be prepared from these functional groups.

Phenols

The phenol functional group is an —OH group bonded directly to a benzene ring. Phenol and its derivatives are weak acids, with pK_a values of approximately 10.0, but are considerably stronger acids than alcohols, which have pK_a values of 16 -18. They react quantitatively with strong bases to give water-soluble phenoxide salts.

Ethers

The ether functional group is an oxygen atom bonded to two carbon atoms that are not also bonded to a heteroatom. In the IUPAC name of an ether, the parent alkane is named, and then the —OR group is named as an alkoxy substituent. Common names are derived by naming the two groups bonded to oxygen, followed by the word 'ether'. Ethers are moderately polar compounds. Their boiling points are close to those of hydrocarbons with a similar number of electrons. Because ethers are hydrogen bond acceptors, they are more soluble in water than are hydrocarbons with a similar number of electrons.

Thiols

A thiol is the sulfur analogue of an alcohol; it contains an —SH (sulfhydryl) group in place of an —OH group. Thiols are named in the same manner as alcohols, but the suffix *-e* is replaced by *-thiol*. Common names for thiols are derived by naming the alkylgroup bonded to —SH and adding the word 'mercaptan'. In compounds containing functional groups of higher precedence, the presence of a thiol is indicated by the prefix *mercapto-*. For thioethers, name the two groups bonded to sulfur, followed by the word 'sulfide'. The S—H bond is nonpolar, and the physical properties of thiols are similar to those of hydrocarbons with a similar number of electrons.

Amines

Amines are classified as primary, secondary or tertiary, depending on the number of hydrogen atoms of ammonia replaced by alkyl or aryl groups. In an aliphatic amine, all carbon atoms bonded to nitrogen are derived from alkyl groups. In an aromatic amine, one or more of the groups bonded to nitrogen are aryl groups. A heterocyclic amine is an amine in which the nitrogen atom is part of a ring. A

heterocyclic aromatic amine is an amine in which the nitrogen atom is part of an aromatic ring.

In IUPAC nomenclature, aliphatic amines are named alkanamines. In the common system of nomenclature, aliphatic amines are named alkylamines, with the alkyl groups listed in alphabetical order in one word ending in the suffix *-amine*.

Amines are polar compounds, and primary and secondary amines associate by intermolecular hydrogen bonding. Because an N—H…N hydrogen bond is weaker than an O—H…O hydrogen bond, amines have lower boiling points than alcohols with a similar number of electrons and structure. All classes of amines form hydrogen bonds with water and are more soluble in water than hydrocarbons with a similar number of electrons.

Reactions of amines

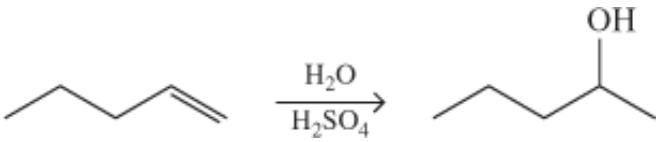
Amines are weak bases, and aqueous solutions of amines are basic. The basicity constant for an amine in water is given the symbol K_b. It is also common to discuss the acid–base properties of amines by reference to the acidity constant, K_a, for the conjugate acid of the amine. Acidity and basicity constants for an amine in water are related by the equation $pK_a + pK_b = 14.00$ at 25 °C.

Amines react with strong acids to produce water-soluble salts, a strategy used by drug companies to enhance the solubility of drugs. Amines can also react as nucleophiles in substitution reactions.

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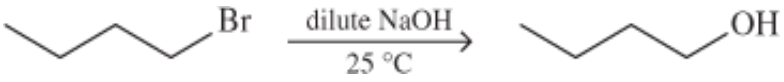
Preparation of alcohols from alkenes *(section 19.1)*

Alcohols can be prepared by the acid-catalysed hydration of alkenes.



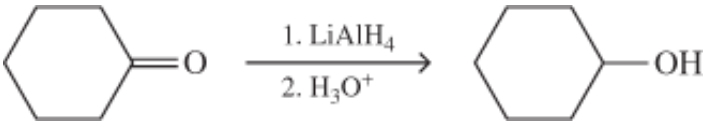
Preparation of alcohols from haloalkanes *(section 19.1)*

Alcohols can be prepared from haloalkanes by the nucleophilic substitution of OH^- or water.



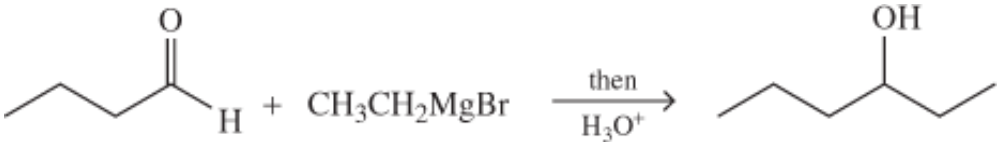
Preparation of alcohols by reduction of carbonyl compounds *(section 19.1)*

Alcohols can be prepared by the reduction of carbonyl compounds. Aldehydes, acids and esters are reduced to primary alcohols, and ketones are reduced to secondary alcohols.



Preparation of alcohols from Grignard reagents *(section 19.1)*

Alcohols can be prepared by the addition of Grignard reagents to carbonyl compounds. Aldehydes give secondary alcohols, while ketones and esters give tertiary alcohols.



Acidity of alcohols *(section 19.2)*

In dilute aqueous solution, methanol and ethanol are comparable in acidity to water. Secondary and tertiary alcohols are weaker acids than water.

$$CH_3OH + H_2O \rightleftharpoons CH_3O^- + H_3O^+ \quad pK_a = 15.5$$

Reaction of alcohols with active metals *(section 19.2)*

Alcohols react with Li, Na, K and other active metals to form metal alkoxides, which are generally stronger bases than NaOH and KOH.

$$2CH_3CH_2OH + 2Na \rightarrow 2CH_3CH_2O^-Na^+ + H_2$$

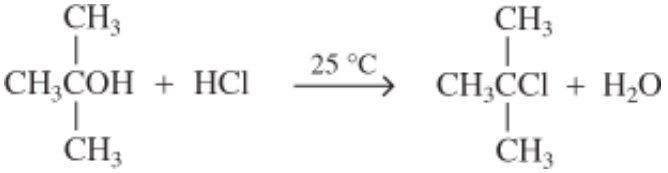
Reaction of alcohols with HCl, HBr and HI *(section 19.2)*

Primary alcohols react with HBr and HI by an S_N2 mechanism.

$$CH_3CH_2CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2CH_2Br + H_2O$$

Tertiary alcohols react with HCl, HBr and HI by an S_N1 mechanism, with the formation of a carbocation

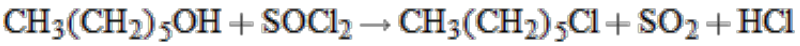
intermediate.



Secondary alcohols may react with HCl, HBr and HI by an S_N2 or an S_N1 mechanism, depending on the alcohol and experimental conditions.

Reaction of alcohols with $SOCl_2$ *(section 19.2)*

The reaction of alcohols with thionyl chloride is often the method of choice for converting an alcohol into an alkyl chloride.



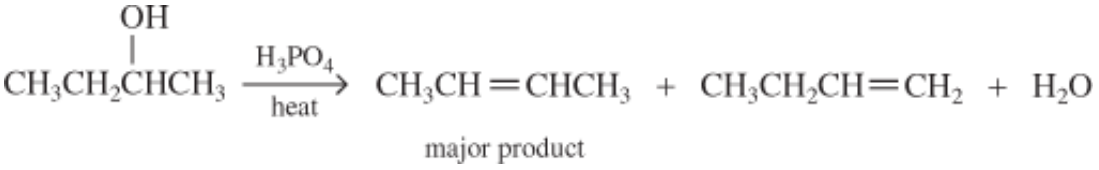
Reaction of alcohols with phosphorus halides *(section 19.2)*

The reaction of alcohols with phosphorus halides is often used for the preparation of alkyl bromides.



Acid-catalysed dehydration of alcohols *(section 19.2)*

When isomeric alkenes are possible, the major product of acid-catalysed dehydration of alcohols is generally the more substituted alkene (Zaitsev's rule).



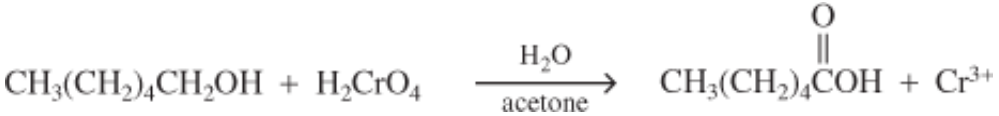
Oxidation of a primary alcohol to an aldehyde *(section 19.2)*

The oxidation of a primary alcohol to an aldehyde is most conveniently carried out using pyridinium chlorochromate (PCC).



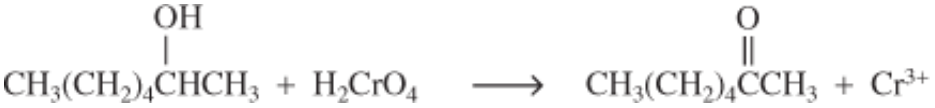
Oxidation of a primary alcohol to a carboxylic acid *(section 19.2)*

A primary alcohol is oxidised to a carboxylic acid by chromic acid.



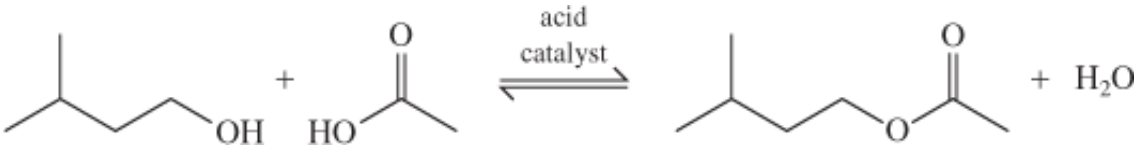
Oxidation of a secondary alcohol to a ketone *(section 19.2)*

A secondary alcohol is oxidised to a ketone by chromic acid and by PCC.

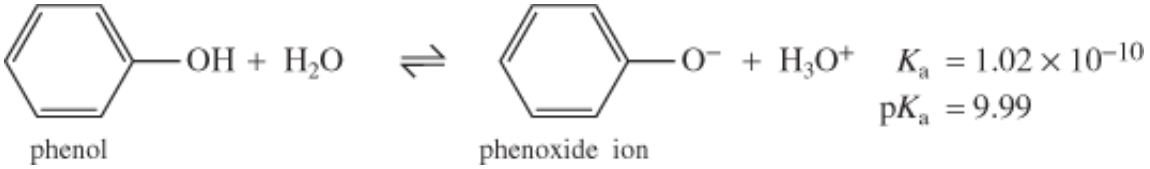


Ester formation *(section 19.2)*

Alcohols react readily with carboxylic acids under acid catalysis to produce esters (this reaction will be discussed in more detail in chapter 23).



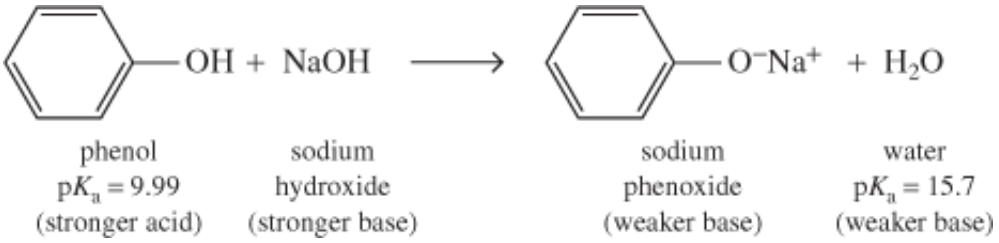
Acidity of phenols *(section 19.3)*



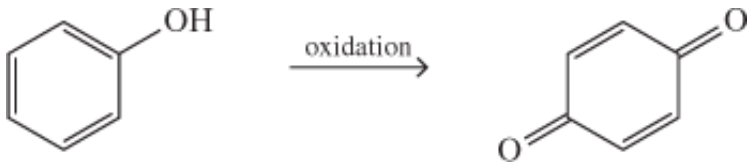
Substitution by electron-withdrawing groups, such as halogens or the nitro group, increases the acidity of phenols.

Reaction of phenols with strong bases *(section 19.3)*

Water-insoluble phenols react quantitatively with strong bases to form water-soluble salts.

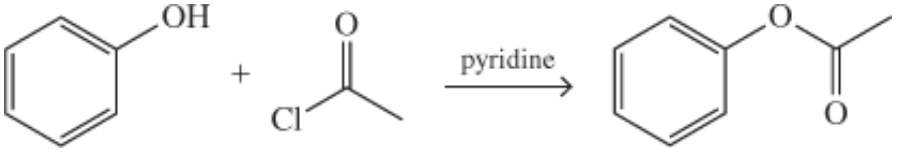


Oxidation of phenols *(section 19.3)*



Ester formation *(section 19.3)*

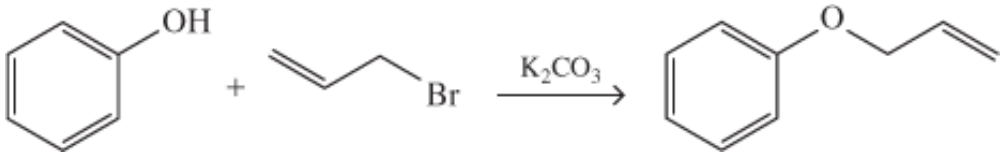
Esters of phenols can be prepared by reaction with acid chlorides or anhydrides.



This reaction is often carried out in the presence of a base to neutralise the HCl as it is formed.

Ether formation *(section 19.3)*

Due to the acidity of phenols, they react with haloalkanes to produce ethers under mildly basic conditions.



Acidity of thiols *(section 19.5)*

Thiols are weak acids, pK_a = 8–9, but are considerably stronger acids than alcohols, pK_a = 16 -18.

$$CH_3CH_2SH + H_2O \rightleftharpoons CH_3CH_2S^- + H_3O^+ \quad pK_a = 8.5$$

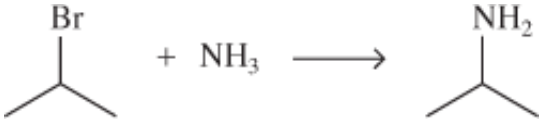
Oxidation to disulfides *(section 19.5)*

Oxidation of a thiol by O_2 gives a disulfide.

$$2RSH + \frac{1}{2}O_2 \rightarrow RS{-}SR + H_2O$$

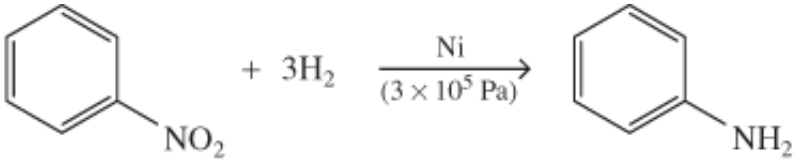
Preparation of amines from haloalkanes *(section 19.6)*

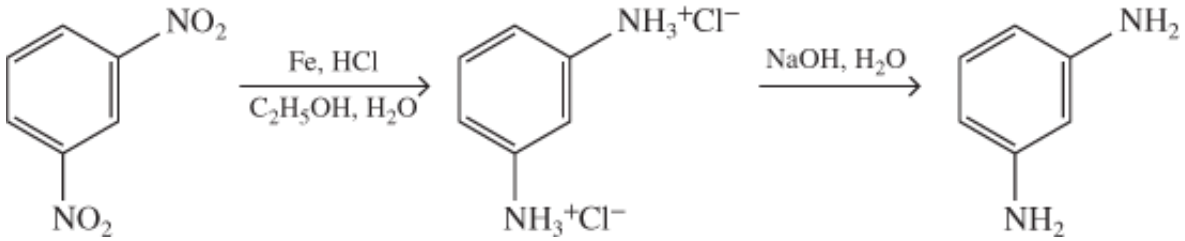
Amines can be prepared from haloalkanes by nucleophilic substitution with an appropriate nucleophile.



Reduction of an aromatic NO_2 group *(section 19.6)*

An NO_2 group on an aromatic ring can be reduced to an amino group by catalytic hydrogenation, or by treatment with a metal and hydrochloric acid, followed by a strong base to liberate the free amine.





Basicity of aliphatic amines *(section 19.7)*

Most aliphatic amines have comparable basicities (pK_b = 3.0-4.0) and are slightly stronger bases than ammonia.

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^- \quad pK_b = 3.36$$

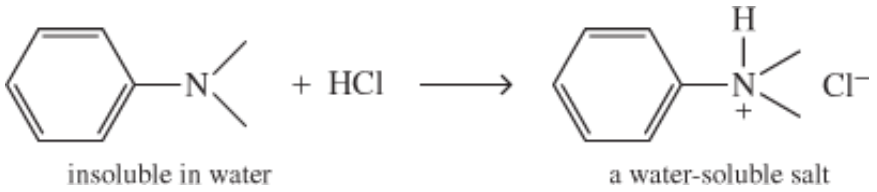
Basicity of aromatic amines *(section 19.7)*

Aromatic amines (pK_b = 9.0–10.0) are considerably weaker bases than aliphatic amines. Reson ance stabilisation from interaction of the unshared electron pair on nitrogen with the φ system of the aromatic ring decreases the availability of that electron pair for reaction with an acid. Substitution on the ring by electron-withdrawing groups further decreases the basicity of the —NH_2 group.



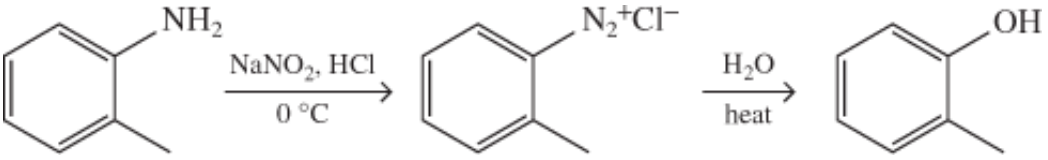
Reaction of amines with strong acids *(section 19.7)*

All amines react quantitatively with strong acids to form water-soluble salts.



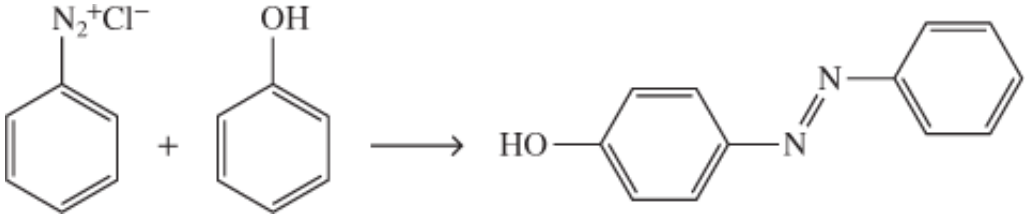
Conversion of a primary aromatic amine to a phenol *(section 19.7)*

Treatment of a primary aromatic amine with nitrous acid gives an arenediazonium salt. Heating the aqueous solution of this salt produces N_2 gas and a phenol.



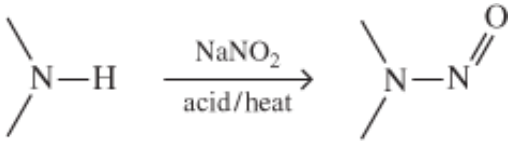
Formation of azo dyes *(section 19.7)*

Arenediazonium salts also couple with phenols and anilines to give azo dyes.



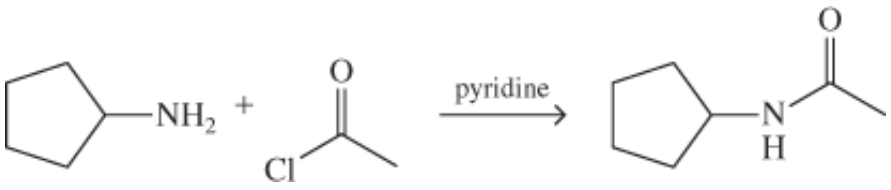
Formation of *N*-nitrosamines *(section 19.7)*

Secondary amines react with nitrites under acidic conditions to produce *N*-nitrosamines.



Formation of amides *(section 19.7)*

Amines can react with acid chlorides and anhydrides to produce amides (this reaction will be discussed in more detail in chapter 23).

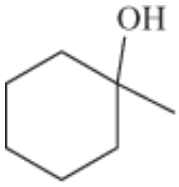


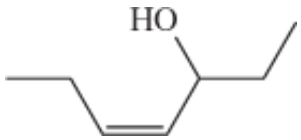
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REVIEW QUESTIONS

Alcohols

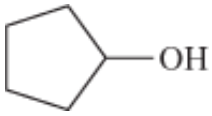
19.1 Classify the following alcohols as primary, secondary or tertiary.

(a) 

(b) 

19.2 Classify the following alcohols as primary, secondary or tertiary.

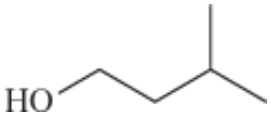
(a) $(CH_3)_3COH$

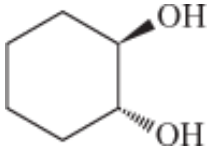
(b) 

19.3 Name the following compounds.

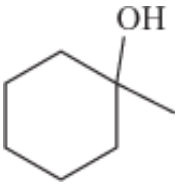
(a) 

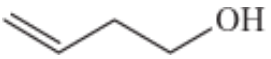
(b) 

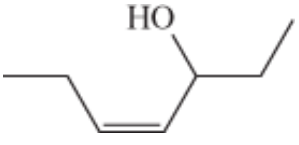
(c) 

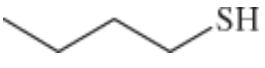
(d) 

19.4 Name the following compounds.

(a) 

(b) 

(c) 

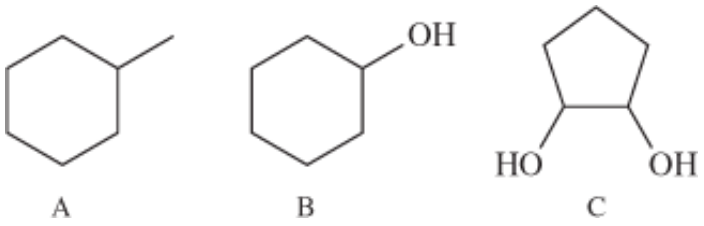
(d) 

19.5 ‘3-butanol’ is not a proper name, but a structure could still be written for it. What is this structure, and what IUPAC name should be used?

19.6 ‘1-chloropentan-4-ol’ is not a proper name, but a structure could still be written for it. What is this structure, and what IUPAC name should be used?

19.7 Explain why $CH_3CH_2CH_2OH$ is more soluble in water than $CH_3CH_2CH_2CH_3$.

19.8 Examine the structures of the following compounds.



A B C

(a) Which has the highest solubility in water? Explain.

(b) Which has the lowest solubility in water? Explain.

19.9 Arrange the compounds in question 19.8 in order of increasing boiling point.

19.10 Arrange these compounds in order of increasing boiling point (values in °C are –42, 78, 117 and 198).

(a) $CH_3CH_2CH_2CH_2OH$

(b) CH_3CH_2OH

(c) $HOCH_2CH_2OH$

(d) $CH_3CH_2CH_3$

19.11 Give the structural formula of an alkene or alkenes from which each of the following alcohols can be prepared.

(a) butan-2-ol

(b) 1-methylcyclohexanol

(c) 2-methylpentan-2-ol

19.12 Give the structural formula of an alkene or alkenes from which each of the following alcohols can be prepared.

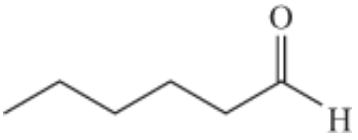
(a) hexan-3-ol

(b) cyclopentanol

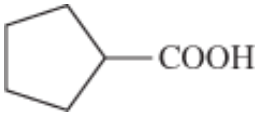
(c) 4-methyloctan-2-ol

19.13 Give the structural formula of the alcohol(s) formed on the reduction of the following carbonyl compounds.

(a)

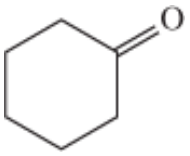


(b)

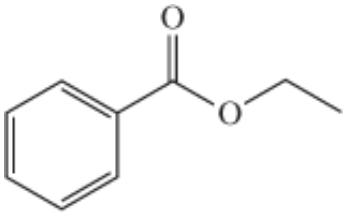


19.14 Give the structural formula of the alcohol(s) formed on the reduction of the following carbonyl compounds.

(a)



(b)



Reactions of alcohols

19.15 Show how to distinguish between cyclohexanol and cyclohexene using a simple chemical test.

19.16 Show how to distinguish between pentan-2-ol and 2-methylpentan-2-ol using a simple chemical test.

19.17 Write equations for the reaction of butan-1-ol, a primary alcohol, with the following reagents.

(a) Na metal

(b) HBr, heat

(c) $K_2Cr_2O_7$, H_2SO_4, heat

(d) $SOCl_2$

(e) pyridinium chlorochromate (PCC)

(f) PBr_3

19.18 Write equations for the reaction of (i) butan-2-ol, a secondary alcohol, and (ii) 1-methylcyclohexanol, a tertiary alcohol, with the following reagents.

(a) Na metal

(b) H_2SO_4, heat

(c) HBr, heat

(d) $K_2Cr_2O_7$, H_2SO_4, heat

(e) $SOCl_2$

(f) pyridinium chlorochromate (PCC)

19.19 Write the equation for the equilibrium that is present in a solution of propanoic acid and methanol with a trace of strong acid.

19.20 When the reaction described in 19.19 is carried out in the laboratory, methanol is used in vast excess, usually as the solvent, even though only one mole equivalent is required. What is the advantage of using such an excess of methanol?

Phenols

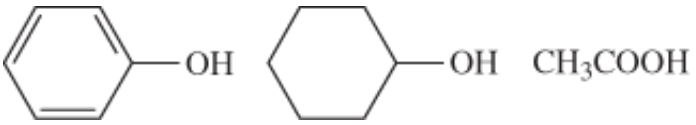
19.21 A monofunctional organic oxygen compound dissolves in aqueous base but not in aqueous acid. To which family of organic compounds that we studied in this chapter does this compound belong? Explain.

19.22 Why do water-insoluble carboxylic acids (pK_a = 4–5) dissolve in 10% sodium bicarbonate with the evolution of a gas, but water-insoluble phenols (pK_a = 9.5–10.5) do not show this chemical behaviour?

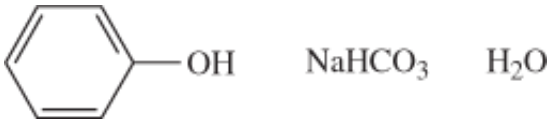
19.23 Use resonance theory to explain why phenol (pK_a = 9.99) is a stronger acid than cyclohexanol (pK_a = 18).

19.24 Arrange the compounds in each of the following sets in order of increasing acidity (from least acidic to most acidic).

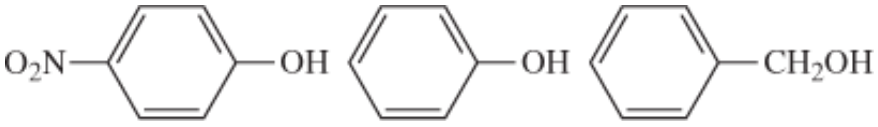
(a)



(b)



(c)



19.25 Give the structure of the expected product formed when 2-bromophenol reacts with each of the following reagents.

(a) sodium hydroxide

(b) chromic acid

(c) acetyl chloride

(d) sodium hydroxide followed by methyl iodide

(e) benzenediazonium chloride *(section* 19.7*)*

19.26 Give the structure of the expected product formed when 4-methoxyphenol reacts with each of the following reagents.

(a) Na metal

(b) $K_2Cr_2O_7$, H_2SO_4

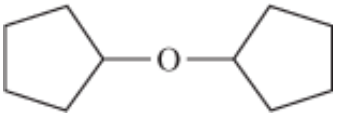
(c) sodium hydroxide followed by 2-bromopropane

(d) benzoyl chloride

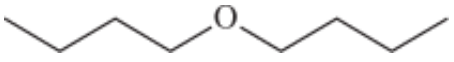
Ethers

19.27 Write names for the following ethers.

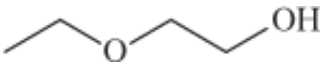
(a)



(b)



(c)



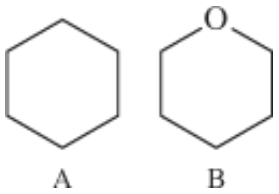
19.28 Draw a structural formula for each of the following ethers.

(a) diisopropyl ether

(b) 1,4-dimethoxybenzene

(c) 3-chloro-1-ethoxybutane

19.29 Which of the following compounds is more soluble in water? Explain.



19.30 Arrange the following compounds in order of increasing boiling point (values in °C are –42, –24, 78 and 118).

A. CH_3CH_2OH

B. CH_3OCH_3

C. $CH_3CH_2CH_3$

D. CH_3COOH

19.31 Each of the following compounds is a common organic solvent. From each pair of compounds, select the solvent with the greater solubility in water.

(a) $CH_3CH_2OCH_2CH_3$ or CH_2Cl_2

(b) $CH_3CH_2OCH_2CH_3$ or CH_3CH_2OH

19.32 Each of the following compounds is a common organic solvent. From each pair of compounds, select the solvent with the greater solubility in water.

(a) $CH_3CH_2OCH_2CH_3$ or $CH_3(CH_2)_3CH_3$

(b) $CH_3CH_2OCH_2CH_3$ or $CH_3OCH_2CH_2OCH_3$

(c) $CH_3CH_2OCH_2CH_3$ or $(CH_3)_2CHOCH(CH_3)_2$

Thiols

19.33 Draw structures corresponding to the following IUPAC names.

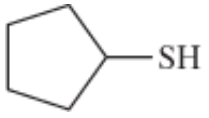
(a) 3-methylbutane-1-thiol

(b) dipropyl sulfide

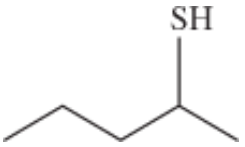
(c) 2-mercaptoethanol

19.34 Name the following compounds.

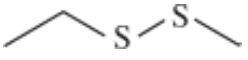
(a)



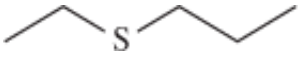
(b)



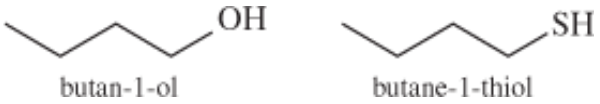
(c)



(d)



19.35 The following are structural formulae for butan-1-ol and butane-1-thiol. One of these compounds has a boiling point of 98.5 °C, the other has a boiling point of 117 °C. Which compound has which boiling point?



butan-1-ol butane-1-thiol

19.36 Which of the two compounds in question 19.35 would you expect to have greater solubility in water? Which would be more soluble in dilute sodium hydroxide solution? Explain.

19.37 From each of the following pairs, select the stronger acid, and write a structural formula for its conjugate base.

(a) H_2O or H_2S

(b) CH_3OH or CH_3SH

(c) CH_3COOH or CH_3CH_2SH

19.38 From each of the following pairs, select the stronger base, and write the structural formula of its conjugate acid.

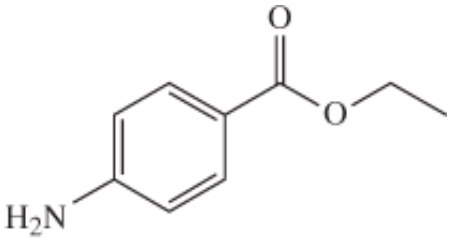
(a) OH^- or $CH_3CH_2O^-$

(b) $CH_3CH_2S^-$ or $CH_3CH_2O^-$

Amines

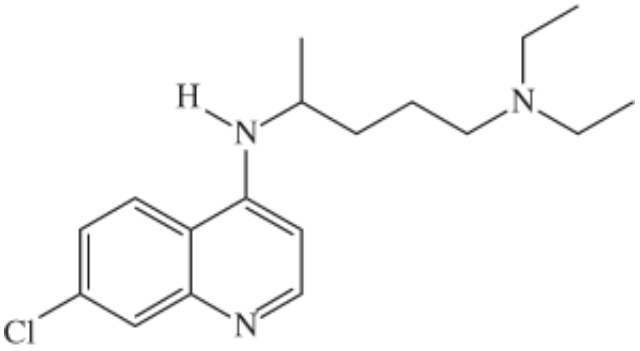
19.39 Classify each amino group in the following compounds as primary, secondary or tertiary, and as aliphatic or aromatic.

(a)



benzocaine
(a topical anaesthetic)

(b)



chloroquine
(a drug for the
treatment of malaria)

19.40 Draw examples of 1°, 2° and 3° amines that contain at least four sp^3 hybridised carbon atoms. Using the same criterion, provide examples of 1°, 2° and 3° alcohols. How does the classification system differ between the two functional groups?

19.41 Draw a structural formula for each of the following amines.

(a) (*R*)-butan-2-amine

(b) octan-1-amine

(c) 2,2-dimethylpropan-1-amine

(d) 2-bromoaniline

19.42 Draw a structural formula for each of the following amines.

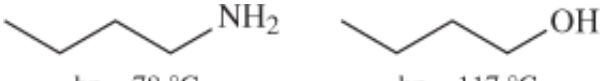
(a) pentane-1,5-diamine

(b) tributylamine

(c) *N*, *N*-dimethylaniline

(d) benzylamine

19.43 Why does butan-1-amine have a lower boiling point than butan-1-ol?



bp = 78 °C
butan-1-amine

bp = 117 °C
butan-1-ol

19.44 Propylamine, ethylmethylamine, and trimethylamine are constitutional isomers with molecular formula C_3H_9N.

$CH_3CH_2CH_2NH_2$	$CH_3CH_2NHCH_3$	$(CH_3)_3N$
bp = 48 °C	bp = 37 °C	bp = 3 °C
propylamine	ethylmethylamine	trimethylamine

Explain why trimethylamine has the lowest boiling point of the three, and propylamine has the highest.

Reactions of amines

19.45 A monofunctional organic nitrogen compound dissolves in aqueous hydrochloric acid but not in aqueous sodium hydroxide. What kind of organic compound is it?

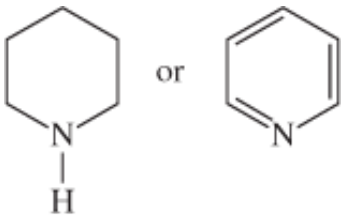
19.46 A crystalline monofunctional organic nitrogen compound readily dissolves in water, but produces a precipitate when this solution is made alkaline with sodium hydroxide. What kind of organic compound is it?

19.47 Use resonance theory to explain why aniline (pK_b = 9.36) is a weaker base than cyclohexylamine (pK_b = 3.34).

19.48 Why does substitution of a nitro group make an aromatic amine a weaker base, but it makes a phenol a stronger acid? For example, 4-nitroaniline is a weaker base than aniline, but 4-nitrophenol is a stronger acid than phenol.

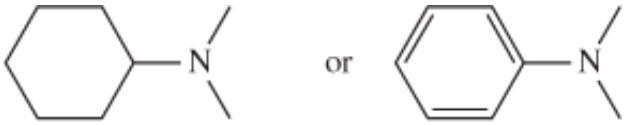
19.49 From each of the following pairs of compounds, select the stronger base.

(a)



A B

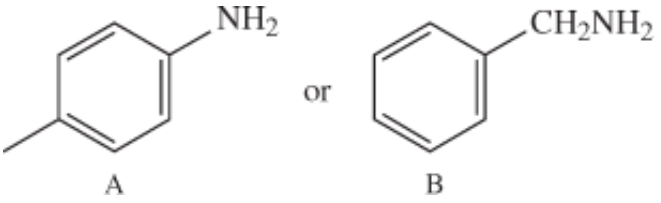
(b)



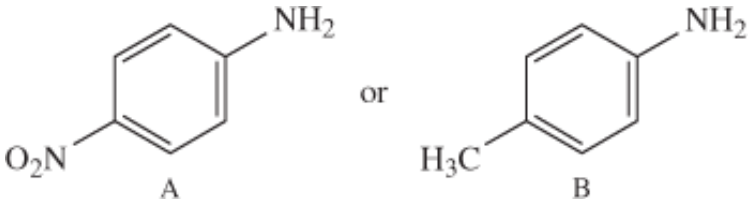
A B

19.50 From each of the following pairs of compounds, select the stronger base.

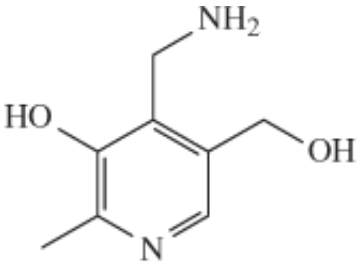
(a)



(b)



19.51 The following is a structural formula of pyridoxamine, one form of vitamin B_6.

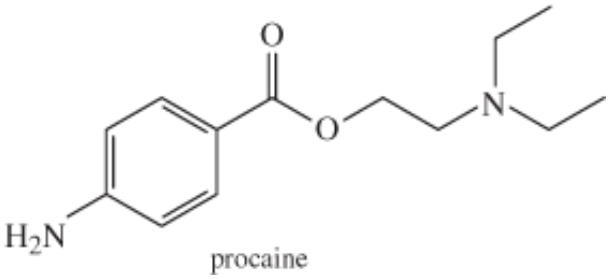


pyridoxamine
(vitamin B_6)

(a) Which nitrogen atom of pyridoxamine is the stronger base?

(b) Draw the structural formula of the hydrochloride salt formed when pyridoxamine is treated with 1 mole of HCl.

19.52 Procaine was one of the first local anaesthetics used for infiltration and regional anaesthesia.



procaine

The hydrochloride salt of procaine is marketed as Novocaine®.

(a) Which nitrogen atom of procaine is the stronger base?

(b) Draw the formula of the salt formed by treating procaine with 1 mole of HCl.

(c) Is procaine chiral? Would a solution of Novocaine in water be optically active or optically inactive?

19.53 Give the structure of the expected product formed when benzylamine reacts with each of the following reagents.

(a) HBr

(b) iodomethane

(c) acetyl chloride

(d) acetic acid

(e) 1-bromobutane

19.54 Give the structure of the expected product formed when aniline reacts with each of the following reagents.

(a) benzoyl chloride

(b) 2-bromopropane

(c) dilute hydrochloric acid solution

(d) nitrous acid

(e) propanoic acid

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REVIEW PROBLEMS

19.55 Draw a structural formula for each of the following compounds.

(a) isopropyl alcohol

(b) propylene glycol

(c) (*R*)-5-methyl-2-hexanol

(d) 4-aminobutanoic acid

(e) 2-aminoethanol (ethanolamine)

(f) 2-aminobenzoic acid

19.56 Draw a structural formula for each of the following compounds.

(a) 2-methyl-2-propyl-1,3-propanediol

(b) 2,2-dimethyl-1-propanol

(c) 2-hydroxybutanoic acid

(d) (*S*)-2-aminopropanoic acid (alanine)

(e) 4-aminobutanal

(f) 4-amino-2-butanone

19.57 Name and draw structural formulae for the eight isomeric alcohols with molecular formula $C_5H_{12}O$. Which of these are chiral?

19.58 There are eight constitutional isomers with molecular formula $C_4H_{11}N$. Name and draw a structural formula for each. Classify each amine as primary, secondary or tertiary.

19.59 Draw a structural formula for each of the following compounds with the given molecular formula.

(a) 2° arylamine, C_7H_9N

(b) 3° arylamine, $C_8H_{11}N$

(c) 1° aliphatic amine, C_7H_9N

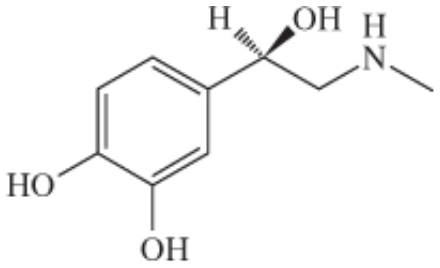
19.60 Draw a structural formula for each of the following compounds with the given molecular formula.

(a) chiral 1° amine, $C_4H_{11}N$

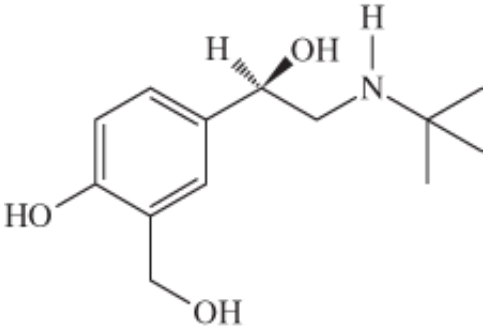
(b) 3° heterocyclic amine, $C_5H_{11}N$

(c) trisubstituted 1° arylamine, $C_9H_{13}N$

19.61 Epinephrine is a hormone secreted by the adrenal medulla. One of epinephrine's actions is as a bronchodilator. Albuterol, sold under several trade names including Ventolin® and Salbutamol®, is one of the most effective and widely prescribed anti-asthma drugs. The *R* enantiomer of albuterol is 68 times more effective in the treatment of asthma than the *S* enantiomer.



(*R*)-epinephrine
(adrenaline)



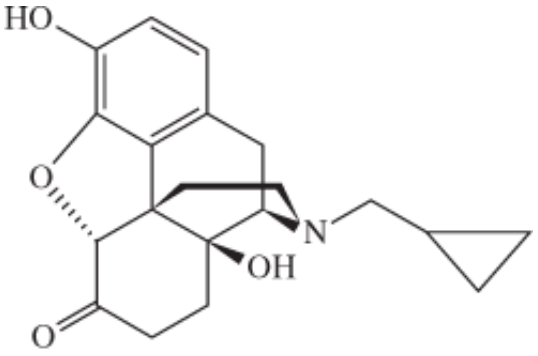
(*R*)-albuterol

(a) Label and name each functional group present.

(b) Classify each alcohol and amino group as primary, secondary or tertiary.

(c) List the similarities and differences between the structural formulae of these compounds.

19.62 Naltrexone is used to help recovering narcotic addicts stay drug free.

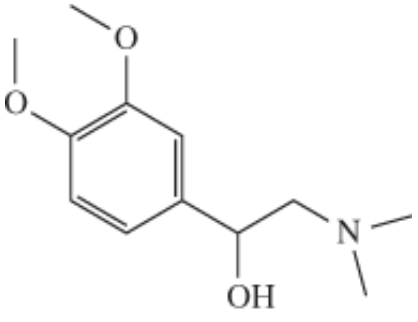


naltrexone

(a) Label and name all the functional groups. Where relevant, indicate whether the group is primary, secondary or tertiary.

(b) Upon addition of dilute hydrochloric acid solution, naltrexone forms a water-soluble salt. Draw the structure of this salt.

19.63 Macromerine has been isolated from the cactus *Coryphantha macromeris* and causes hallucinogenic reactions in animals.

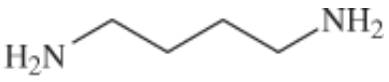


macromerine

(a) Label and name all the functional groups. Where relevant, indicate whether the group is primary, secondary or tertiary.

(b) Upon addition of dilute hydrochloric acid solution, macromerine forms a water-soluble salt. Draw the structure of this salt.

19.64 Explain why putrescine, a foul-smelling compound produced by rotting flesh, ceases to smell upon treatment with two equivalents of HCl.

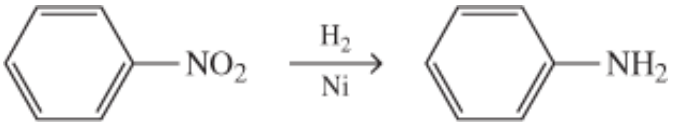


butane-1,4-diamine
(putrescine)

19.65 Draw all possible staggered conformations of ethane-1,2-diol, $HOCH_2CH_2OH$. Explain why the *syn* conformation is more stable than the *anti* conformation by approximately 4 kJ mol^{-1}?

19.66 Describe a procedure for separating a mixture of hexan-1-ol and 2-methylphenol (*o*-cresol) and recovering each in pure form. Both are insoluble in water but are soluble in diethyl ether.

19.67 Aniline is prepared by the catalytic reduction of nitrobenzene.



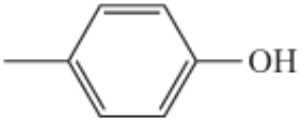
Devise a chemical procedure based on the basicity of aniline to separate it from any unreacted nitrobenzene.

19.68 Suppose that you have a mixture of the following three compounds.



4-nitrotoluene
(*p*-nitrotoluene)

4-methylaniline
(*p*-toluidine)

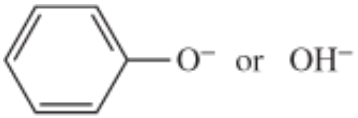


4-methylphenol
(*p*-cresol)

Devise a chemical procedure based on their relative acidity or basicity to separate and isolate each in pure form.

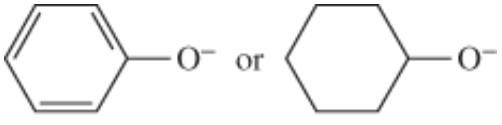
19.69 From each of the following pairs, select the stronger base.

(a)



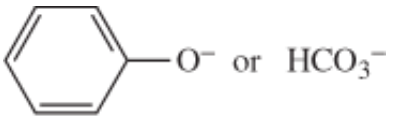
A B

(b)



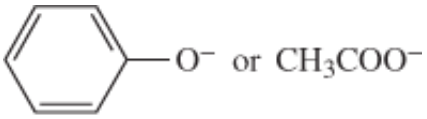
A B

(c)



A B

(d)



A B

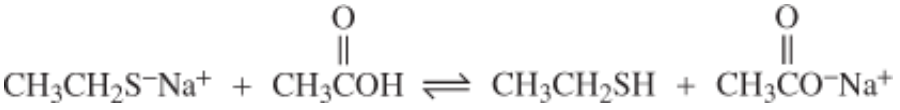
19.70 Predict the position of equilibrium for each of the following acid–base reactions; that is, does each lie considerably to the left, does each lie considerably to the right, or are the concentrations evenly balanced?

(a) $CH_3CH_2OH + Na^+OH^- \rightleftharpoons CH_3CH_2O^-Na^+ + H_2O$

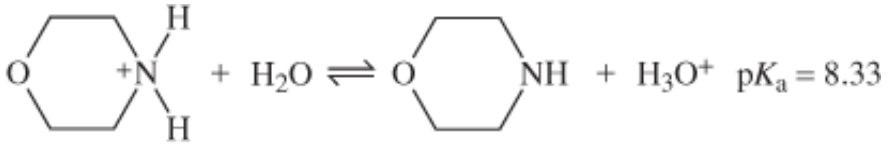
(b) $CH_3CH_2SH + Na^+OH^- \rightleftharpoons CH_3CH_2S^-Na^+ + H_2O$

(c) $CH_3CH_2OH + CH_2CH_2S^-Na^+ \rightleftharpoons CH_3CH_2O^-Na^+ + CH_3CH_2SH$

(d)



19.71 The pK_a value of the morpholinium ion is 8.33.



morpholinium ion morpholine

(a) Calculate the ratio of morpholine to morpholinium ion in aqueous solution at pH 7.0.

(b) At what pH are the concentrations of morpholine and morpholinium ion equal?

19.72 The pK_b of amphetamine is approximately 3.2. Calculate the ratio of amphetamine to its conjugate acid at pH 7.4, the pH of blood plasma.

19.73 Calculate the ratio of amphetamine to its conjugate acid at pH 1.0, such as might be present in stomach acid.

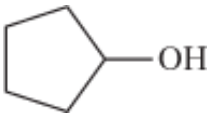
19.74 Arrange the compounds in each of the following sets in order of decreasing solubility in water.

(a) ethanol, butane, diethyl ether

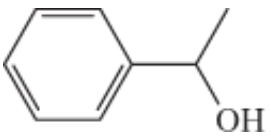
(b) hexan-1-ol, hexane-1,2-diol, hexane

19.75 Write the structures of the products of the acid-catalysed dehydrations of the following compounds.

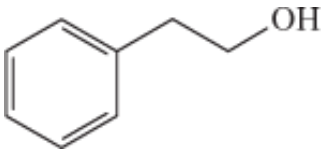
(a)



(b)

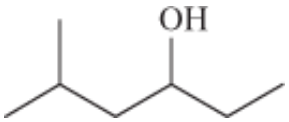


(c)

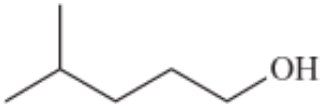


19.76 Write the structures of the products of the acid-catalysed dehydrations of the following compounds. If more than one alkene is possible show them all, and indicate which isomer would predominate.

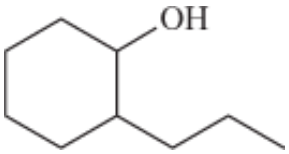
(a)



(b)



(c)



19.77 Write the structures of the substitution products that form when the alcohols in question 19.75 are heated with concentrated hydroiodic acid.

19.78 Write the structures of the substitution products that form when the alcohols in question 19.76 are heated with thionyl chloride ($SOCl_2$).

19.79 Write the structures of the products that can be prepared by the oxidation of the compounds in question 19.75 using pyridinium chlorochromate (PCC).

19.80 Write the structures of the products that can be prepared by the oxidation of the compounds in question 19.76 using chromic acid (H_2CrO_4).

19.81 Write the structure of the product of the acid-catalysed dehydration of propan-2-ol. Write the mechanism of the reaction.

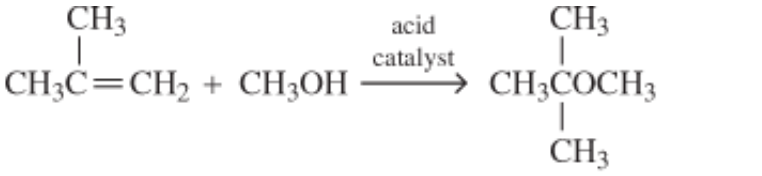
19.82 When (*R*)-butan-2-ol is left in aqueous acid, it slowly loses its optical activity. When the organic material is recovered from the aqueous solution, only butan-2-ol is found. Account for the observed loss of optical activity.

19.83 What is the most likely mechanism of the following reaction?



Draw a structural formula for the intermediate(s) formed during the reaction.

19.84 In the commercial synthesis of methyl *tert*-butyl ether (MTBE), once used as an antiknock, octane-improving petrol additive, 2-methylpropene and methanol are passed over an acid catalyst to give the ether as shown below.

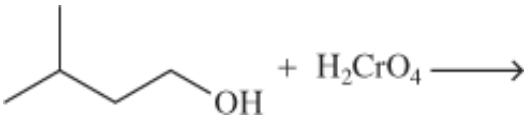


2-methylpropene methanol 2-methoxy-2-methylpropane (methyl *tert*-butyl ether, MTBE)

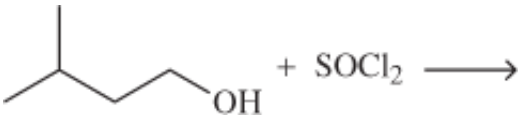
Propose a mechanism for this reaction.

19.85 Complete the equations for the following reactions.

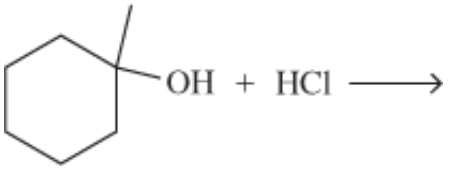
(a)



(b)

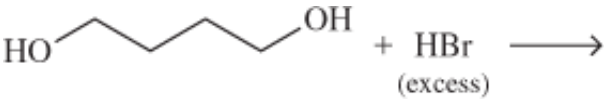


(c)

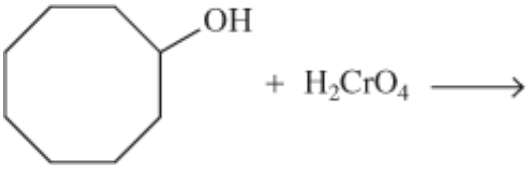


19.86 Complete the equations for the following reactions.

(a)

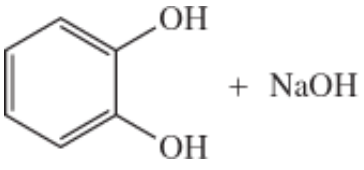


(b)

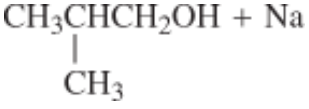


19.87 Write equations showing the reaction between the following pairs of substances.

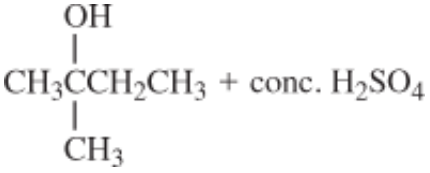
(a)



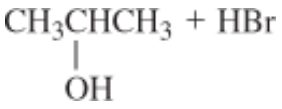
(b)



(c)

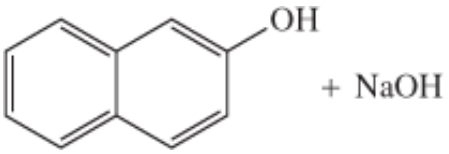


(d)

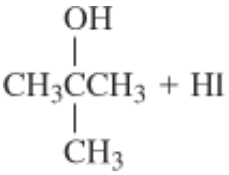


19.88 Write equations showing the reaction between the following pairs of substances.

(a)

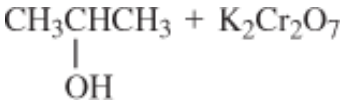


(b)

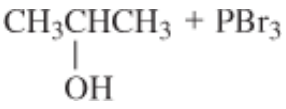


(c) $CH_3CH_2CH_2OH + SOCl_2$

(d)

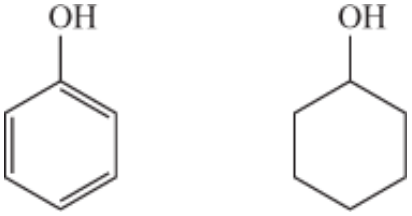


(e)

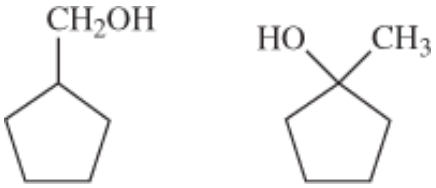


19.89 Explain how you could use simple chemical tests to distinguish between the following sets of compounds. Explain your observations and give equations where necessary.

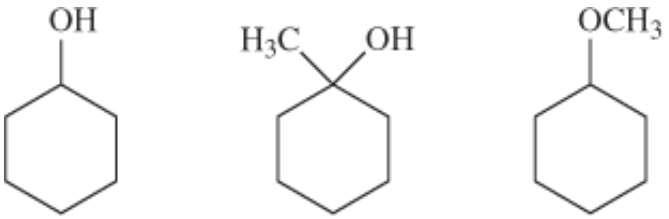
(a)



(b)



19.90 Explain how you could use simple chemical tests to distinguish between the following set of compounds. Explain your observations and give equations where necessary.



19.91 Show how to convert cyclohexanol to the following compounds.

(a) cyclohexene

(b) cyclohexane

(c) cyclohexanone

19.92 Show how to convert:

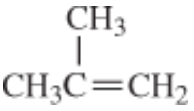
(a) propan-1-ol to propan-2-ol in two steps

(b) cyclohexene to cyclohexanone in two steps

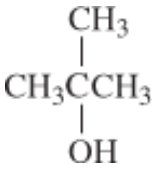
(c) propene to acetone (propanone) in two steps.

19.93 Show how to prepare each of the following compounds from 2-methylpropan-1-ol.

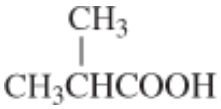
(a)



(b)



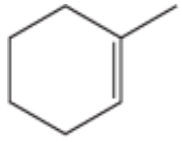
(c)



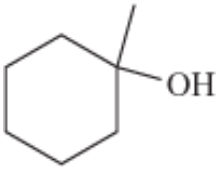
For any preparation involving more than one step, show each intermediate compound formed.

19.94 Show how to prepare each of the following compounds from 2-methylcyclohexanol.

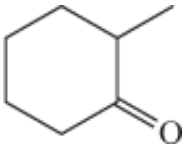
(a)



(b)

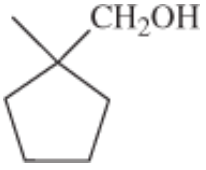


(c)

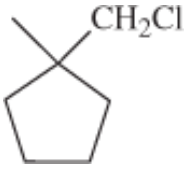


For any preparation involving more than one step, show each intermediate compound formed.

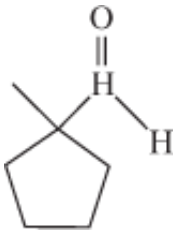
19.95 Show how to convert the alcohol on the left to compounds (a), (b) and (c).



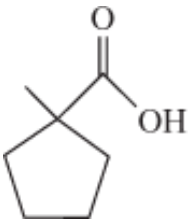
(a)



(b)



(c)



19.96 Show reagents and experimental conditions that can be used to synthesise the following compounds from propan-1-ol (any derivative of propan-1-ol prepared in an earlier part of this question may be used for a later synthesis).

(a) propanal

(b) propanoic acid

(c) propene

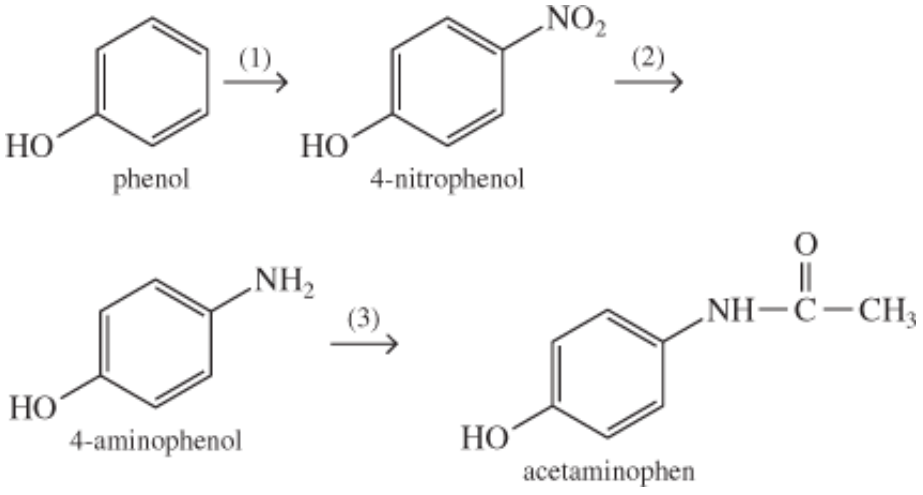
(d) propan-2-ol

(e) 2-bromopropane

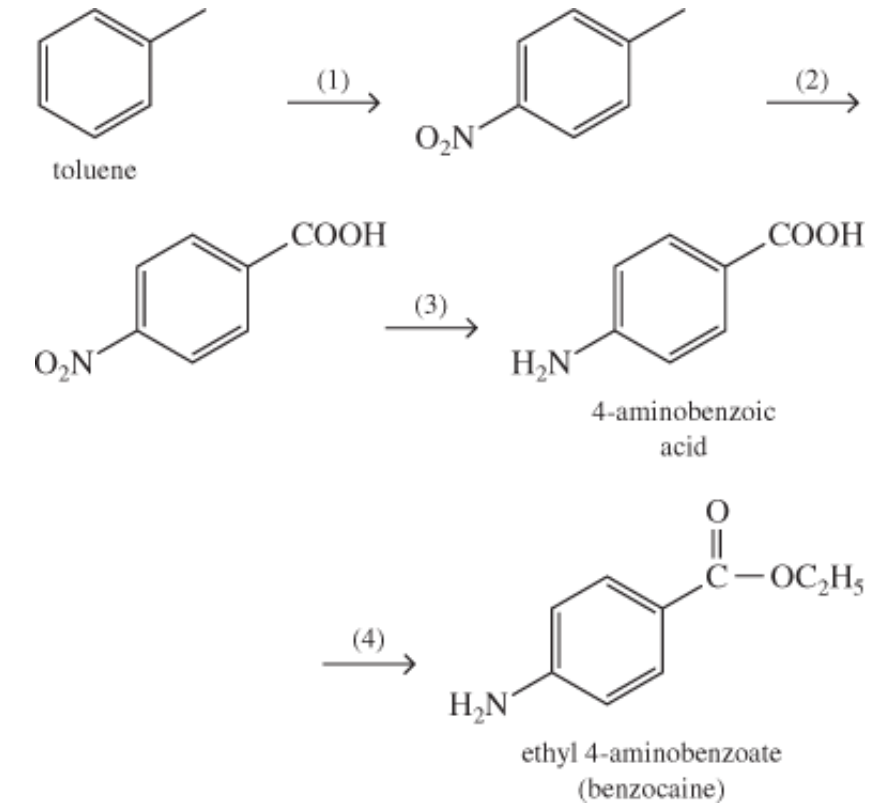
(f) 1-chloropropane

(g) acetone

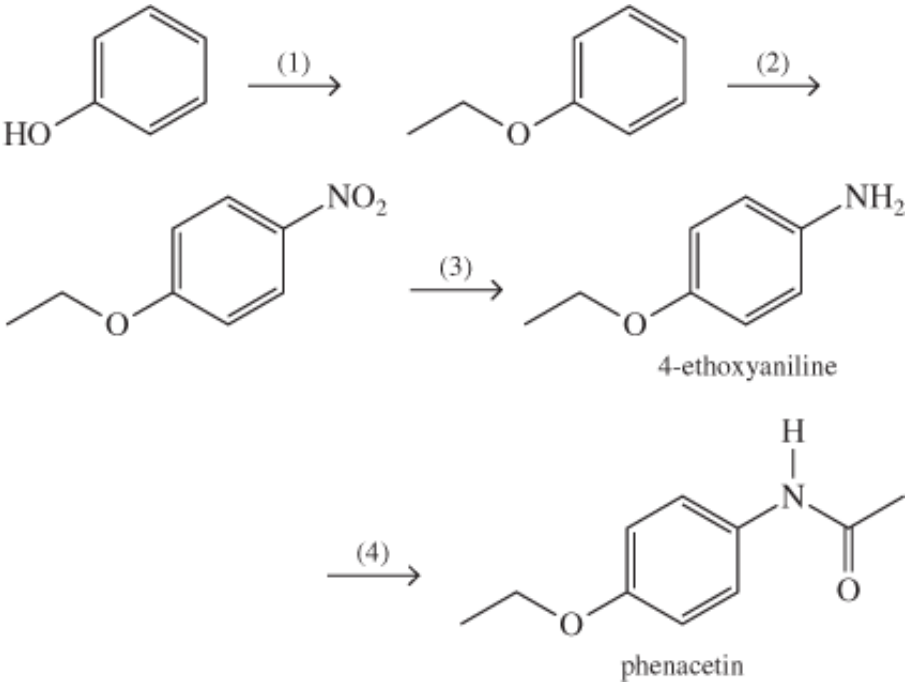
19.97 The compound 4-aminophenol is a building block in the synthesis of the analgesic acetaminophen. Show how this building block can be used in the synthesis of acetaminophen in three steps from phenol.



19.98 The topical anaesthetic benzocaine can be synthesised in four steps from toluene. Show how this can be achieved.

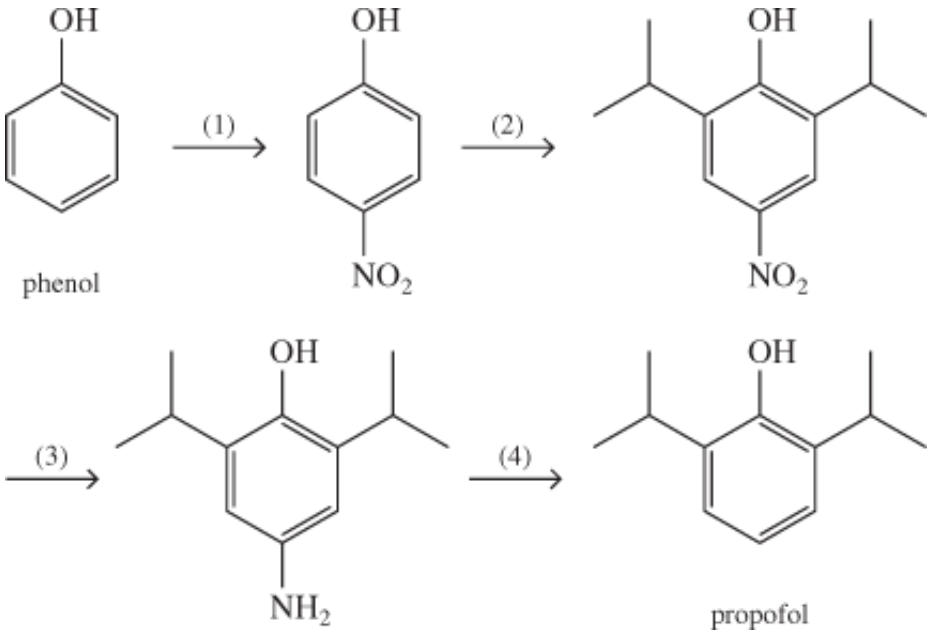


19.99 The over-the-counter analgesic phenacetin is synthesised in four steps from phenol.



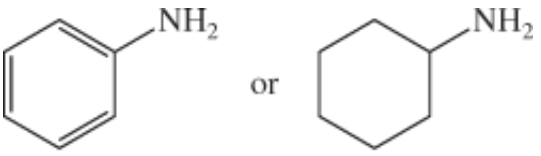
Show reagents for each step of the synthesis of phenacetin.

19.100 The intravenous anaesthetic propofol is synthesised from phenol in four steps. Show the reagents required for steps (1) to (3).



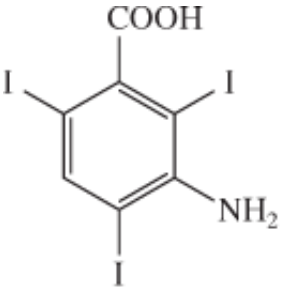
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19.101 Which of the following compounds is a better nucleophile? Give reasons for your answer.

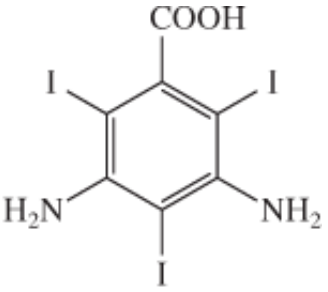


aniline cyclohexanamine

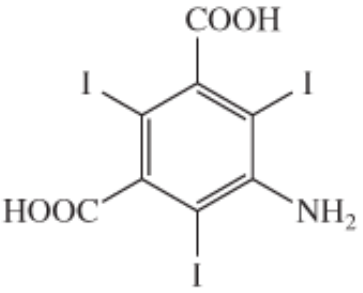
19.102 Radiopaque imaging agents are substances, administered either orally or intravenously, that absorb X-rays more strongly than body material does. One of the best known of these agents is barium sulfate, the key ingredient in the 'barium cocktail' used for imaging the gastrointestinal tract. Among other X-ray imaging agents are the triiodoaromatics. You can get some idea of the kinds of imaging they are used for from the following selection of trade names: Angiografin®, Gastrografin, Cardiografin, Cholografin, Renografin, and Urografin®. The most common of the triiodoaromatics are derivatives of the following three triiodobenzenecarboxylic acids.



3-amino-2,4,6-triiodobenzoic acid

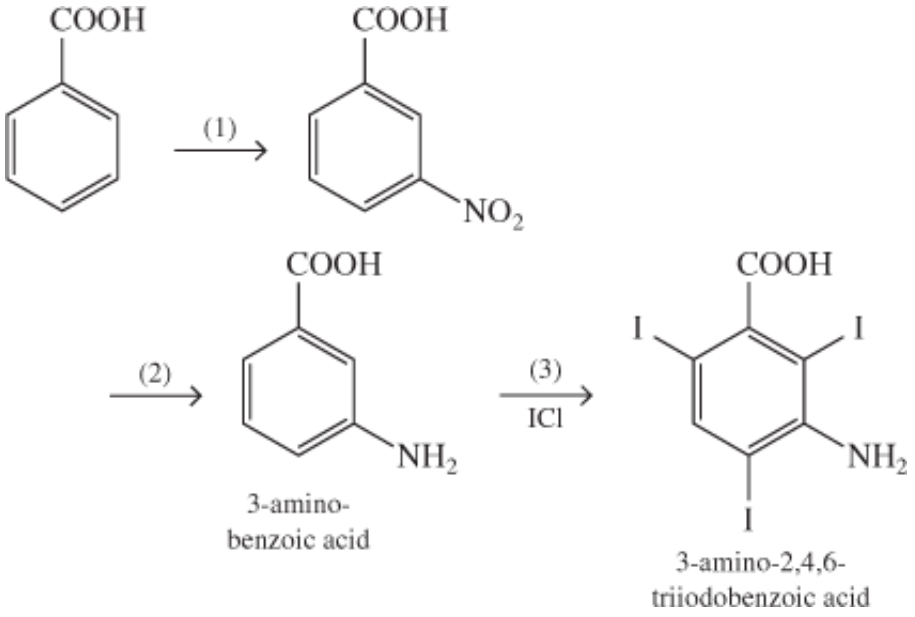


3,5-diamino-2,4,6-triiodobenzoic acid



5-amino-2,4,6-triiodoisophthalic acid

The compound 3-amino-2,4,6-triiodobenzoic acid is synthesised from benzoic acid in three steps.



(a) Show the reagents required for steps (1) and (2).

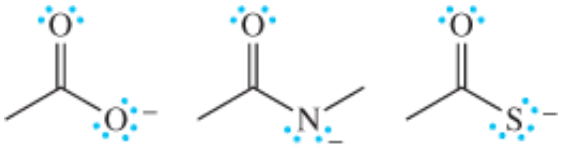
(b) Iodine monochloride, ICl, a black crystalline solid with a melting point of 27.2 °C and a boiling point of 97 °C, is prepared by mixing equimolar amounts of I_2 and Cl_2. Propose a mechanism for the iodination of 3-aminobenzoic acid using this reagent.

(c) Show how to prepare 3,5-diamino-2,4,6-triiodobenzoic acid from benzoic acid.

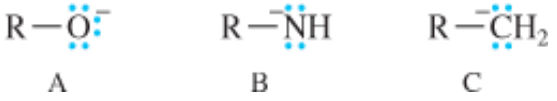
(d) Show how to prepare 5-amino-2,4,6-triiodoisophthalic acid from benzene-1,3-dicarboxylic acid.

19.103 Rank the members in each of the following sets of reagents from most to least nucleophilic.

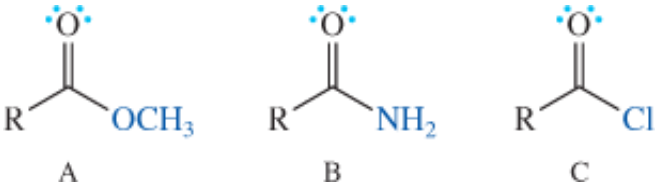
(a)



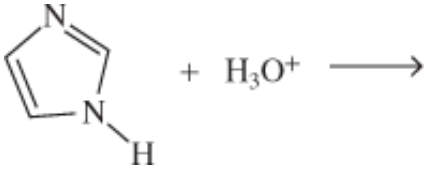
(b)



19.104 In chapter 23 we will see that the reactivity of the following carbonyl compounds is directly proportional to the stability of the leaving group. Using this, rank the order of reactivity of the carbonyl compounds from most reactive to least reactive.



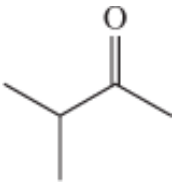
19.105 Predict the product of the following acid–base reaction.



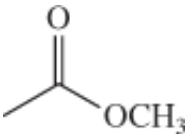
19.106 Amines can act as nucleophiles. For each of the following molecules, circle the atom that would

most likely be attacked by the nitrogen atom of an amine.

(a)



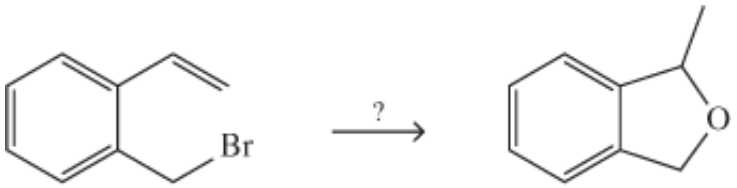
(b)



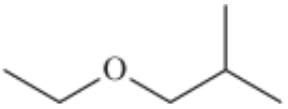
(c)



19.107 How can the following transformation be accomplished? (*Hint:* This is a two-step process involving an alcohol intermediate.)



19.108 Give at least two chemically reasonable syntheses of ethyl 2-methylpropyl ether (ethyl isobutyl ether) using ethanol and methylpropan-1-ol as your starting materials.



ethyl 2-methylpropyl ether

19.109 A pure liquid, *X*, reacts with sodium to produce hydrogen. It also reacts with phosphorus pentachloride to yield compound *Y*, which on treatment with alcoholic potassium hydroxide solution gives pent-1-ene only. What are the structures of *X* and *Y* and the reactions involved?

19.110 When neopentyl alcohol (2,2-dimethylpropan-1-ol), $(CH_3)_3CCH_2OH$, is heated with acid, it is slowly converted into an 85 : 15 mixture of two alkenes with the formula C_5H_{10}. What are these alkenes and how are they formed? What do you think is the major product and why?

19.111 Compound *A*, $C_5H_{10}O$, absorbs 1 mole of hydrogen on catalytic hydrogenation to give *B*. Both *A* and *B* react with sodium metal to produce hydrogen gas. *B*, when treated with phosphorus tribromide, gives *C*, $C_5H_{11}Br$, which when treated with lithium aluminium hydride gives *D*, C_5H_{12}. Compound *A* contains no methyl groups. Draw a cyclic and an acyclic structure for *A*, and explain all reactions involved.

19.112 An unknown compound *X*, C_7H_9N, is only sparingly soluble in water, but dissolves readily in dilute hydrochloric acid. The resulting solution, on treatment with sodium nitrite, does not form an azo dye when added to an alkaline solution of 2-naphthol. However, *X* gives a positive test for a primary amine. Deduce the structure of *X*.

19.113 Acid-catalysed hydration of 1-methylcyclohexene yields two alcohols. The major product does not undergo oxidation, while the minor product does undergo oxidation. Explain.

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KEY TERMS

hydroxyl group
alcohol
aliphatic amine
alkoxy
alkylamines
aniline
aromatic amine
azo compounds
cyclic ether
dehydration
diol
disulfide
ether
glycol
heteroatom
heterocyclic amine
heterocyclic aromatic amine
hydrogen bonding
mercaptan
phenol
pyridinium chlorochromate (PCC)
thiol
triol
zwitterion

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CHAPTER

20 Spectroscopy

We have encountered numerous reactions and compounds in the earlier chapters of this book. Have you ever wondered how chemists know the structure of the compounds used or produced in the various reactions? Remember that chemistry is an experimental science and evidence must be provided to support any claimed results. Until the mid-twentieth century, the determination of the structure of a compound was a difficult and time-consuming exercise. With the advent of modern instrumental techniques, this process has been greatly simplified (but it is *not* as easy as depicted on forensic science TV shows). In this chapter we will discuss the three most commonly used tools: mass spectrometry (MS), infrared (IR) spectroscopy and nuclear magnetic res onance (NMR) spectroscopy. These techniques have the advantages that only a small amount of material is required, complex structures can be readily analysed, and the process is relatively quick. We will introduce some of the features and applications of these techniques that aid in the determination of the structure of molecules.



One of the most powerful diagnostic tools in modern medicine is magnetic resonance imaging (MRI), a technique founded on the principles of NMR spectroscopy. MRI differentiates the different tissues in the body by detecting the hydrogen nuclei of water molecules in the differing environments within those tissues. Analogously, the different environments that nuclei such as hydrogen, carbon or phosphorus reside in give rise to different NMR signals. As a testament to the importance of MRI in modern medicine, the

2003 Nobel Prize in physiology or medicine was awarded to Paul Lauterbur and Sir Peter Mansfield for developing this technique.

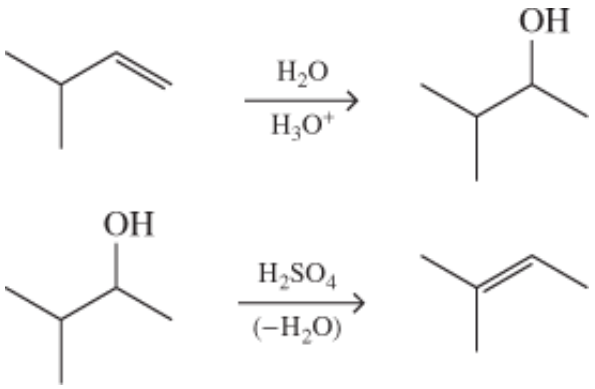
KEY TOPICS

20.1 Tools for determining structure
20.2 Mass spectrometry
20.3 Infrared spectroscopy
20.4 Interpreting infrared spectra
20.5 Nuclear magnetic resonance spectroscopy
20.6 Interpreting NMR spectra
20.7 Other tools for determining structure

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20.1 Tools for Determining Structure

Let us consider two reactions we have studied previously: the hydration of 3-methylbut-1-ene and the dehydration of 3-methylbutan-2-ol.



How do chemists determine that the product formed is an alcohol in the first reaction and an alkene in the second? Furthermore, they need to determine the position of the —OH group and the alkene group. How can this be done? Answering the first question by classical methods (those methods available to the early chemists) is not so hard; there are numerous test-tube tests available to identify an alcohol or alkene group. The second question can also be answered by classical techniques, but this is not so simple. Today, chemists rely almost exclusively on instrumental methods of analysis for structure determination. Although in this chapter we will focus on mass spectrometry (MS), infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy, these are by no means the only tools chemists use. Some other tools used by chemists include X-ray crystallography, UV/visible spectroscopy and electron spin resonance. The general application of these other techniques will be described briefly in section 20.7.

The Index of Hydrogen Deficiency

We can obtain valuable information about the structural formula of an unknown compound by inspecting its molecular formula. In addition to learning the number of each type of atom in a molecule of the compound, we can determine its **index of hydrogen deficiency (IHD)** (also known as **double bond equivalents** or degrees of unsaturation), which is the sum of the number of rings and π bonds in a molecule. For a hydrocarbon, we can determine this quantity by comparing the number of hydrogen atoms in the molecular formula of a compound of unknown structure with the number of hydrogen atoms in a **reference compound** with the same number of carbon atoms and with no rings or π bonds. The molecular formula of the reference hydrocarbon is C_nH_{2n+2}.

$$\text{index of hydrogen deficiency} = \frac{(H_{\text{reference}} - H_{\text{molecule}})}{2}$$

Let us consider, for example, the alkanes (C_nH_{2n+2}), cycloalkanes (C_nH_{2n}), alkenes (C_nH_{2n}) and alkynes (C_nH_{2n-2}) (see chapter 16). These have an IHD of 0, 1, 1 and 2 respectively. The IHD (sometimes called the 'unsaturation index' or the 'double bond equivalents') can be very useful in determining the structure of a molecule. If an unknown compound has an IHD of 0, we know immediately it does not contain any rings or π bonds, while an IHD of 1 would indicate the presence of either a ring or a π bond. Since benzene has an IHD of 4 (one ring and the equivalent of three double bonds), compounds containing a benzene ring must have an IHD ≥ 4; an IHD < 4 indicates that such a ring is not present in the molecule.

Calculating the IHD of Hydrocarbons

Calculate the index of hydrogen deficiency for isopropylbenzene (cumene) with the molecular formula C_9H_{12} and account for this deficiency by reference to the structural formula of the compound.

Analysis

The molecular formula of the reference hydrocarbon with nine carbon atoms is C_9H_{20}.

Solution

The index of hydrogen deficiency of cumene is (20 - 12)/2 = 4 and is accounted for by the three ‘double bonds’ and one ring in cumene.

Is our answer reasonable?

Draw the structure of the compound and count the number of ‘double bonds’ and rings. Benzenoid compounds (compounds based on benzene) must have an IHD of at least 4.

PRACTICE EXERCISE 20.1

Calculate the index of hydrogen deficiency of cyclohexene, C_6H_{10}, and account for this deficiency by reference to the structural formula of the compound.

To determine the molecular formula of a reference compound containing elements other than carbon and hydrogen, write the formula of the reference hydrocarbon, add to it other elements contained in the unknown compound, and make the following adjustments to the number of hydrogen atoms:

1. For each atom of a monovalent group 17 element (F, Cl, Br, I) added to the reference hydrocarbon, subtract one hydrogen atom; halogen substitutes for hydrogen and reduces the number of hydrogen atoms by one per halogen atom. The general formula of an acyclic monochloroalkane, for example, is $C_nH_{2n+1}Cl$.
2. No correction is necessary for the addition of atoms of group 16 elements (O, S, Se) to the reference hydrocarbon. Inserting a divalent group 16 element into a reference hydrocarbon does not change the number of hydrogen atoms.
3. For each atom of a trivalent group 15 element (N and P) added to the formula of the reference hydrocarbon, add one hydrogen atom. Inserting a trivalent group 15 element adds one hydrogen atom to the molecular formula of the reference compound. The general molecular formula for an acyclic alkylamine, for example, is $C_nH_{2n+3}N$.

Calculating the IHD

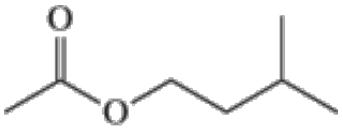
Isopentyl acetate (3-methylbutyl acetate), a compound with a banana-like odour, is a component of the alarm pheromone of honey bees. Its molecular formula is $C_7H_{14}O_2$. Calculate the index of hydrogen deficiency of this compound.

Analysis

The molecular formula of the reference hydrocarbon with seven carbon atoms is C_7H_{16}. Adding oxygen atoms to this formula does not change the number of hydrogen atoms.

Solution

The molecular formula of the reference compound is $C_7H_{16}O_2$, and the index of hydrogen deficiency is (16 - 14)/2 = 1, indicating either one ring or one π bond. As can be seen from the structural formula of isopentyl acetate, it contains one π bond, the carbon–oxygen double bond.



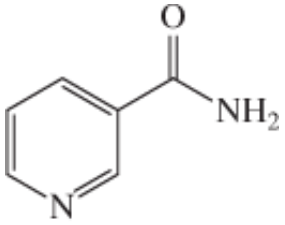
isopentyl acetate

Is our answer reasonable?

Draw the structure of the compound and count the number of double bonds and rings.

PRACTICE EXERCISE 20.2

The index of hydrogen deficiency of nicotinamide is 5. Account for this value by reference to the structural formula of nicotinamide:



nicotinamide

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20.2 Mass Spectrometry

In chapter 10 you learned that the colligative properties of solutions can be used to determine the molar mass of the dissolved solutes. An alternative and more widely used method is **mass spectrometry**. This technique allows us to determine the mass of molecules and fragments of molecules. The three key steps in mass spectrometry are (1) ionisation of the sample, (2) separ ation of the resulting ions and (3) detection of the ions. The fundamental principle is that, when a molecule is ionised, it can be accelerated through an electric or magnetic field where ions of different mass are deflected to different extents. The ions are then counted by the detector and their abundance is plotted on a graph against their mass to charge ratios (*m*/*z*). A schematic representation of a mass spectrometer is given in figure 20.1.

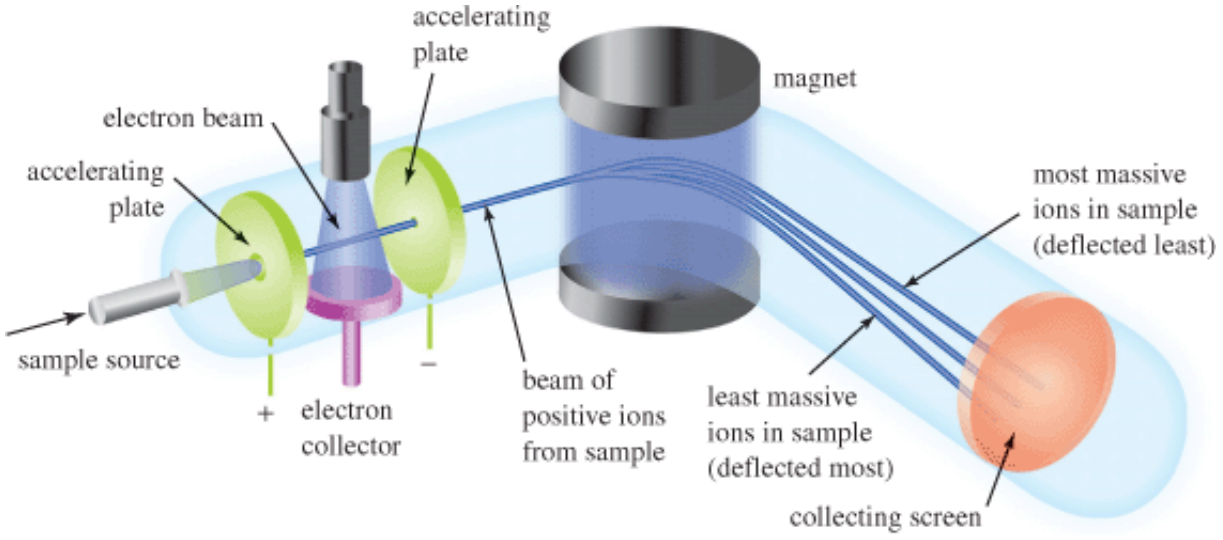


FIGURE 20.1 Schematic representation of one type of mass spectrometer. In the sample source, an electron beam ionises gas molecules into positively charged ions. The ions are accelerated and then deflected by a magnet. Each fragment follows a trajectory that depends on its mass to charge ratio (*m*/*z*). Cameron Kepert

When a sample is introduced into a mass spectrometer, it is bombarded with a stream of highenergy electrons, which causes some of the molecules to be ionised by the ejection of an electron. This produces ions that are **radical cations** (‘radical’ because there is an unpaired electron and ‘cation’ because of the positive charge). These ions are termed **molecular ions** (or parent ions) and have essentially the same mass as the original molecules because the mass of the lost electron is negligible.

$$\underset{\text{molecule}}{M} + \underset{\substack{\text{high}\\\text{energy}\\\text{electron}}}{e^-} \rightarrow \underset{\substack{\text{molecular}\\\text{ion}}}{(M)^{+\bullet}} + 2e^-$$

The peak due to the molecular ion can be used to quickly differentiate between molecules of similar mass (usually the one with the highest *m*/*z* value). Consider, for example, the problem of differentiating between samples of hexane and cyclohexane. Mass spectrometry will allow identification because they have different molecular masses (86 and 84, respectively) as shown in figure 20.2. In chapter 1, we defined atomic mass as the mass of one atom, measured in amu. We can do the same for a single molecule. Thus, molecular mass is the mass of one molecule, measured in amu.

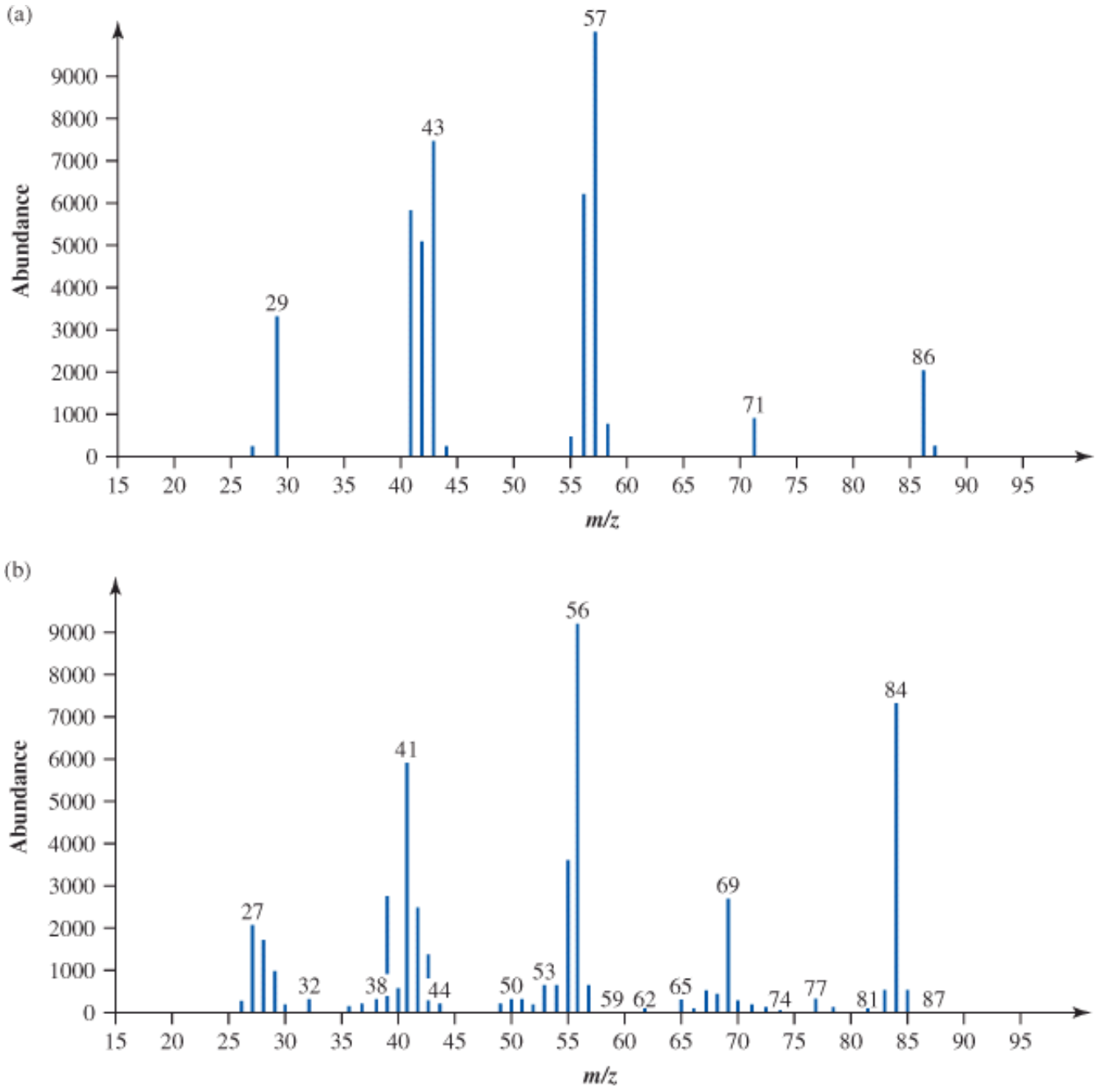


FIGURE 20.2 The mass spectra of hexane and cyclohexane:
(a) The molecular ion signal at *m/z* 86 indicates that this spectrum is of hexane,
(b) while *m/z* 84 indicates cyclohexane. The other peaks in the spectra are due to fragmentation products (see p. 868). Cameron Kepert

chemistry Research

Identification and Structural Analysis of Biomolecules

Professor Mark A Buntine, Curtin University

Mass spectrometry is an extremely powerful tool for determining the mass of molecules and the sequence in which various functional groups are joined together within a molecule. Laser spectroscopy, through the excitation of electrons (electronic spectroscopy) or the promotion of vibrations (vibrational spectroscopy), is an effective way of learning about the shape of molecules and the strength of the various bonds that hold the atoms together within a molecule. When the two techniques are combined, chemists can study molecular shape and

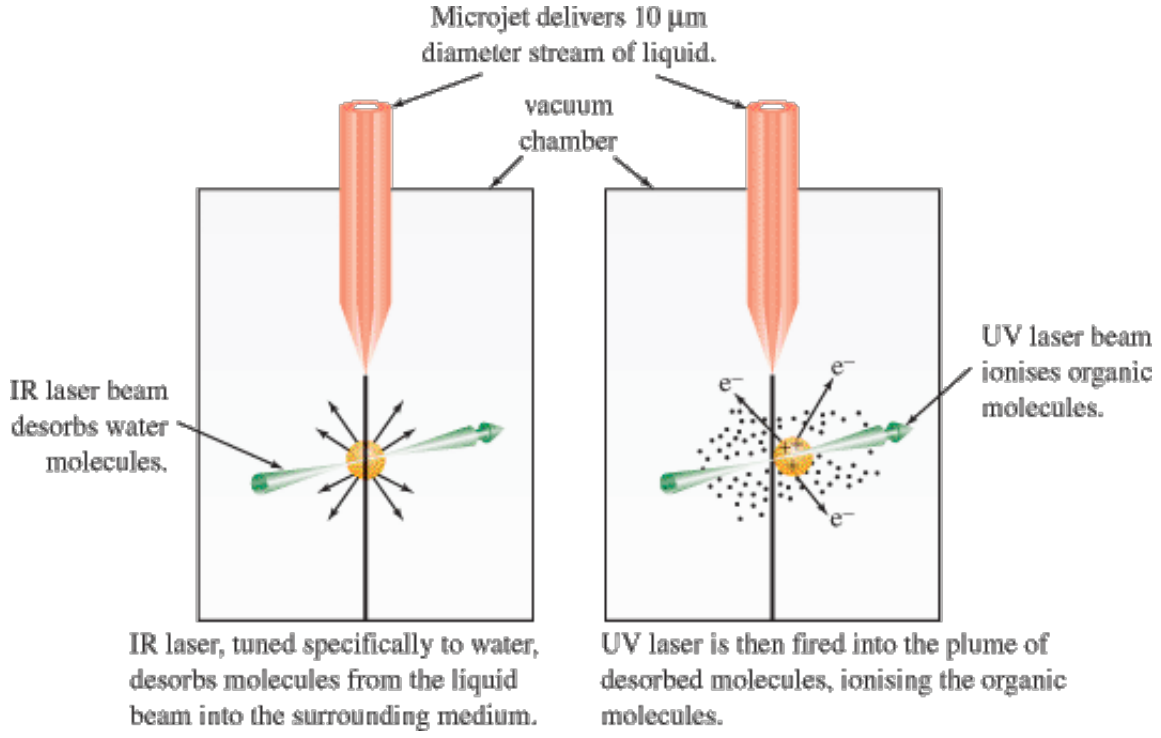
function with great sensitivity and accuracy.

However, mass spectrometry and the highest resolution laser spectroscopy require molecules to be in the gas phase. The ions created in a mass spectrometer would react very quickly if they were not isolated in the collision-free conditions of a vacuum chamber. In solution, solute–solvent and other intermolecular interactions blur much of the detail provided by laser spectroscopy of gaseous molecules. One common way that chemists have introduced molecules into the gas phase for study by these techniques has been to heat them to obtain the sample vapour. However, heating larger molecules, such as those of biological interest, usually causes them to decompose.

It is a major challenge for mass spectrometry to develop methods to introduce nonvolatile molecules into the gas phase. Two of the best approaches to date are electrospray ionisation (ESI) and matrix-assisted laser desorption and ionisation (MALDI). The developers of these techniques, John Fenn (for ESI) and Koichi Tanaka (for MALDI) shared the Nobel Prize in chemistry in 2002 for their contributions to the field.

ESI and MALDI do suffer from some limitations, however. Often salts or sugars need to be mixed with the biological molecules of interest to help get them into the gas phase. These additives can significantly alter the normal intermolecular bonding environments, thereby changing their molecular shape.

Chemists at Curtin University are researching the use of *liquid microjets* as an alternative large-molecule introduction technology that does not require any additives that might affect molecular shape. A very thin stream of liquid (10 micrometres in diameter — approximately the thickness of a human hair) is injected directly into a vacuum chamber. A pulsed infrared laser specifically tuned to an absorption band of the water solvent rapidly heats the liquid sample and thereby ejects molecules into the gas phase. Following this, a pulsed ultraviolet laser removes an electron from the molecule, creating an ion detectable by mass spectrometric analysis. A schematic of this technique is shown below. Measuring the efficiency with which a biomolecule is ionised as a function of the UV laser photon energy gives details of its molecular shape. Unambiguous mass identification is obtained by the mass spectrometric detection of the ions.



One significant application of the liquid microjet technique being studied by the Perth researchers is an investigation of the shape of biomolecules, which often controls their biological activity and function. It is known that the bonds that form between biomolecules and the water solvent control this shape. However, very little is known about the strength and structure of these bonds at different sites around the biomolecule. Some experiments have informed us about the strength of the bonds; others have told us where the bonds occur. The Western Australian team is gathering both pieces of information in a single experiment, allowing a better understanding of biochemical interactions.

WORKED EXAMPLE 20.3

Determining Molecular Formulae from Mass Spectra

The mass spectrum of an unknown alkane showed a molecular ion peak at *m*/*z* 128. What is the molecular formula of this compound?

Analysis

As this is an alkane we know it contains only C and H and it has the general formula C_nH_{2n+2}.

Solution

Substituting our known values into C_nH_{2n+2} gives the equation $12 \times n + [1 \times (2n + 2)] = 128$. Solving for n gives $n = 9$. Therefore, the molecular formula of the compound is C_9H_{20}.

Is our answer reasonable?

You should check that the molecular mass of C_9H_{20} is 128.

PRACTICE EXERCISE 20.3

(a) The mass spectrum of an unknown alkane showed a molecular ion peak at *m*/*z* 198. What is the molecular formula of this compound?

(b) The mass spectrum of an unknown cycloalkane showed a molecular ion peak at *m*/*z* 140. What is the molecular formula of this compound?

When ionising the sample in a mass spectrometer, many of the resulting molecular ions fragment to give

cations of lower mass (sometimes called daughter ions) and neutral radicals (which are not detected as they are not charged). These fragment cations are sorted according to their mass to charge ratios (*m*/*z*). As the charge is almost always +1 when molecules are ionised in this way, *m*/*z* is equivalent to the mass of the ion. Analysis of these fragmentation patterns can be used to help determine the structure of a compound; however, details of this process will not be covered here. Instead, we will focus on the use of mass spectrometry to determine molar masses and molecular formulae.

Isotopes in Mass Spectrometry

Upon inspection of the spectra in figure 20.2, you will notice that the *m*/*z* values for all the peaks are given as whole numbers. This is sufficient for most purposes. However, it does not allow us to differentiate between molecules with the same mass (when quoted in whole numbers) but different formulae. The accurate mass of the molecular ion, and consequently the molecular formula, of a compound can be determined by using a technique called **high resolution mass spectrometry**. In this process, the mass to charge ratio of ions (including the molecular ion) is measured with a high degree of precision (usually to four decimal places). For example, consider the four compounds listed in table 20.1, all of which have different molecular formulae but the same nominal molecular mass. You will also notice that the molecular mass and the accurate mass are not the same. This is because, in determining the accurate mass, we use the accurate mass of the most abundant isotope of each element, rather than the atomic mass of the element. Table 20.2 lists some accurate masses for the elements commonly encountered in organic chemistry, along with their natural abundances.

TABLE 20.1 Comparison of the masses of four compounds with molecular mass of 88

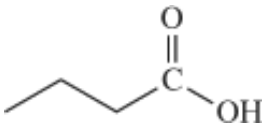
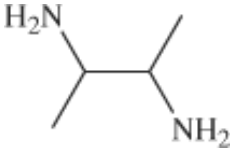
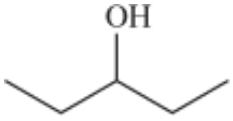
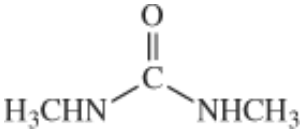
Name	Structure	Molecular formula	Molecular mass (amu)	Accurate mass (amu)
butanoic acid		$C_4H_8O_2$	88.11	88.0524
butane-2,3-diamine		$C_4H_{12}N_2$	88.15	88.1001
pentan-3-ol		$C_5H_{12}O$	88.15	88.0888
N,*N*′-dimethylurea		$C_3H_8N_2O$	88.11	88.0637

TABLE 20.2 Isotope abundance and accurate mass of selected elements that are commonly encountered in organic chemistry

Element	Atomic mass (amu)	Isotope	% Natural abundance	Accurate mass (amu)
hydrogen	1.0079	^{1}H	99.985	1.0078
		^{2}H	0.015	2.0140
carbon	12.011	^{12}C	98.89	12.0000
		^{13}C	1.11	13.0034
nitrogen	14.0067	^{14}N	99.64	14.0031

		^{15}N	0.36	15.0001
oxygen	15.9994	^{16}O	99.76	15.9949
		^{17}O	0.04	16.9991
		^{18}O	0.20	17.9992
phosphorus	30.9738	^{31}P	100.00	30.9738
sulfur	32.064	^{32}S	95.00	31.9721
		^{33}S	0.76	32.9715
		^{34}S	4.22	33.9679
		^{36}S	0.02	35.9671
fluorine	18.9984	^{19}F	100.00	18.9984
chlorine	35.453	^{35}Cl	75.77	34.9688
		^{37}Cl	24.23	36.9659
bromine	79.904	^{79}Br	50.69	78.9183
		^{81}Br	49.31	80.9163
iodine	126.9044	^{127}I	100.00	126.9044

WORKED EXAMPLE 20.4

Determining Molecular Formulae from High Resolution Mass Spectra

Which of the molecular formulae C_7H_{16}, $C_6H_{14}N$, $C_5H_{12}N_2$, $C_6H_{12}O$ and $C_5H_8O_2$ corresponds to an accurate mass of *m*/*z* 100.0888?

Analysis

As a starting point, you will notice all of these molecular formulae have a nominal molecular mass of 100. To solve this problem, simply determine the accurate mass corresponding to each formula using the accurate mass value for the most abundant isotope of each element.

Solution

$C_6H_{12}O$

Is our answer reasonable?

Double-check your calculations for the accurate mass. It is possible to work backwards from an accurate mass to determine the molecular formula, but this requires a computer program (or extensive trial and error).

PRACTICE EXERCISE 20.4

Which of the molecular formulae C_8H_{18}, $C_7H_{14}O$, $C_7H_{16}N$, $C_6H_{14}N_2$, $C_6H_{12}NO$ and $C_6H_{10}O_2$ corresponds to an accurate mass of 114.1158?

You may have noticed that, of the elements listed in table 20.2, many had one isotope with a natural abundance of more than 99%. In the other cases, we can use the isotope abundance to help determine the presence of particular elements. Bromine is particularly easy to recognise by the presence of two signals of equal intensity and a mass difference of 2, due to the ^{79}Br (M^+ ion) and ^{81}Br [$(M + 2)^+$ ion] isotopes, which are nearly equally abundant. The presence of a chlorine atom in a molecule will give rise to an $(M + 2)^+$ signal one-third the height of the M^+ signal (the ratio of ^{35}Cl to ^{37}Cl is 3 : 1). Isotope distribution has also been used to help identify many metallic and organometallic materials in the environment. For example, the pollutants lead, mercury and tin have four, seven and ten natural isotopes respectively.

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20.3 Infrared Spectroscopy

Spectroscopic techniques, including infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy, involve the interaction of molecules with electromagnetic radiation. Thus, to understand the fundamentals of spectroscopy, we must first review some of the fundamentals of electromagnetic radiation.

Electromagnetic Radiation

In section 4.2, we studied the characteristics of light, a form of electromagnetic radiation, and we will provide only a summary here. Gamma rays, X-rays, ultraviolet light, visible light, **infrared radiation**, microwaves and radio waves are all examples of **electromagnetic radiation** and part of the electromagnetic spectrum. Because electromagnetic radiation behaves as a wave travelling at the speed of light, it is described in terms of its wavelength and frequency. Figure 20.3 summarises the wavelengths and frequencies of some regions of the electromagnetic spectrum.

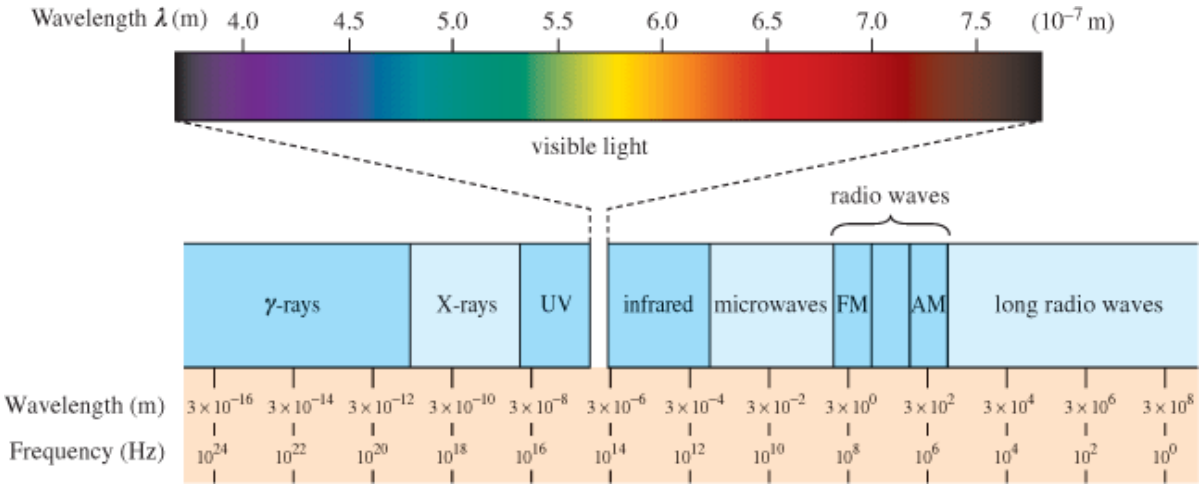
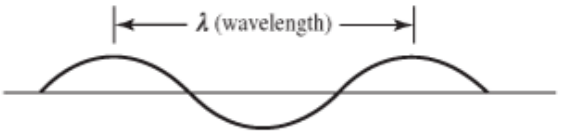


FIGURE 20.3 Wavelength and frequency of some regions of the electromagnetic spectrum.

Wavelength is the distance between any two consecutive equivalent points on the wave (for example, crest to crest). Wavelength is given the symbol λ (Greek lowercase *lambda*) and is usually expressed in the SI base unit of metres. Other derived units commonly used to express wavelength are given in table 20.3.

TABLE 20.3 Common units used to express wavelength (λ)

Unit	Relation to metre
metre (m)	
millimetre (mm)	1 mm = 10^{-3} m
micrometre (μm)	1 μm = 10^{-6} m
nanometre (nm)	1 nm = 10^{-9} m



The **frequency** of a wave is the number of full cycles of the wave that pass a given point in a second. Frequency is given the symbol ν (Greek lowercase *nu*) and is reported in s^{-1}, also called **hertz (Hz)**. Wavelength and frequency are inversely proportional, and we can calculate one from the other using the relationship:

$$c = \nu\lambda$$

where ν is frequency in s^{-1}, c is the velocity of light (2.998×10^8 m s^{-1}), and λ is the wavelength in metres.

An alternative way to describe electromagnetic radiation is in terms of particles. We call these particles photons. The energy of a photon and the frequency of radiation are related by the equation:

$$E = h\nu = h\frac{c}{\lambda}$$

where E is the energy in kJ and h is Planck's constant, 6.626×10^{-34} J s. This equation tells us that high-energy radiation corresponds to short wavelengths, and vice versa. Thus, ultraviolet light (higher energy) has a shorter wavelength

(approximately 10^{-7} m) than infrared radiation (lower energy), which has a wavelength of approximately 10^{-5} m.

The Vibrational Infrared Spectrum

As we discussed in chapter 5, molecules are flexible structures with atoms and groups of atoms able to rotate around covalent single bonds. Covalent bonds stretch and bend just as if the atoms were joined by flexible springs. We know from experimental observations and from theories of molecular structure that all energy changes within a molecule are quantised; that is, they are subdivided into small, but well-defined, increments. For example, vibrations of bonds within molecules can undergo transitions only between allowed vibrational energy levels.

We can cause atoms or molecules to undergo a transition from energy state E_1 to a higher energy state E_2 by irradiating them with electromagnetic radiation corresponding to the energy difference between states E_1 and E_2 as illustrated schematically in figure 20.4. When these atoms or mol ecules return to the ground state, an equivalent amount of energy is emitted. When a sample is irradiated with electromagnetic radiation of various wavelengths, it absorbs energy of particular wavelengths, while the wavelengths not absorbed simply pass through or are reflected from the sample unchanged. In infrared (IR) spectroscopy (figure 20.5), when we irradiate a sample with infrared radiation, this radiation is absorbed when its energy (frequency) is exactly equal to the energy required to excite the molecules to a higher energy state. Because different functional groups have different bond strengths, the energy required to bring about these transitions varies from one functional group to another. Thus, in infrared spectroscopy, we detect functional groups by the vibrations of their bonds.

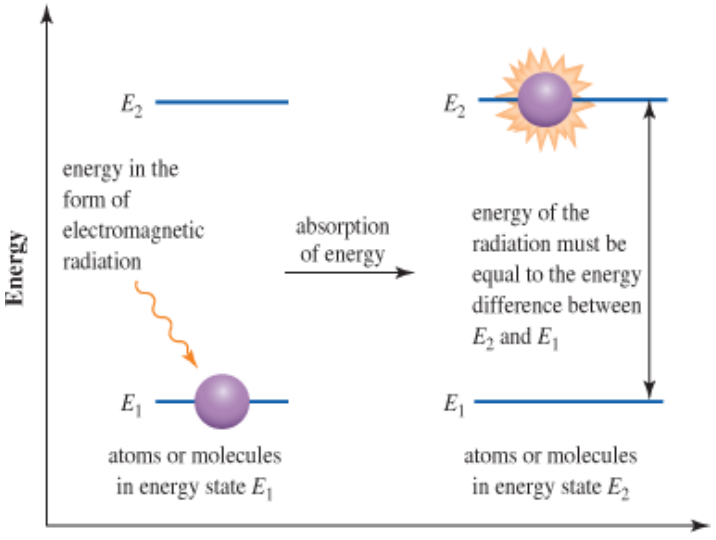


FIGURE 20.4 Absorption of energy in the form of electromagnetic radiation excites atoms or molecules in energy state E_1 to a higher energy state E_2.

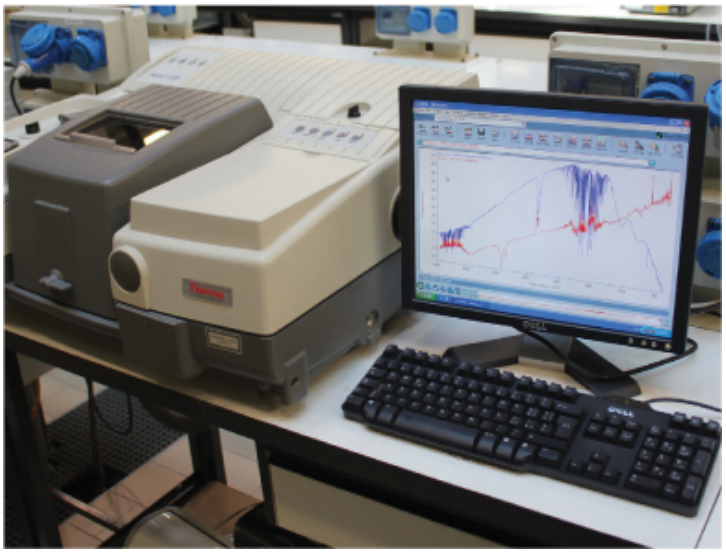


FIGURE 20.5 An infrared spectrophotometer. Spectra are shown on the monitor.

The infrared region of the electromagnetic spectrum (figure 20.3) covers the range of wavelengths from 7.8×10^{-7} m (just longer than the visible region) to 2.0×10^{-3} m (just shorter than the microwave region). In chemistry, however, we routinely use only the portion that extends from 2.5×10^{-6} to 2.5×10^{-5} m. This region is often called the **vibrational infrared** region and we commonly refer to radiation in this region by its **wavenumber** ($\tilde{\nu}$), the number of waves per centimetre. To convert wavelength to wavenumber, simply calculate the reciprocal of the wavelength (in cm). Expressed in wavenumbers, the vibrational region of the infrared spectrum extends from 4000 to 400 cm^{-1} (the unit cm^{-1} is read 'reciprocal centimetre'). An advantage of using wavenumbers is that they are directly proportional to energy; the higher the wavenumber, the higher the energy of radiation.

Figure 20.6 shows an infrared spectrum of aspirin. The horizontal axis is calibrated in wave-numbers (cm^{-1}). The wavenumber scale is often divided into two or more linear regions. For all spectra reproduced in this text, it is divided into three linear regions: 4000 –2200 cm^{-1}, 2200 -1000 cm^{-1} and 1000 - 450 cm^{-1}. The vertical axis measures transmittance, with 100% transmittance at the top and 0% transmittance at the bottom. Thus, the baseline for an infrared spectrum (100% transmittance of radiation through the sample = 0% absorption) is at the top of the chart, and the absorption of radiation corresponds to a trough or valley. Strange as it may seem, we commonly refer to infrared absorptions as peaks, even though they are actually troughs. They are also called 'bands' or signals. If absorption of light is used on the vertical axis instead of transmittance, the signals are actually peaks.

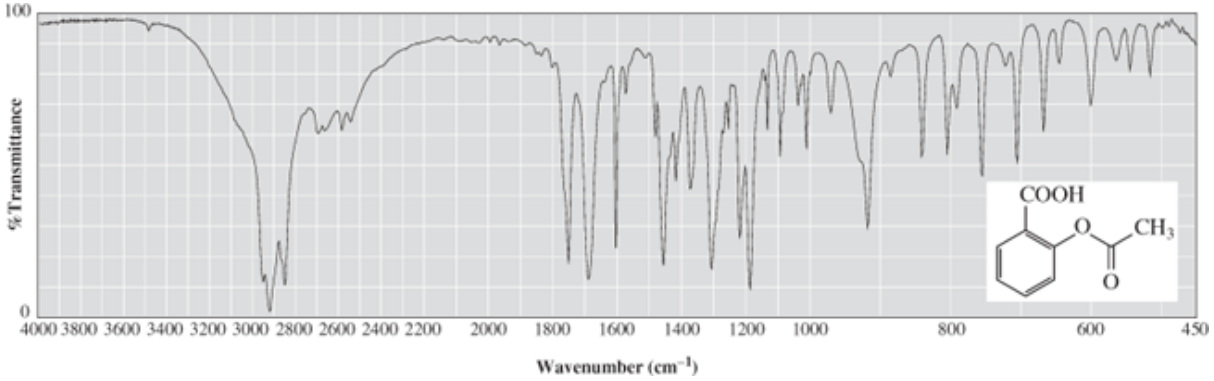


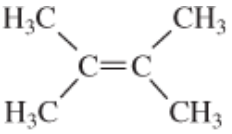
FIGURE 20.6 Infrared spectrum of aspirin.

Molecular Vibrations

Atoms joined by covalent bonds are not permanently fixed in one position but, instead, undergo continuous vibrations relative to each other. The energies associated with transitions between vibrational energy levels in most covalent molecules range from 8 to 40 kJ mol^{-1}. Such transitions can be induced by the absorption of radiation in the infrared region of the electromagnetic spectrum.

For molecules to absorb infrared radiation, the bonds undergoing vibration must be polar, and their vibration must cause a periodic change in the bond dipole; the greater the polarity of the bonds, the more intense is the absorption. Any vibration that meets these criteria is said to be **infrared active**. Covalent bonds in homonuclear diatomic molecules, such as H_2 and Br_2, and some carbon–carbon double or triple bonds in symmetrical alkenes and alkynes do not absorb infrared radiation because they are not polar bonds. The multiple bonds in the following two compounds, for example, do not have a dipole moment so are not infrared active.

Neither the double nor the triple bond in these compounds is infrared active.



2,3-dimethylbut-2-ene



but-2-yne

For nonlinear molecules containing *n* atoms, 3*n* - 6 allowed fundamental vibrations exist. For a compound as simple as ethanol, CH_3CH_2OH, there are 21 fundamental vibrations, and for hexanoic acid, $CH_3(CH_2)_4COOH$, there are 54. Thus, even for relatively simple molecules, a large number of vibrational energy levels exist, and the patterns of energy absorption for these and larger molecules are quite complex.

The simplest vibrational motions in molecules giving rise to the absorption of infrared radiation are **stretching** and **bending** motions. The fundamental stretching and bending vibrations for a methylene group are illustrated in figure 20.7.

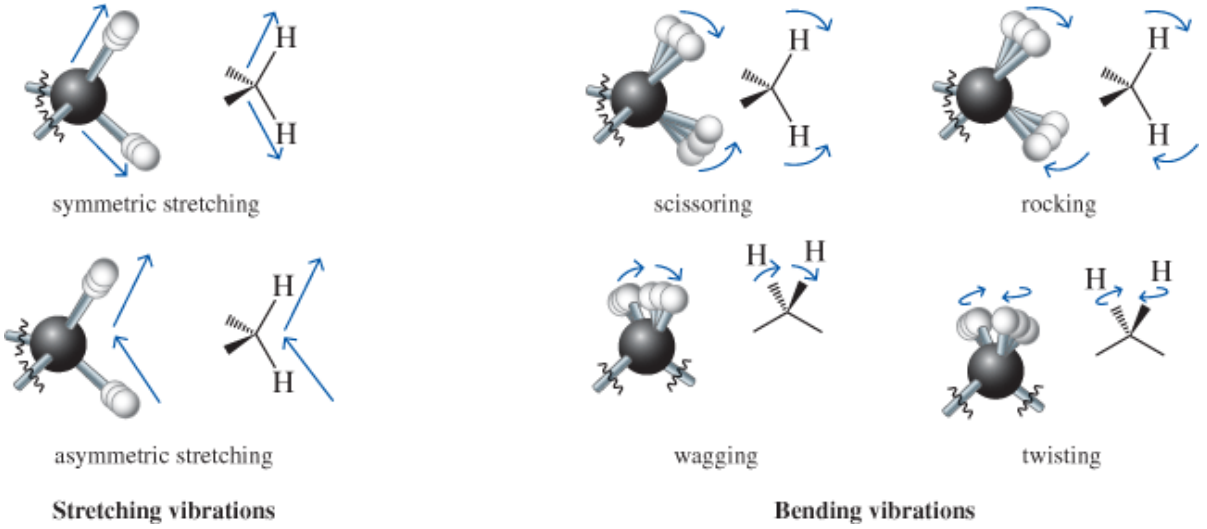


FIGURE 20.7 Fundamental modes of vibration for a methylene group.

To someone skilled in the interpretation of infrared spectra, absorption patterns can yield an enormous amount of information about chemical structure. The value of infrared spectra for us, however, is that we can use them to determine the presence or absence of particular functional groups. Carbonyl groups, for example, typically show strong absorption at approximately 1630 -1800 cm^{-1} m. The position of absorption for a particular carbonyl group depends principally on the functional group to which it belongs (aldehyde, ketone, carboxylic acid, anhydride, acid chloride, ester or amide). Other factors influencing the frequency of absorption include ring strain (if the carbonyl group is part of a ring) and conjugation (having an alkene or aromatic ring immediately adjacent to the carbonyl group).

Correlation Tables

Data on absorption patterns of selected functional groups are collected in tables called **correlation tables** Table 20.4 gives the characteristic infrared vibrational frequencies for the types of bonds and functional groups we deal with most often. Appendix H contains a cumulative correlation table. In these tables, we refer to the intensity of a particular absorption as strong (s), medium (m) or weak (w).

TABLE 20.4 Characteristic IR vibrational frequencies of selected functional groups

Bond	Frequency (cm^{-1})	Intensity
O—H	3200–3500	strong and broad
N—H	3100–3500	medium

C—H	2850–3100	medium to strong
C≡C	2100–2260	weak
C=O	1630–1800	strong
C=C	1600–1680	weak
C—O	1050–1250	strong

In general, we will pay most attention to the region from 3650 to 1500 cm^{-1}, where the characteristic stretching vibrations for most functional groups are found. Vibrations in the region from 1500 to 400 cm^{-1} can arise from phenomena such as combinations of two or more bands or harmonics of fundamental absorption bands. Such vibrations are much more complex and far more difficult to analyse. Because even slight variations in molecular structure lead to differences in absorption patterns in this region, it is often called the **fingerprint region**. If two compounds have even slightly different structures, the differences in their infrared spectra are most clearly discernible in the fingerprint region.

WORKED EXAMPLE 20.5

Identifying Functional Groups Using IR Spectroscopy

Determine the functional group that is most likely present if a compound gives an IR signal at:

(a) 1705 cm^{-1}

(b) 2150 cm^{-1}.

Analysis

Check the correlation tables for signals in the required regions. In this example, table 20.4 provides sufficient information.

Solution

(a) A carbonyl C=O group (signals between 1630 and 1800 cm^{-1})

(b) An alkyne C≡C group (signals between 2100 and 2260 cm^{-1})

Is our answer reasonable?

Check that the signal falls within the required range. Check also if there is more than one possibility.

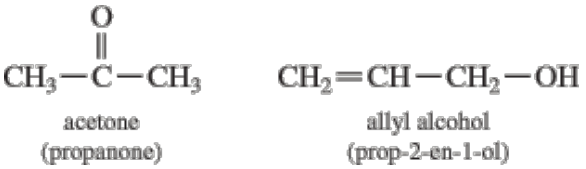
PRACTICE EXERCISE 20.5

A compound gives a strong, very broad IR signal in the region from 3200 to 3500 cm^{-1} and a strong signal at 1715 cm^{-1}. Which functional group accounts for both of these signals?

WORKED EXAMPLE 20.6

Distinguishing Between Isomers Using IR Spectroscopy

Acetone (propanone) and allyl alcohol (prop-2-en-1-ol) are constitutional isomers. Show how these may be distinguished by IR spectroscopy.



Analysis

Firstly, you need to identify the key functional group differences: in this case, a ketone (C═O) in acetone and an alcohol (OH) and alkene (C≡C) in allyl alcohol. Now consult table 20.4.

Solution

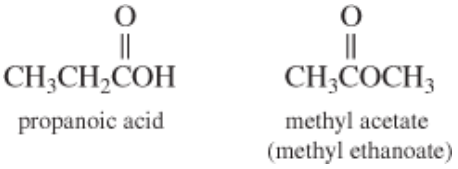
Only acetone gives a strong signal in the C═O stretching region, 1630 -1800 cm^{-1}. Alternatively, only allyl alcohol gives a strong signal in the O—H stretching region, 3200–3500 cm^{-1}.

Is our answer reasonable?

Check that you have chosen the appropriate strong signals (alkenes often display weak signals and are, therefore, not always a good choice).

PRACTICE EXERCISE 20.6

Propanoic acid and methyl acetate are constitutional isomers. Show how these may be distinguished by IR spectroscopy.



chemistry Research

The spectroscopy of fingerprints

Associate Professor Simon W Lewis, Curtin University

Fingermarks are the most widely used method of personal identification in law enforcement. Their presence at a crime scene or on an object is instrumental in connecting individuals to a case; they are a prime example of Locard's exchange principle that ‘every contact leaves a trace’. The most common form of these are latent (hidden) fingermarks, and successful recovery from a scene or an object relies upon their detection. On deposition, the fingermark can be considered as a mixture of the natural secretions present on the skin, an emulsion of waxes, oils and aqueous components, and whatever surface contaminants may be present. Detection methods target differences between the latent fingermark and the surface upon which it is laid and are based either on physical attraction or a chemical reaction. For example, latent fingermarks on paper can be detected by treating with the chemical 1,2-indanedione, which reacts with the amino acids present in the latent fingermark to give pink impressions, which are luminescent when illuminated with blue-green light (505 nm) and viewed through orange goggles (see figure 20.8).

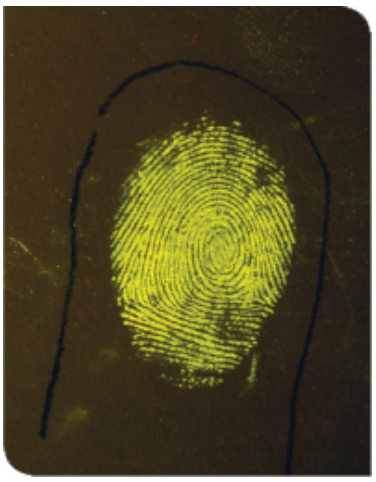


FIGURE 20.8 A1,2-indanedione treated fingermark viewed in photoluminescence mode. Simon Lewis

The successful development of latent fingermarks relies heavily upon the chemistry of the latent fingermark residue. With time, the chemical nature of the latent deposit will change due to evaporation of volatile components, bacterial action and oxidation. The rate of change will depend on the initial chemical composition of the residue and the environmental conditions. This ageing process can have a significant effect on the successful development of a latent fingermark. Despite these issues, most fingermark detection techniques have been developed on the basis of knowledge of the components of human skin secretions, without regard for the potential for ageing of the print. In addition, there is currently no reliable technique for estimating the age of a latent fingermark.

The ability to make future improvements to current fingermark detection methods and the development of new approaches to the visualisation of latent fingermarks depends critically upon a greater understanding of the chemistry of the fingermark residue. The majority of studies on the composition of skin secretions have been for medical purposes and have focused on the collection of the secretions from the body rather than from the latent fingermark deposit. Such studies therefore produce results that are not representative of a true latent fingermark. More recent studies have looked at the forensic aspects of fingermark chemistry. However, these approaches often require the removal of the latent fingermark deposit from its substrate, thus destroying its context and also preventing ageing studies on the latent mark.

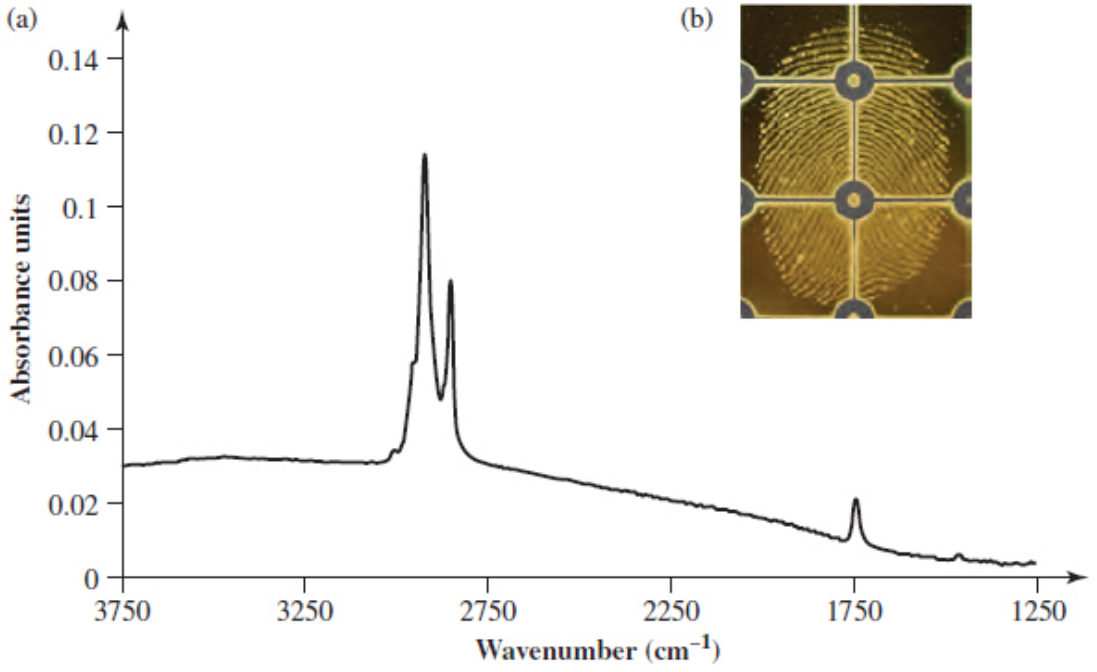


FIGURE 20.9 (a) Typical synchrotron IR spectrum of a latent fingermark; (b) latent fingermark on gold-plated glass. Simon Lewis

Researchers at Curtin University, in collaboration with scientists at the infra-red (IR) beamline at the Australian Synchrotron, have been using synchrotron IR microscopy to investigate the chemistry of latent fingermarks and how this changes with time. Fingermarks from donors of different age and gender were deposited on gold-plated glass and subjected to IR analysis at regular intervals over a period of 12 months. The synchrotron source is much brighter than conventional IR spectrometers, and this significantly enhances the signal-to-noise ratios and thereby reduces the time required to produce the spectra. In addition, the synchrotron also provides much higher spatial resolution; this enables skin cell debris to be avoided by selecting very small areas for analysis. This approach has been very useful for monitoring the variation in lipid content of deposited latent fingermarks.

Future research will include investigation of the potential of mass spectral imaging in combination with IR data to obtain a better understanding of the fundamental chemistry of latent fingermark chemistry. This will provide a platform for the development of the next generation of latent fingermark detection methods. Observed changes in chemical composition over time and under different environmental conditions will also provide a valuable insight into the fingermark ageing process. In addition, the knowledge gained will provide a step towards the development of a ‘standard’ latent fingermark, vital for establishing the effectiveness of new detection methods and for quality assurance and quality control in fingermark detection.

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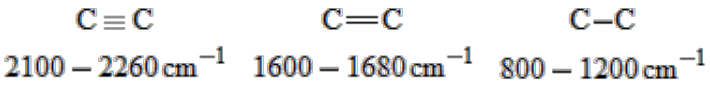
20.4 Interpreting Infrared Spectra

Interpreting spectroscopic data is a skill that is easy to acquire through practice and exposure to examples. An IR spectrum will reveal not only the functional groups that are present in a sample, but also those that can be excluded from consideration. Often, we can determine the structure of a compound solely from the data in the spectrum of the compound. At other times, we may need additional information, such as the molecular formula of the compound or knowledge of the reactions used to synthesise the molecule. In this section, we will see specific examples of IR spectra for characteristic functional groups. Familiarising yourself with them will help you to master the technique of spectral interpretation.

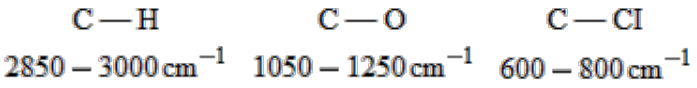
General Rules for Interpretation of IR Spectra

Below is a set of general rules and guidelines for the analysis and interpretation of IR spectra.

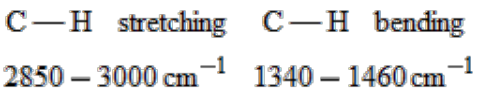
- The stronger the bond, the higher is the vibrational frequency.



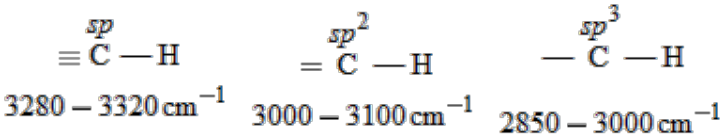
- The C—Y stretching frequency decreases with an increase in mass of Y.



- Bending usually occurs at a lower frequency than stretching.



- Hybridisation effects cause the stretching frequency to increase as we move from sp^3 to sp



Alkanes

Infrared spectra of alkanes are usually simple, with few signals, the most common of which are given in table 20.5.

TABLE 20.5 Characteristic IR signals of alkanes, alkenes and alkynes

Hydrocarbon	Vibration	Frequency (cm^{-1})	Intensity
Alkane			
C—H	stretching	2850–3000	strong
CH_2	bending	1450	medium
CH_3	bending	1375 and 1450	weak to medium
Alkene			
C—H	stretching	3000–3100	weak to medium
C=C	stretching	1600–1680	weak to medium
Alkyne			
C—H	stretching	3300	medium to strong
C≡C	stretching	2100–2260	weak to medium

Figure 20.10 shows an infrared spectrum of decane. The strong signal with multiple splittings between 2850 and 3000 cm^{-1} is characteristic of alkane C—H stretching. The C—H signal is strong in this spectrum because there are so many C—H bonds and no other functional groups. The other prominent signals in the spectrum are those due to methylene bending at 1465 cm^{-1} and methyl bending at 1380 cm^{-1}. Because alkane CH, CH_2 and CH_3 groups are present in many organic compounds, these peaks are among the most commonly encountered in infrared spectroscopy, and consequently they are usually not very useful as a diagnostic tool.

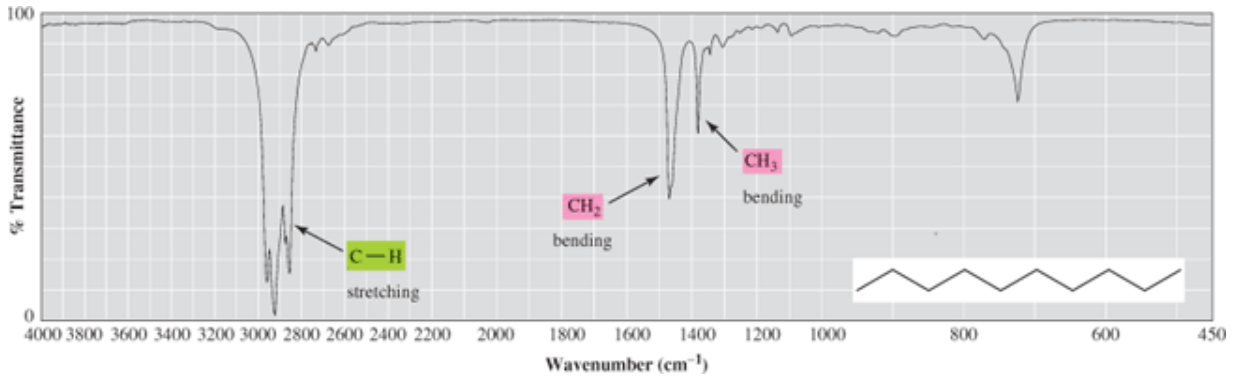


FIGURE 20.10 Infrared spectrum of decane.

Alkenes

An easily recognised alkene signal is the stretching band for the vinylic C—H in C═C—H at a slightly higher frequency (at 3000 –3100 cm^{-1}) than the alkane C—H frequency (vinylic hydrogen atoms are those on a carbon atom of a carbon–carbon double bond). Also characteristic of alkenes is the C═C stretching band at 1600–1680 cm^{-1}. This vibration, however, is often weak and diffi-cult to observe. Signals for both C—H stretching in vinylic C═C—H and C═C stretching can be seen in the infrared spectrum of cyclopentene (figure 20.11). Also visible are the signals for aliphatic C—H stretching near 2900 cm^{-1} and the methylene bending near 1440 cm^{-1}.

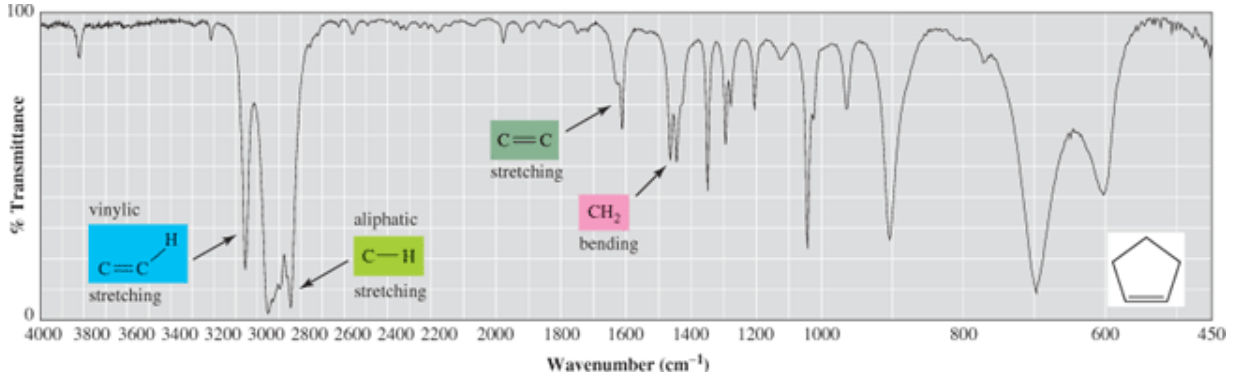


FIGURE 20.11 Infrared spectrum of cyclopentene.

Alkynes

The IR spectra of terminal alkynes exhibit a strong signal at 3300 cm^{-1} due to C—H stretching in C≡C—H. This absorption band is absent in internal alkynes because the triple bond is not bonded to a proton (terminal alkynes have the C≡C group at the end of the chain; in internal alkynes, the C≡C group is not at the end of the chain). Alkynes give a weak signal between 2100 –2260 cm^{-1}, due to C≡C stretching. The signal for this stretching is shown clearly in the spectrum of oct-1-yne (figure 20.12) but is absent in oct-4-yne.

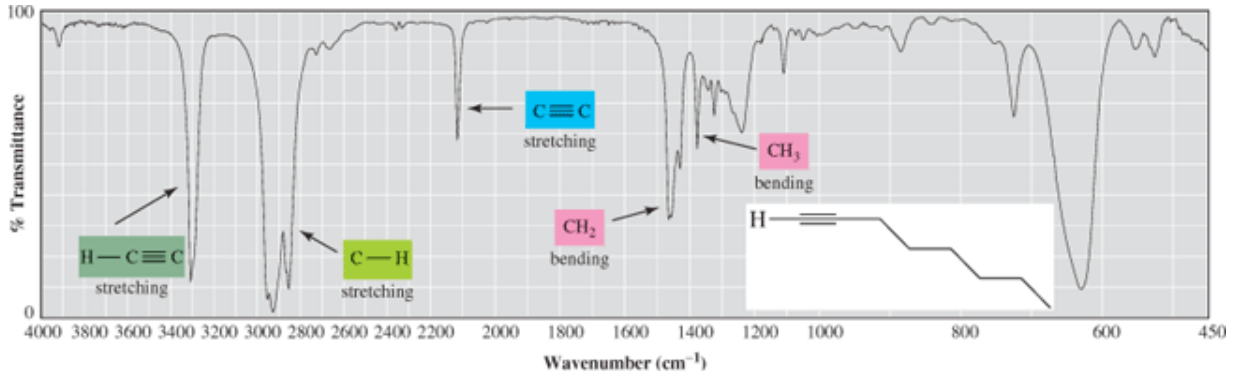


FIGURE 20.12 Infrared spectrum of oct-1-yne.

Alcohols

Alcohols are easily recognised by their characteristic O—H stretching signal in their IR spectra (table 20.6). Both the position of this signal and its intensity depend on the extent of hydrogen bonding (section 6.8). Under normal conditions, where there is extensive hydrogen bonding between alcohol molecules, O—H stretching occurs as a broad signal at 3200 –3500 cm^{-1}. The signal due to the C—O stretching vibration of alcohols appears in the range 1050 -1250 cm^{-1}.

TABLE 20.6 Characteristic IR signals of alcohols

Bond	Frequency (cm^{-1})	Intensity
O—H (hydrogen bonded)	3200–3500	medium and broad
C—O	1050 -1250	medium

Figure 20.13 shows an infrared spectrum of pentan-1-ol. The hydrogen-bonded O—H stretching appears as a strong, broad signal centred at 3340 cm^{-1}. The signal for C—O stretching appears near 1050 cm^{-1}, a value characteristic of primary alcohols.

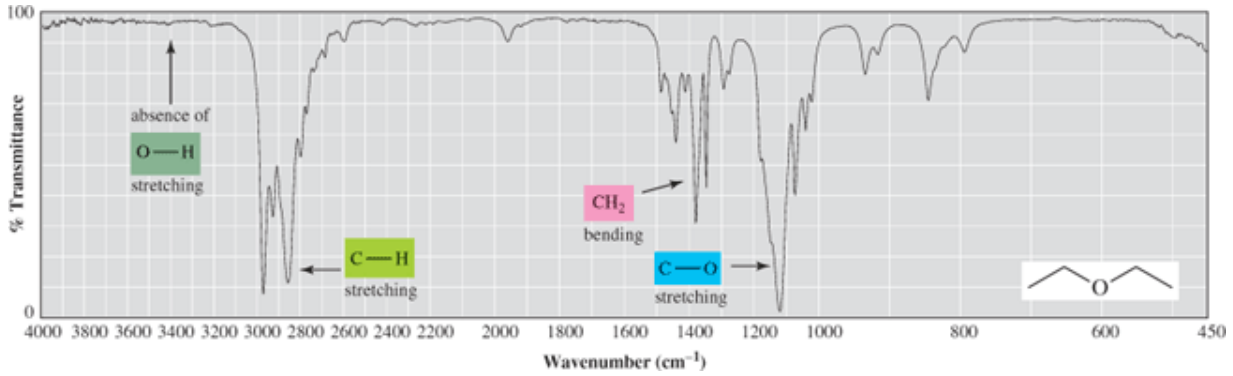


FIGURE 20.13 Infrared spectrum of pentan-1-ol.

Ethers

The C—O stretching frequencies of ethers are similar to those observed in alcohols and esters. Dialkyl ethers typically

show a single signal in this region between 1070 and 1150 cm^{-1}. The presence or absence of a signal for O—H stretching at 3200–3500 cm^{-1} for a hydrogen-bonded O—H can be used to distinguish between an ether and an alcohol. The C—O stretching vibration is also present in esters. In this case, we can use the presence or absence of a signal for C═O stretching (1735 to 1750 cm^{-1}) to distinguish between an ether and an ester. Figure 20.14 shows an infrared spectrum of diethyl ether. Notice the absence of a signal for O—H stretching.

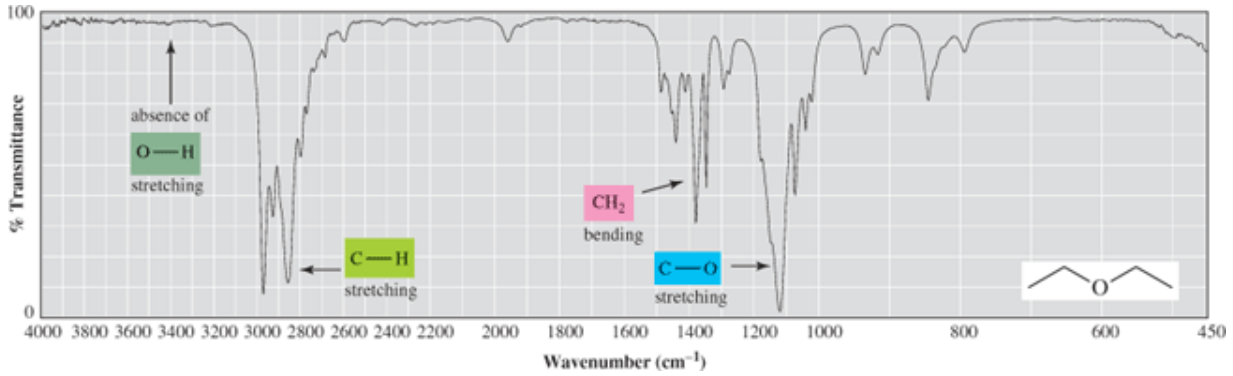


FIGURE 20.14 Infrared spectrum of diethyl ether.

Benzene and Its Derivatives

The IR spectra of aromatic rings show a medium to weak signal in the C—H stretching region at approximately 3030 cm^{-1}, characteristic of C—H bonds on sp^2 carbon atoms. They also show several signals due to C═C stretching between 1450 and 1600 cm^{-1}. In addition, they show strong signals in the region from 690 to 900 cm^{-1} due to C—H bending of the aromatic rings (table 20.7). Finally, the presence of weak, broad bands between 1700 and 2000 cm^{-1} can be an indicator of a benzene ring (often these are so weak that they are not observed).

TABLE 20.7 Characteristic IR signals of aromatic hydrocarbons

Bond	Vibration	Frequency (cm^{-1})	Intensity
C—H	stretching	3030	medium to weak
C—H	bending	690–900	strong
C═C	stretching	1475 and 1600	strong to medium

The C—H and C═C signal patterns characteristic of aromatic rings can be seen in the infrared spectrum of toluene (figure 20.15).

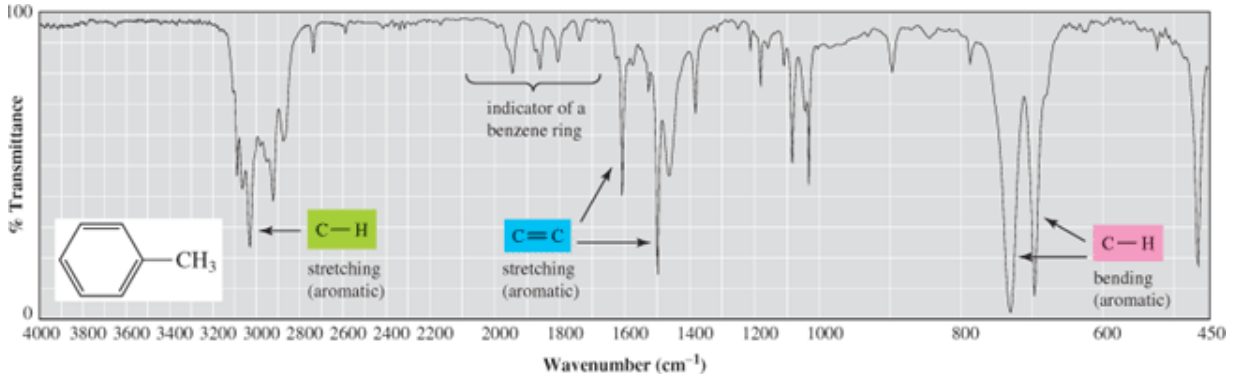


FIGURE 20.15 Infrared spectrum of toluene.

Amines

The most important and readily observed infrared signals of primary and secondary amines are due to N—H stretching

vibrations, which appear in the region from 3100 to 3500 cm^{-1}. Primary amines have two signals in this region, one caused by symmetric stretching vibration and the other by asymmetric stretching. The two N—H stretching bands characteristic of a primary amine can be seen in the IR spectrum of butylamine (figure 20.16). Secondary amines give only one band in this region. Tertiary amines have no N—H and so are transparent in this region of the infrared spectrum.

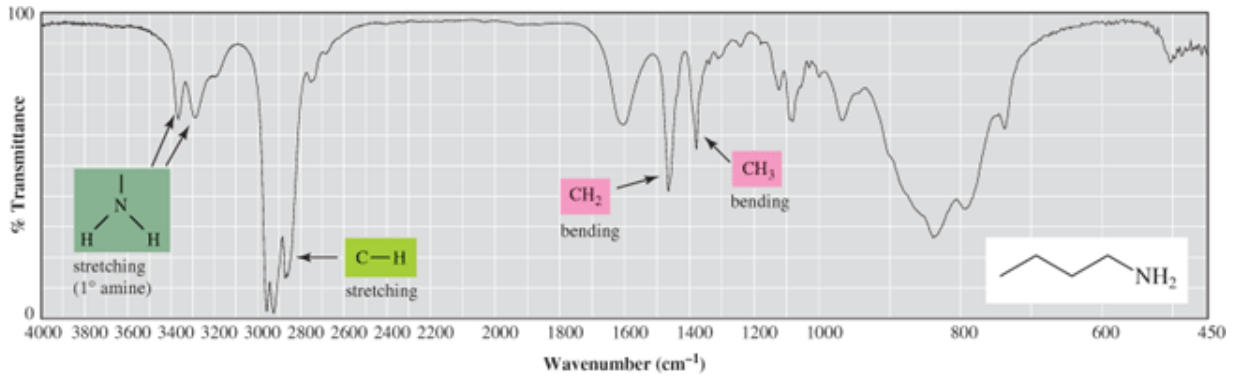


FIGURE 20.16 Infrared spectrum of butylamine, a primary amine.

Aldehydes and Ketones

Aldehydes and ketones show characteristic strong infrared signals between 1705 and 1780 cm^{-1} associated with the stretching vibration of the carbon–oxygen double bond. The stretching vibration for the carbonyl group of menthone occurs at 1705 cm^{-1} (figure 20.17).

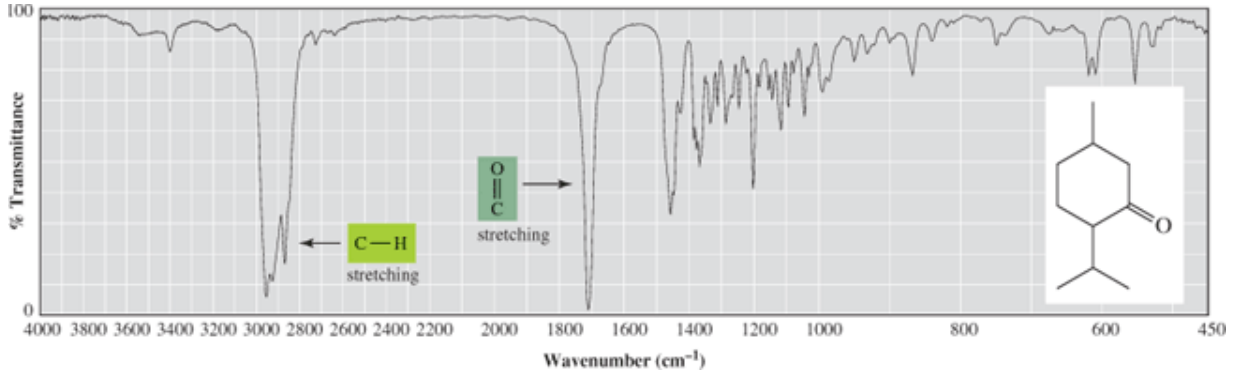


FIGURE 20.17 Infrared spectrum of menthone.

Because several different functional groups contain a carbonyl group, it is often not possible to tell from signals in this region alone whether the carbonyl-containing compound is an aldehyde, a ketone, a carboxylic acid or an ester.

Carboxylic Acids and Their Derivatives

The most important infrared signals of carboxylic acids and their functional derivatives are due to the C═O stretching vibration; these signals are summarised in table 20.8.

TABLE 20.8 Characteristic IR signals of carboxylic acids, esters and amides

Compound	C═O vibrational frequency (cm^{-1})	Additional signals (cm^{-1})
$RCNH_2$	1630–1680	N—H stretching at 3200 and 3400 (1° amides have two N—$_H$ peaks) (2° amides have one N—H peak)
RCOH	1700–1725	O—H very broad stretching at 2400 –3400 C—O stretching at 1210 -1320

O ‖ RCOR	1735–1750	C—O stretching at 1000 -1100 and 1200 -1250

The carboxyl group of a carboxylic acid gives rise to two characteristic signals in the infrared spectrum. One of these occurs in the region from 1700 to 1725 cm^{-1} and is associated with the stretching vibration of the carbonyl group. This region is essentially the same as that observed for the carbonyl groups of aldehydes and ketones. The other infrared signal characteristic of a carboxyl group is a band between 2400 and 3400 cm^{-1} due to the stretching vibration of the O—H group. This signal, which often overlaps the C—H stretching band, is generally very broad due to hydrogen bonding between molecules of the carboxylic acid. Both C═O and O—H stretchings can be seen in the infrared spectrum of butanoic acid, shown in figure 20.18.

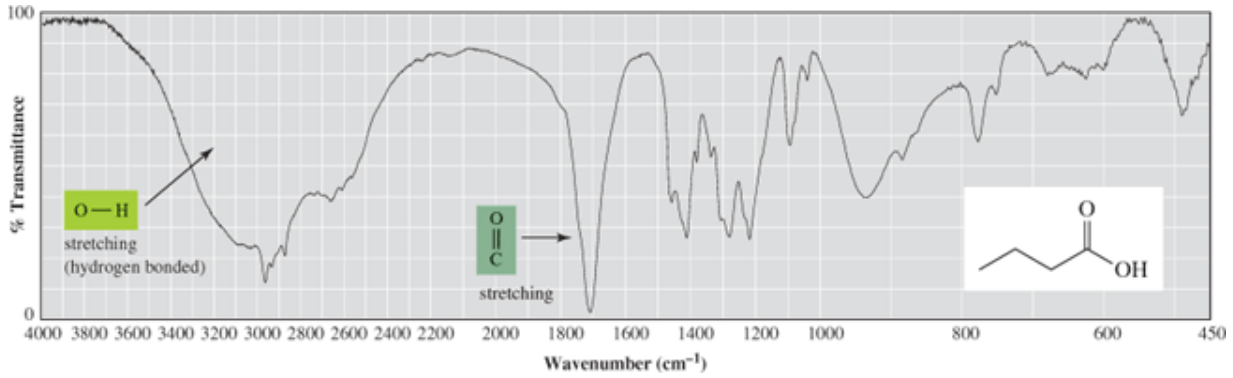


FIGURE 20.18 Infrared spectrum of butanoic acid.

The IR spectra of esters display strong signals for C═O stretching in the region between 1735 and 1750 cm^{-1} m. In addition, they display strong signals for C—O stretching in the region from 1000 to 1250 cm^{-1} (figure 20.19).

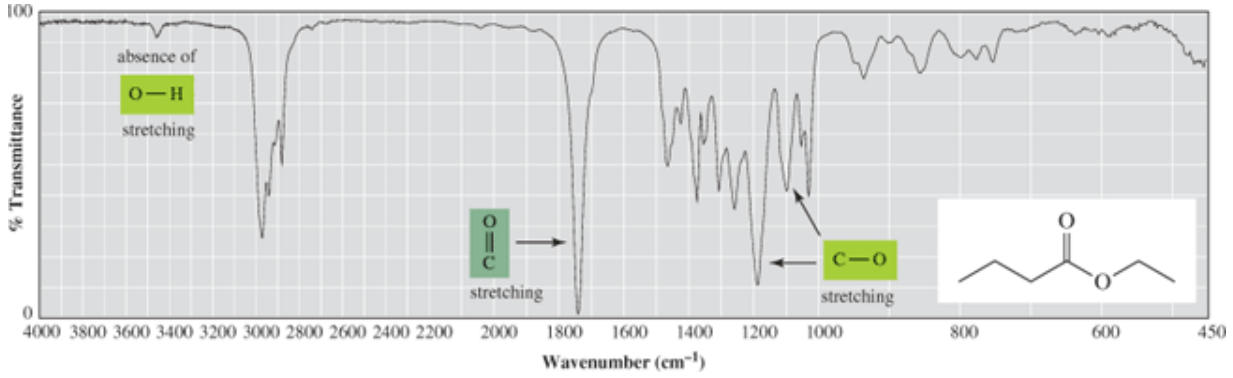


FIGURE 20.19 Infrared spectrum of ethyl butanoate.

The signal due to carbonyl stretching of amides occurs at lower wavenumbers (1630 -1680 cm^{-1}) than other carbonyl compounds. Like the amines, primary and secondary amides show N—H stretching in the region from 3200 to 3400 cm^{-1} m ; primary amides ($RCONH_2$) show two N—H signals, whereas secondary amides (RCONHR) show only a single N—H signals. Tertiary amides, of course, do not show N—H stretching absorptions. Compare the three spectra in figure 20.20.

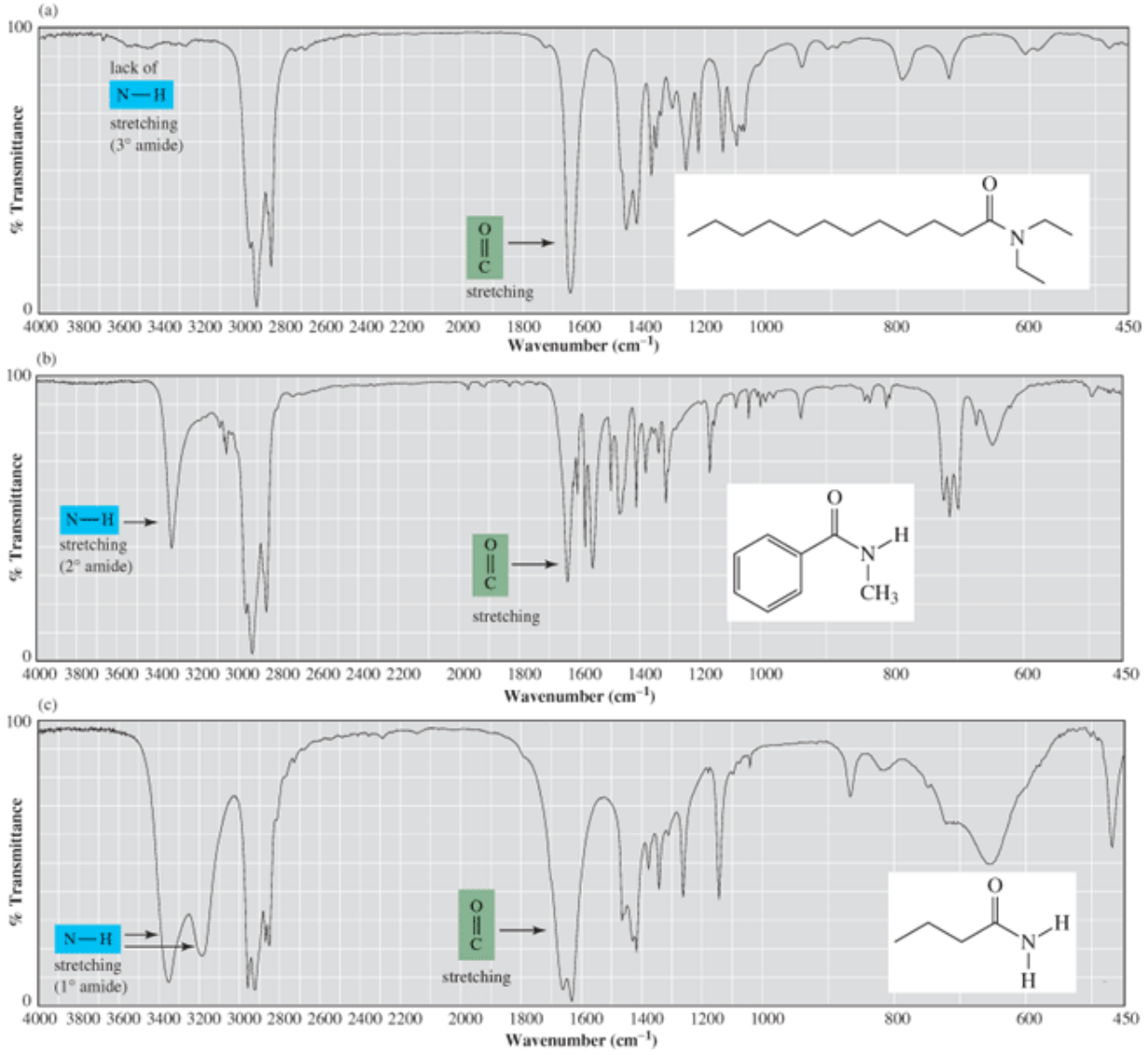
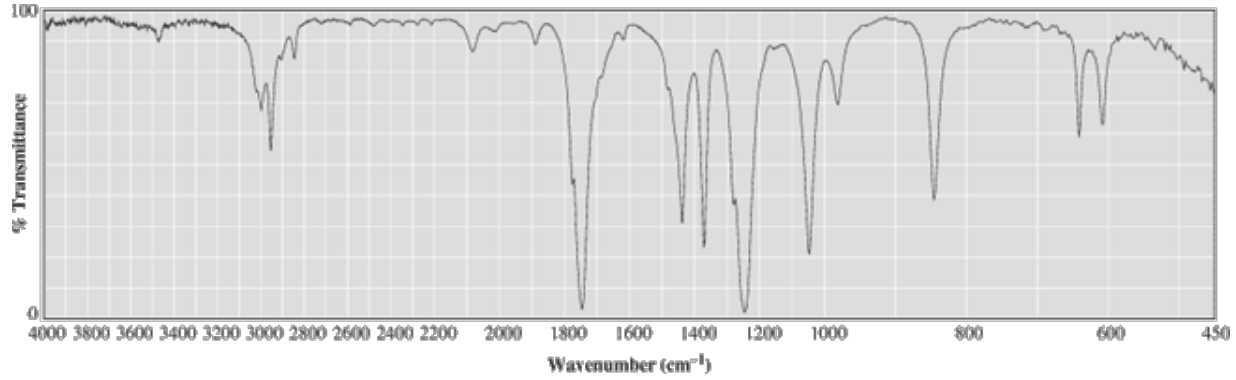


FIGURE 20.20 Infrared spectra of
(a) *N*,*N*-diethyldodecanamide, a tertiary amide,
(b) *N*-methylbenzamide, a secondary amide, and
(c) butanamide, a primary amide.

WORKED EXAMPLE 20.7

Determining a Compound From an IR Spectrum and Molecular Formula

An unknown compound with the molecular formula $C_3H_6O_2$ yields the following IR spectrum. Draw possible structures for the compound.

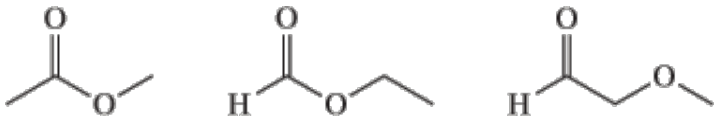


Analysis

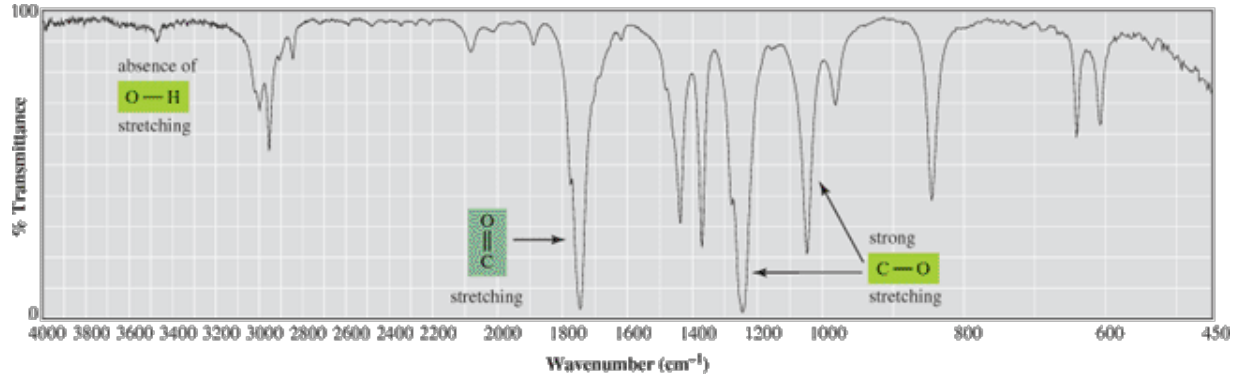
There are many ways to solve this sort of problem. We should start by determining the index of hydrogen deficiency (IHD). Based on the reference formula of C_3H_8, the IHD = 1. This means we have either one ring or one double bond. Now we can inspect the spectrum for key functional group signals (see table 20.4) and then draw possible isomers that would match the data. Do not forget to also consider missing signals. For example, in this case, there is no signal for an O—H stretch at ~3300 cm^{-1}, which automatically excludes carboxylic acids and alcohols.

Solution

The IR spectrum shows a strong signal at approximately 1750 cm^{-1}, which is indicative of a C═O group and, therefore, we cannot have an alkene or a ring (IHD = 1). The spectrum also shows strong C—O signals peaks at 1250 and 1050 cm^{-1}. Furthermore, there are no signals above 3000 cm^{-1}, which eliminates the possibility of an O—H group. Now, let's put the information together so we can propose some structures. Since we cannot have an acid or alcohol (no O—H signal), the two oxygen atoms must be part of an ester, or an ether and an aldehyde (we do not have enough carbon atoms for an ether and a ketone). On the basis of this data, three structures are possible for the given molecular formula:



The given spectrum can now be annotated as follows:



Is our answer reasonable?

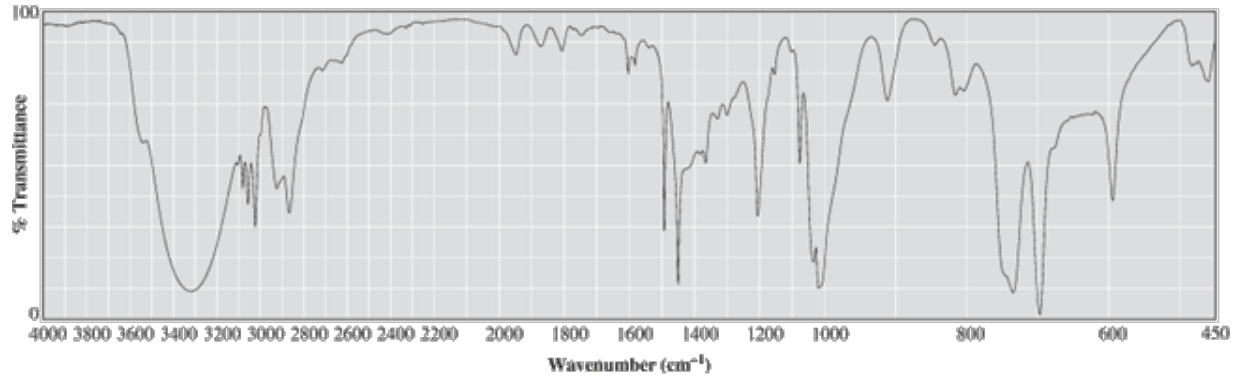
Check that the compounds suggested would give the appropriate signals. Check also that the compounds have the correct molecular formula.

PRACTICE EXERCISE 20.7

What does the value of the wavenumber of the stretching frequency for a particular functional group indicate about the relative strength of the bond in that functional group?

Interpreting IR Spectra

Determine possible structures for a compound that yields the following IR spectrum and has a molecular formula of C_7H_8O.

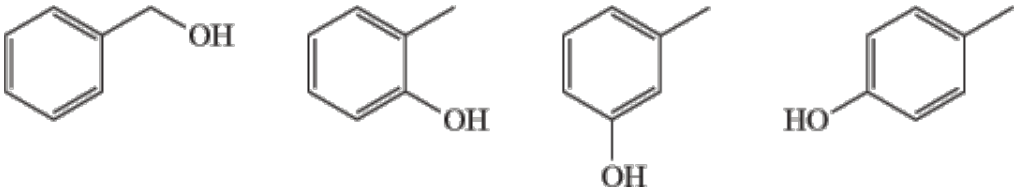


Analysis

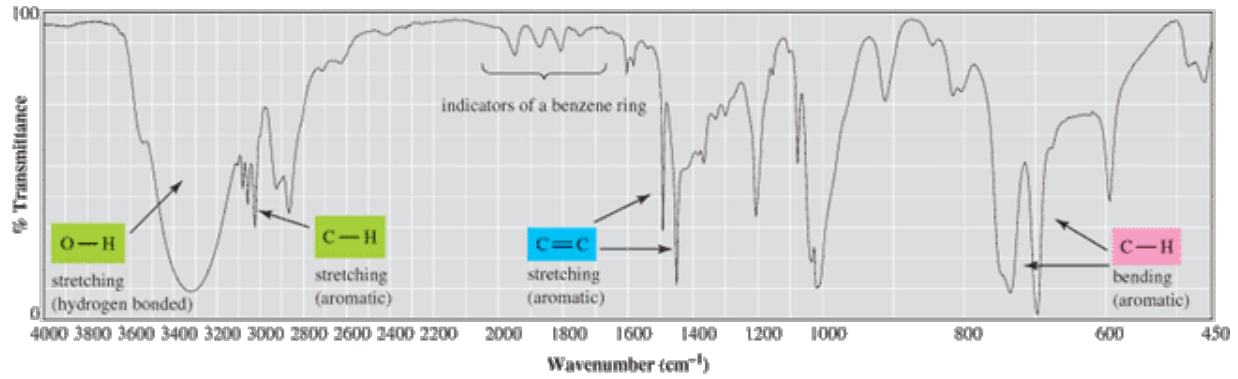
Given the molecular formula of C_7H_8O, you should determine the index of hydrogen deficiency to be 4, based on the reference formula of C_7H_{16}. While accounting for this value may seem daunting at first (consider the possible combinations of four rings or π bonds), recall that the benzene ring has an index of hydrogen deficiency of 4. Look for characteristic bands for aromatic compounds in the IR spectrum; if they are present, you know that there are no other double bonds or rings in the molecule. The oxygen atom may be present as an alcohol/phenol, ether, aldehyde or ketone (the last two would not be possible if there was an aromatic ring present).

Solution

A quick inspection of the spectrum indicates a strong, broad signal at approximately 3310 cm^{-1} due to O—H stretching and the absence of a signal due to a carbonyl group between 1700 and 1800 cm^{-1}. Because we must have an —OH group, we cannot propose any structures with an ether group (or an aldehyde or a ketone). Closer inspection of the spectrum shows the characteristic aromatic C—H bending bands at 690 and 740 cm^{-1} and the weak, broad bands between 1700 and 2000 cm^{-1}, which support the existence of a benzene ring. Also, a signal for sp^2 C—H stretching is present just above 3000 cm^{-1}. Aromatic C═C stretching absorption bands at 1450 and 1490 cm^{-1} also indicate a benzene ring. Now, given that the molecular formula is C_7H_8O and we have a benzene ring and an —OH group, we have to account for only one more carbon atom. This last carbon atom must be bonded to the benzene ring. There are only four possible places we can attach an —OH group to toluene (methylbenzene) and these structures are given below.



The given spectrum can now be annotated as follows:



Is our answer reasonable?

You should check that all of the proposed compounds have the correct IHD and that the key signals for each compound are present in the spectrum.

The preceding examples illustrate the power and limitations of IR spectroscopy. The power lies in its ability to provide us with information about the functional groups in a molecule. IR spectroscopy does not, however, provide us with information on how those functional groups are connected. Fortunately, another type of spectroscopy — nuclear magnetic resonance (NMR) spectroscopy — does provide us with connectivity information. NMR spectroscopy is the next topic of this chapter.

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20.5 Nuclear Magnetic Resonance Spectroscopy

We began this chapter with an introduction to mass spectrometry and we saw how it could be used to determine molecular masses and molecular formulae. We then discussed infrared spectroscopy and saw how infrared light could be used to determine the types of functional groups present in an unknown compound. Now we will concentrate on the technique known as nuclear magnetic resonance (NMR) spectroscopy. The phenomenon of nuclear magnetic resonance was first detected in 1946 by Felix Bloch and Edward Purcell, who shared the 1952 Nobel Prize in physics for their discoveries. NMR spectroscopy has become the most important tool in the determination of organic structures. The particular value of **nuclear magnetic resonance (NMR) spectroscopy** is that it gives us information about the number and types of atoms in a molecule and can also provide information on how they are connected. **^{1}H-NMR spectroscopy** gives information about the number and types of hydrogen atoms within a molecule while **^{13}C-NMR spectroscopy** tells us about the number and types of carbon atoms. Although we will consider only hydrogen and carbon NMR, it is also possible to obtain NMR spectra of many other elements.

The Origin of Nuclear Magnetic Resonance

From our study in chapter 4, we are already familiar with the concept that an electron has a spin and that a spinning charge creates an associated magnetic field. In effect, an electron behaves as if it is a tiny bar magnet. An atomic nucleus that has an odd mass or an odd atomic number also has a spin (a nuclear spin) and also behaves as if it is a tiny bar magnet. Recall that, when designating isotopes, a superscript represents the mass of the element. Thus, the nuclei of ^{1}H and ^{13}C, isotopes of the two elements most common in organic compounds, also have a nuclear spin, whereas the nuclei of ^{1}2C and ^{1}6O do not have a nuclear spin. Accordingly, in this sense, nuclei of ^{1}H and ^{1}3C are quite different from nuclei of ^{1}2C and ^{16}O.

WORKED EXAMPLE 20.9

Determining Whether an Atomic Nucleus Has a Spin

Which of the following nuclei has a spin?

(a) $^{14}_{6}C$

(b) $^{14}_{7}N$

Analysis

Recall that to have a nuclear spin an isotope must have either an odd atomic number or an odd mass.

Solution

(a) ^{14}C, a radioactive isotope of carbon, has neither an odd mass number nor an odd atomic number and, therefore, does not have a spin.

(b) ^{14}N, the most common naturally occurring isotope of nitrogen (99.63% of all nitrogen atoms), has an odd atomic number and, therefore, has a spin.

Is our answer reasonable?

Check that either the mass number or the atomic number is odd.

PRACTICE EXERCISE 20.8

Which of the following nuclei has a spin?

(a) $^{31}_{15}P$

(b) $^{195}_{78}Pt$

Within a collection of ^{1}H and ^{13}C atoms, the spins of their nuclei are completely random in orientation. When we place them in a powerful magnetic field, however, interactions between their nuclear spins and the applied magnetic field are quantised, and only two orientations are allowed (figure 20.21).

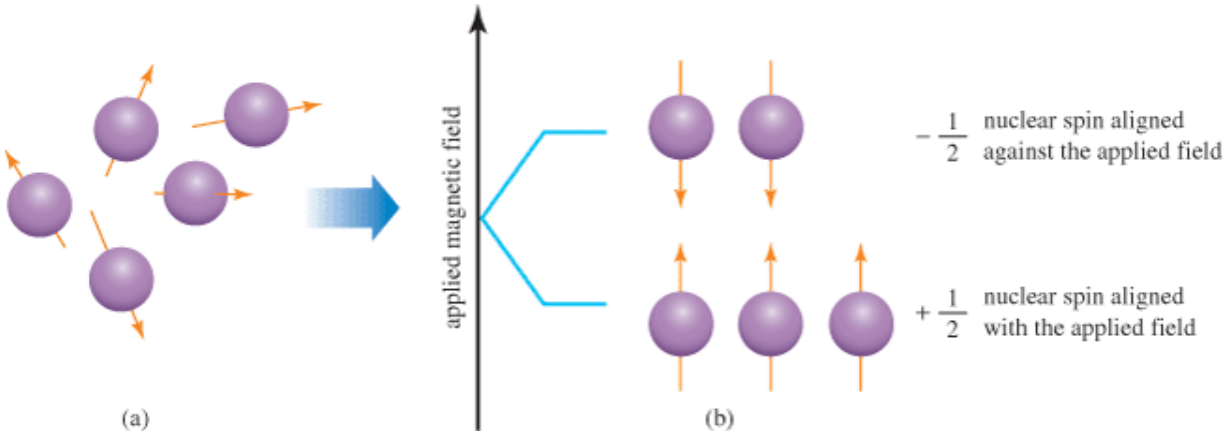


FIGURE 20.21 ^{1}H and ^{13}C nuclei
(a) in the absence of an applied magnetic field and
(b) in the presence of an applied field. ^{1}H and ^{13}C nuclei with spin $+\frac{1}{2}$ are aligned with the applied magnetic field and are in the lower spin energy state; those with spin $-\frac{1}{2}$ are aligned against the applied magnetic field and are in the higher spin energy state.

When hydrogen nuclei are placed in an applied magnetic field, a small majority of their nuclear spins align with the applied field in the lower energy state. Irradiation of nuclei with **radio-frequency radiation** of the appropriate energy causes some of those in the lower energy spin state to absorb energy and results in their nuclear spins flipping from the lower energy state to the higher energy state, as illustrated in figure 20.22. In this context, **resonance** is defined as the absorption (or emission when the nuclei return to equilibrium) of electromagnetic radiation by a spinning nucleus and the resulting flip of its nuclear spin state. (*Note:* (Resonance used in this context is completely different from the resonance theory of chemical structures discussed earlier.)

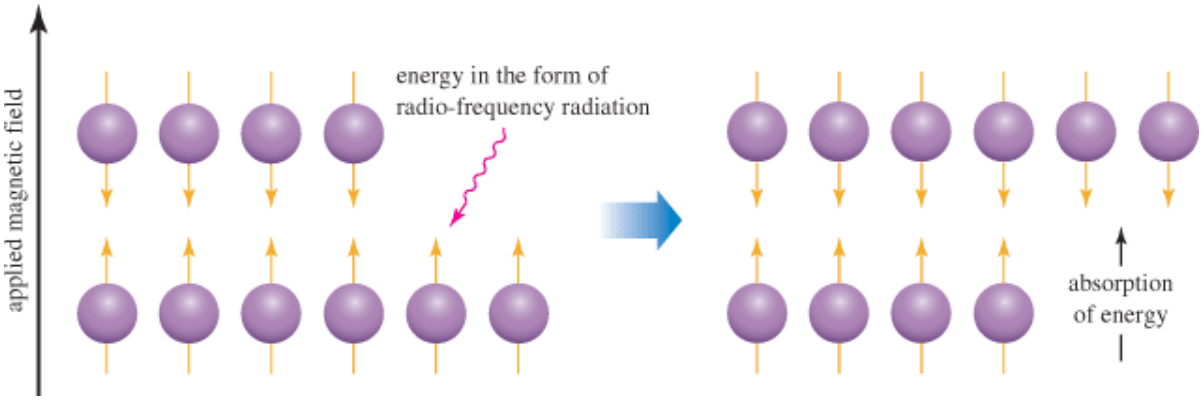


FIGURE 20.22 An example of resonance for nuclei of spin $+\frac{1}{2}$ and $-\frac{1}{2}$.

If a strong enough magnetic field is used, then the energy required to cause this flipping corresponds to that of radiowaves. For example, an applied field strength of 7.05 tesla (T) is readily available with present-day superconducting electromagnets (for comparison, the magnitude of the Earth's magnetic field is approximately 30–60 microtesla). In such fields, the difference in energy between nuclear spin states for ^{1}H is 0.120 J mol^{-1}, which corresponds to electromagnetic radiation of approximately 300 MHz (300 000 000 Hz). At the same magnetic field

strength, the difference in energy between nuclear spin states for $^{1}3C$ is 0.035 J mol^{-1}, which corresponds to electromagnetic radiation of 75 MHz. Thus, we can use electromagnetic radiation in the radio-frequency range to detect changes in nuclear spin states for ^{1}H and ^{13}C. In the next several sections, we describe how these measurements are made for nuclear spin states of these two isotopes and then how this information can be correlated with molecular structure.

Shielding

If we were dealing with ^{1}H nuclei isolated from all other atoms and electrons, any combination of applied field and electromagnetic radiation that produces a resonance signal for one hydrogen nucleus would produce the same resonance signal for all other hydrogen nuclei. In other words, the same amount of energy would cause all hydrogen atoms to resonate, and the hydrogen atoms would be indistinguishable from one another. NMR would then be an ineffective technique for determining the structure of a molecule because all the hydrogen atoms in a compound would resonate at the same frequency, giving rise to one and only one NMR signal.

Fortunately, hydrogen atoms in organic molecules are surrounded by electrons and by other atoms. The electrons that surround a nucleus also have spin so they create **local magnetic fields** that oppose the applied field. Consequently, the magnetic field experienced by a hydrogen atom in a molecule is slightly less than that of the applied magnetic field of the instrument. Although these local magnetic fields created by electrons are orders of magnitude weaker than the applied magnetic fields used in NMR spectroscopy, they are nonetheless significant at the molecular level. The result of these local magnetic fields is that hydrogen atoms are **shielded** from the applied field. The greater the shielding of a particular hydrogen atom by local magnetic fields, the greater is the energy (frequency of radiowaves) required to bring that hydrogen atom into resonance.

As we learned in previous chapters, the electron density around a nucleus can be influenced by the atoms that surround the nucleus. For example, the electron density around the hydrogen atoms in fluoromethane (figure 20.23) is less than that around the hydrogen atoms in chloromethane (figure 20.24), due to the greater electronegativity of fluorine relative to chlorine. Thus, we can say that the hydrogen atoms in chloromethane are *more shielded* than the hydrogen *d* atoms in fluoromethane. Conversely, we can say the hydrogen atoms in fluoromethane are more **deshielded** (reduced electron density around each hydrogen atom) than those in chloromethane.

The differences in resonance frequencies between the various ^{1}H nuclei within a molecule caused by shielding are generally very small. The difference between the resonance frequencies of hydrogen atoms in chloromethane compared with those in fluoromethane, for example, is only 360 Hz under an applied field of 7.05 tesla. Considering that the radio-frequency radiation used at this applied field is approximately 300 MHz, the difference in resonance frequencies between these two sets of hydrogen atoms is only slightly greater than 1 part per million (1 ppm) compared with the irradiating frequency.



FIGURE 20.23 Fluorine's greater electronegativity produces a larger inductive effect and, therefore, reduces the electron density around each hydrogen atom. We say that these hydrogen atoms are deshielded.

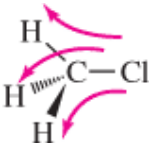


FIGURE 20.24 Chlorine is less electronegative than fluorine, resulting in a smaller inductive effect and, therefore, a greater electron density around each hydrogen atom. We say that the hydrogen atoms in chloromethane are more shielded (by their local environment) than those in fluoromethane.

$$\frac{360\,\text{Hz}}{300 \times 10^{6}\,\text{Hz}} = \frac{1.2}{10^{6}} = 1.2\,\text{ppm}$$

The importance of shielding for elucidating the structure of a molecule will be discussed later in this section.

An NMR Spectrometer

Modern NMR spectrometers (figure 20.25) work by irradiating a sample with a short pulse of radiation that covers the entire range of relevant radiowave frequencies. All hydrogen atoms are simultaneously excited and then begin to return (or decay) to their original spin state. As each atom decays, it releases energy of a particular frequency that is detected as an electrical impulse in the receiver coils. The resulting combination of electrical impulses generated from all decay frequencies is called a free induction decay (FID). Typically an FID can be recorded every 1–2 seconds, and many are collected and then averaged to generate a spectrum using a mathematical technique called Fourier transformation. This signal averaging allows us to easily measure the NMR spectrum of very small amounts of sample (as little as 1 mg).

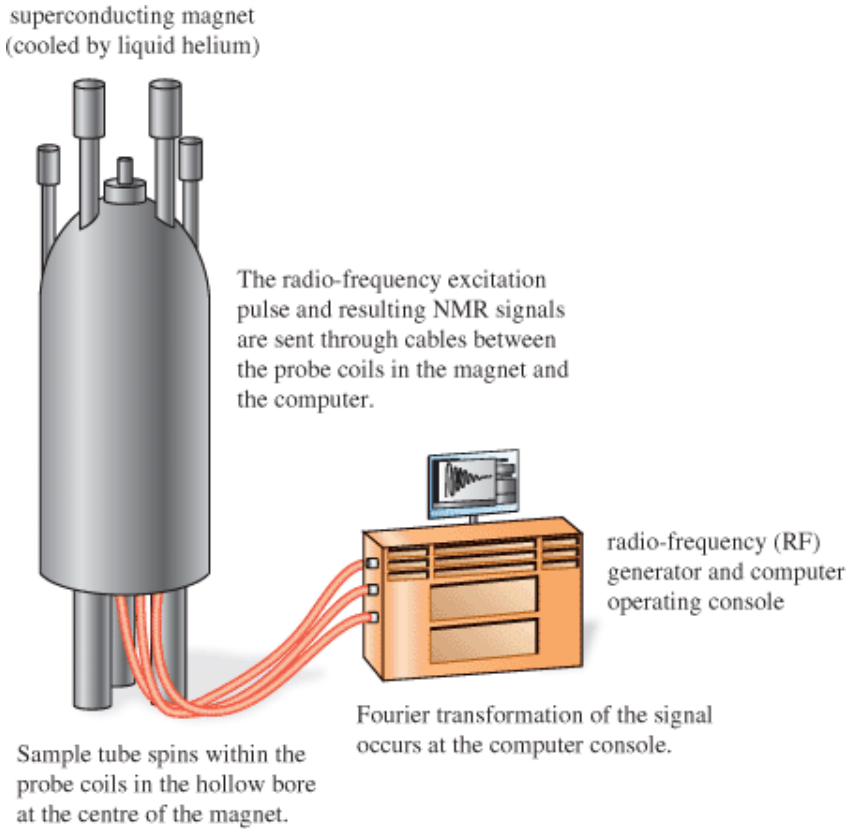


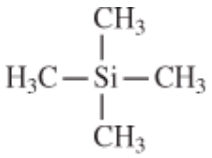
FIGURE 20.25 Schematic diagram of a nuclear magnetic resonance spectrometer.

To record a spectrum, the sample is dissolved in a solvent having no 1H hydrogen atoms, most commonly deutero chloroform, $CDCl_3$, or deuterium oxide, D_2O (deuterium, D, is the ^2H isotope of hydrogen). The sample cell is a small glass tube suspended in the hollow bore at the centre of the magnet and set spinning on its long axis to ensure that all parts of the sample experience a homogeneous applied field (figure 20.26).



FIGURE 20.26 An NMR sample tube in its spinning assembly.

It is customary to measure the resonance frequencies of individual nuclei relative to the resonance frequency of the same nuclei in a reference compound. The reference compound now universally accepted for ^{1}H-NMR and ^{13}C-NMR spectroscopy in organic solvents is **tetramethylsilane (TMS)**:



tetramethylsilane (TMS)

When we determine a ^{1}H-NMR spectrum of a compound, we report how far the resonance signals of its hydrogen atoms are shifted from the resonance signal of the hydrogen atoms in TMS. When we determine a ^{13}C-NMR spectrum, we report how far the resonance signals of its carbon atoms are shifted from the resonance signal of the four carbon atoms in TMS.

To standardise reporting of NMR data, scientists have adopted a quantity called the **chemical shift (δ)** expressed in parts per million:

$$\delta = \frac{\text{shift in frequency of a signal from TMS (Hz)}}{\text{operating frequency of the spectrometer (MHz)}}$$

In a typical ^{1}H-NMR spectrum, the horizontal axis represents the δ (delta) scale, with values from 0 on the right to 10 on the left, but values can fall outside this range (for example, see figures 20.31 and 20.47 and table 20.9). The vertical axis represents the intensity of the resonance signal. Figure 20.27 shows a ^{1}H-NMR spectrum of methyl acetate, a compound used in the manufacture of artificial leather. The small signal at δ 0 in this spectrum represents the hydrogen atoms of the reference compound, TMS. The remainder of the spectrum consists of two signals: one for the hydrogen atoms of the —OCH_3 group and one for the hydrogen atoms of the methyl attached to the carbonyl group. It is not our purpose at the moment to determine which hydrogen atoms give rise to which signal but only to recognise the form in which we record an NMR spec-trum and to understand the meaning of the calibration marks.

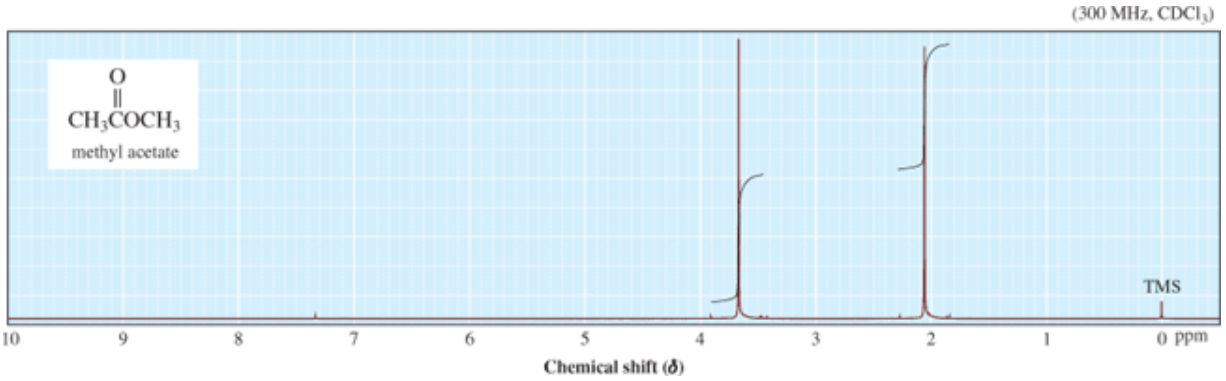


FIGURE 20.27 ^{1}H-NMR spectrum of methyl acetate.

A note on terminology: If a signal is shifted towards the left of the spectrum, we say that the nuclei giving rise to that signal are deshielded (also often referred to as shifted **downfield**). Conversely, if a signal is shifted towards the right of the spectrum, we say that the nuclei giving rise to that signal are shielded (also often referred to as shifted **upfield**). Figure 20.28 summarises some of the common NMR terms.

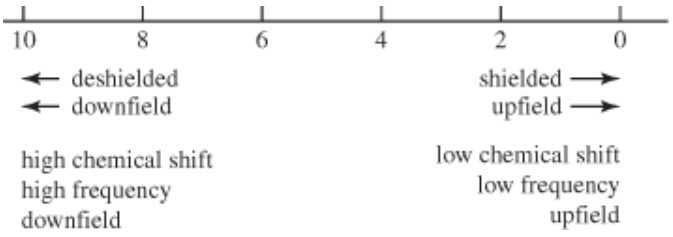
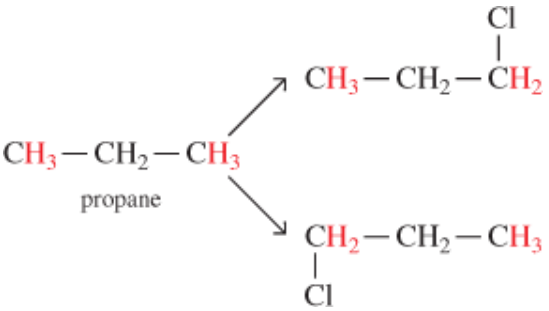


FIGURE 20.28 A summary of some common NMR terms.

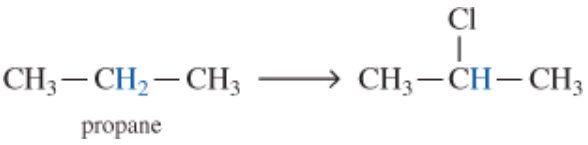
Equivalent Hydrogen Atoms

Given the structural formula of a compound, how do we know how many signals to expect? The answer is that **equivalent hydrogen atoms** give the same ^{1}H-NMR signal; conversely, nonequivalent hydrogen atoms give different ^{1}H-NMR signals. A direct way to determine which hydrogen atoms in a molecule are equivalent is to replace each in turn by a test atom, such as a halogen atom. If replacement of two hydrogen atoms in turn gives the same compound, the two hydrogen atoms are equivalent. If replacement gives different compounds, the two hydrogen atoms are nonequivalent.

Using this substitution test, we can show that propane contains two sets of equivalent hydrogen atoms: a set of six equivalent 1° hydrogen atoms (hydrogen atoms attached to a 1° carbon atom) and a set of two equivalent 2° hydrogen atoms (hydrogen atoms attached to a 2° carbon atom). Thus we would expect to see two signals: one for the six equivalent methyl hydrogen atoms and one for the two equivalent methylene (—CH_2—) hydrogen atoms.



Replacement of any of the red hydrogen atoms by a chlorine atom gives 1-chloropropane; thus, all of the red hydrogen atoms in propane are equivalent.

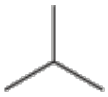


Replacement of either of the blue hydrogen atoms by a chlorine atom gives 2-chloropropane; thus, both of the blue hydrogen atoms in propane are equivalent.

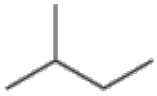
WORKED EXAMPLE 20.10

EQuivalent Hydrogen Atoms

Determine the number of sets of equivalent hydrogen atoms in each of the following compounds and the number of hydrogen atoms in each set.

(a) 

2-methylpropane

(b) 

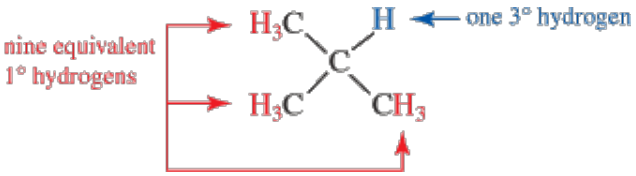
2-methylbutane

Analysis

You should start by identifying all the hydrogen atoms in the molecules. Compound (a) has 10 and compound (b) has 12. Now apply the substitution process described previously to identify equivalent hydrogen atoms.

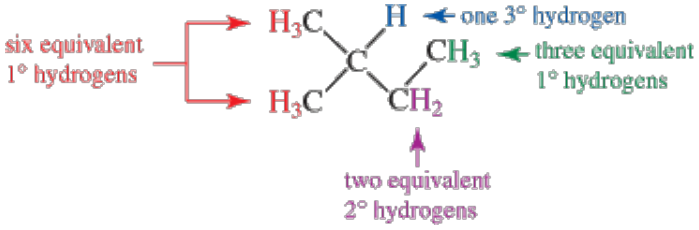
Solution

(a) There are two sets of equivalent hydrogen atoms in 2-methylpropane — a set of nine equivalent 1° hydrogen atoms and one 3° hydrogen atom.



Replacing any one of the red hydrogen atoms with a chlorine atom yields 1-chloro-2-methylpropane. Replacing the blue hydrogen atom with a chlorine atom yields 2-chloro-2-methylpropane.

(b) There are four sets of equivalent hydrogen atoms in 2-methylbutane — two different sets of 1° hydrogen atoms, one set of 2° hydrogen atoms and one 3° hydrogen atom.



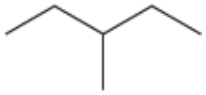
Replacing any of the red hydrogen atoms with a chlorine atom yields 1-chloro-2-methylbutane. Replacing the blue hydrogen atom with a chlorine atom yields 2-chloro-2-methylbutane. Replacing a purple hydrogen atom with a chlorine atom yields 2-chloro-3-methylbutane. Replacing a green hydrogen atom with a chlorine atom yields 1-chloro-3-methylbutane.

Is our answer reasonable?

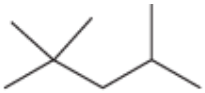
Check that you have identified all hydrogen atoms and that the different groups are actually different.

PRACTICE EXERCISE 20.9

Determine the number of sets of equivalent hydrogen atoms in each of the following compounds and the number of hydrogen atoms in each set.

(a) 

3-methylpentane

(b) 

2,2,4-trimethylpentane

Here are four organic compounds, each of which has one set of equivalent hydrogen atoms and gives one signal in its ^{1}H-NMR spectrum:



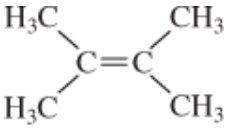
acetone
(propanone)



1,2-dichloroethane



cyclopentane

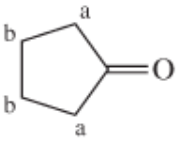


2,3-dimethylbut-2-ene

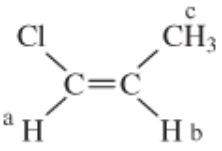
The structures below show that molecules with two or more sets of equivalent hydrogen atoms give rise to a different resonance signal for each set. For example, 1,1-dichloroethane has (a) three equivalent 1° hydrogen atoms and (b) one 3° hydrogen atom, so there are two resonance signals in its ^{1}H-NMR spectrum.



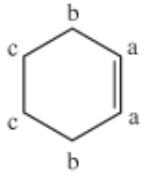
1,1-dichloroethane
(two signals)



cyclopentanone
(two signals)

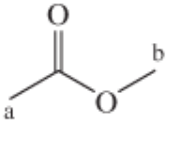


(*Z*)-1-chloropropene
(three signals)

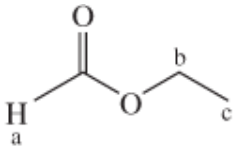


cyclohexene
(three signals)

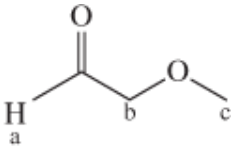
You should see immediately that valuable information about a compound's molecular structure can be obtained simply by counting the number of signals in a ^{1}H-NMR spectrum of that compound. Consider, for example, the two constitutional isomers with molecular formula $C_2H_4Cl_2$. The compound 1,2-dichloroethane has four equivalent 2° hydrogen atoms and shows one signal in its ^{1}H-NMR spectrum. Its constitutional isomer 1,1-dichloroethane has three equivalent 1° hydrogen atoms and one 3° hydrogen atom; this isomer shows two signals in its ^{1}H-NMR spectrum. Thus, simply counting signals can allow you to distinguish between these constitutional isomers. For example, in worked example 20.7 we narrowed down three possible candidates with a molecular formula of $C_3H_6O_2$ that could have produced the IR spectrum. Now, if we consider the number of signals in the ^{1}H-NMR spectrum of these compounds, we see that they give rise to two, three and three signals respectively.



methyl acetate
(methyl ethanoate)



ethyl formate
(ethyl methanoate)



methoxyacetaldehyde
(2-methoxyethanal)

Later we will see how we can distinguish between ethyl formate and methoxyacetaldehyde.

Structural Formulae From Number of Signals in ^{1}H-NMR Spectra

Each of the following compounds gives only one signal in its ^{1}H-NMR spectrum. Propose a structural formula for each.

(a) C_2H_6O

(b) $C_3H_6Cl_2$

(c) C_6H_{12}

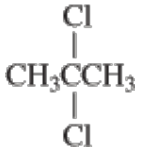
Analysis

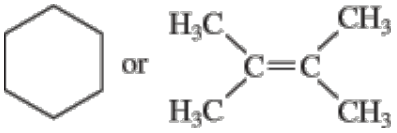
We should start by determining the IHD as this will tell you if you need to consider rings or double bonds. With this information, you then need to consider how you can put the atoms in the formulae together so that all hydrogen atoms are equivalent (drawing possible isomers and checking the number of different hydrogen atoms is probably the easiest way).

Solution

Given that the IHD for the three compounds are 0, 0 and 1, respectively, we know that we need to consider a ring or alkene only for (c). The following are structural formulae for each of the given compounds. Notice that, for each structure, the replacement of any hydrogen atom with a chlorine atom will yield the same compound regardless of the hydrogen being replaced.

(a) CH_3OCH_3

(b) 

(c) 

Is our answer reasonable?

Check that, for each structure, the replacement of any hydrogen atom with a chlorine atom will yield the same compound regardless of the hydrogen atom being replaced.

PRACTICE EXERCISE 20.10

Each of the following compounds gives only one signal in its ^{1}H-NMR spectrum. Propose a structural formula for each compound.

(a) C_3H_6O

(b) C_5H_{10}

(c) C_5H_{12}

(d) $C_4H_6Cl_4$

Signal Areas

We have just seen that the number of signals in a ^{1}H-NMR spectrum gives us information about the number of sets of equivalent hydrogen atoms. Signal areas in a ^{1}H-NMR spectrum can be measured by a mathematical technique called **integration**. In most of the spectra shown in this text, this information is displayed in the form of a **line of integration** superimposed on the original spectrum. The vertical rise of the line of integration over each signal is proportional to the area under that signal, which, in turn, is proportional to the number of hydrogen atoms giving rise to the signal.

Figure 20.29 shows an integrated ^{1}H-NMR spectrum of the petrol additive *tert*-butyl acetate, $C_6H_{12}O_2$. The spectrum shows signals at δ 1.4 and 2.0. The integrated area of the more shielded signal (to the right: 67 chart divisions) is nearly three times that of the less shielded signal (to the left: 23 chart divisions). We have used the horizontal lines on the chart as a unit of measure (10 chart divisions are equivalent to the distance between two consecutive solid horizontal lines)—alternatively, we could measure the line separation with a ruler). This relationship corresponds to a ratio of 3 : 1. We know from the molecular formula that there is a total of 12 hydrogen atoms in the molecule. The ratios obtained from the integration lines are consistent with the presence of one set of nine equivalent hydrogen atoms and one set of three equivalent hydrogen atoms. We will often make use of shorthand notation in referring to an NMR spectrum of a molecule. The notation lists the chemical shift of each signal, beginning with the most deshielded signal and followed by the number of hydrogen atoms that give rise to each signal (based on the integration). The shorthand notation describing the spectrum of *tert*-butyl acetate (figure 20.29) would be δ 2.0 (3H) and δ 1.4 (9H).

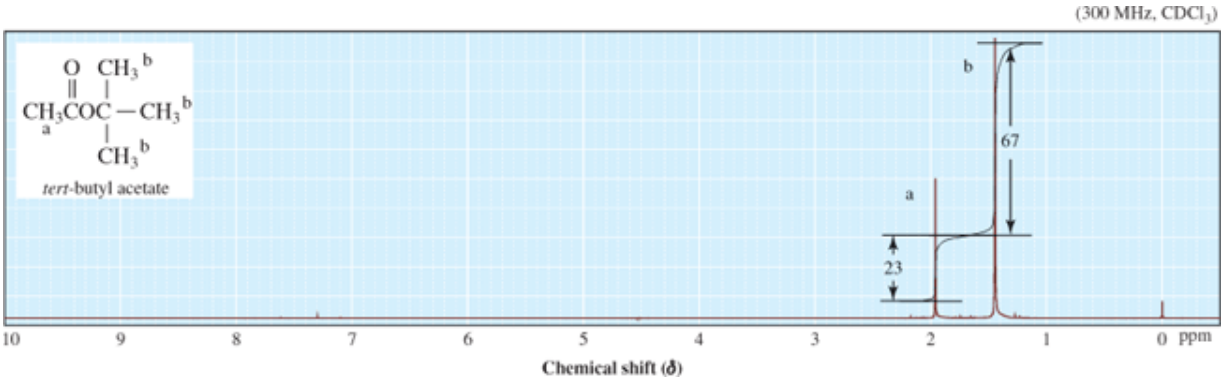


FIGURE 20.29 ^{1}H-NMR spectrum of *tert*-butyl acetate, $C_6H_{12}O_2$, showing a line of integration. The ratio of signal areas for the two peaks is 3 : 1, which, for a molecule possessing 12 hydrogen atoms, corresponds to nine equivalent hydrogen atoms of one set and three equivalent hydrogen atoms of another set.

An alternative way of representing integration values is to have the integration values printed below the horizontal scale axis. It is quite normal for the numerical values provided not to exactly match the ratio, but this is not a problem as we know we must have integer values for the number of hydrogen atoms. As an example, the spectrum of benzyl alcohol is given in figure 20.30.

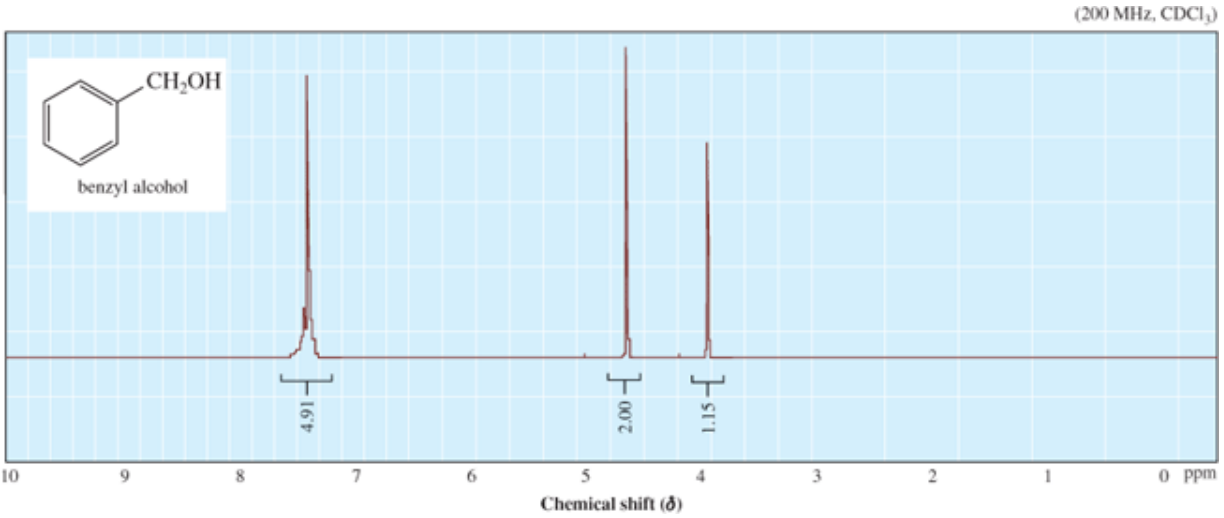
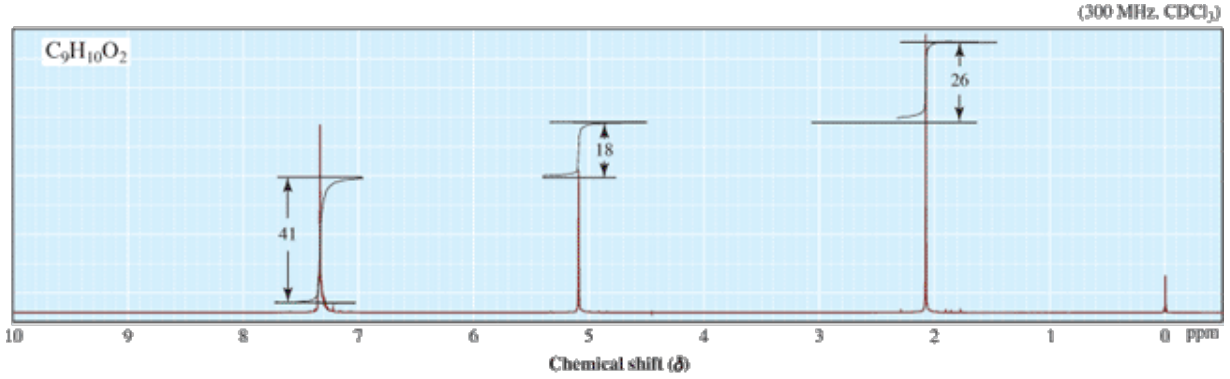


FIGURE 20.30 ^{1}H-NMR spectrum of benzyl alcohol, C_7H_8O, showing the integration values. The ratio of signal area for the three peaks is 5 : 2 : 1 (from left to right). Although the numerical values provided do not exactly match the ratio, this is not a problem as the number of hydrogen atoms must be integers.

WORKED EXAMPLE 20.12

Determining Integration Values

The following is a ^{1}H-NMR spectrum of a compound with the molecular formula $C_9H_{10}O_2$. From an analysis of the integration data, calculate the number of hydrogen atoms giving rise to each signal.



Analysis

Determine the relative ratio of the three signals, bearing in mind that there is a total of 10 hydrogen atoms in the molecule. Remember also that each signal must represent a whole number of hydrogen atoms (e.g. you cannot have 0.2 hydrogen atoms).

Solution

The ratio of the relative signal heights (obtained from the number of horizontal chart divisions) is 5 : 2 : 3. The molecular formula indicates that there are ten hydrogen atoms. Thus, the signal at δ 7.3 represents five hydrogen atoms, the signal at δ 5.1 represents two hydrogen atoms, and the signal at δ 2.1 represents three hydrogen atoms. Consequently, the signals and the number of hydrogen atoms each signal represents are δ 7.3 (5H), δ 5.1 (2H) and δ 2.1 (3H).

Is our answer reasonable?

Check that the sum of the number of hydrogen atoms for each signal equals the total number of hydrogen atoms in the molecule.

PRACTICE EXERCISE 20.11

The integration values of the two signals in the ^{1}H-NMR spectrum of a ketone with molecular formula $C_7H_{14}O$ are given as a ratio of 6.2 to 1.0. Calculate the number of hydrogen atoms giving rise to each signal, and propose a structural formula for this ketone.

Chemical Shift

The position of a signal along the *x*-axis of an NMR spectrum is known as the chemical shift of that signal. The chemical shift of a signal in a ^{1}H-NMR spectrum can give us valuable information about the type of hydrogen atoms giving rise to that absorption. Hydrogen atoms on methyl groups bonded to sp^3 hybridised carbons, for example, typically give a signal near δ 0.8 -1.0 (see figure 20.33 for an example). Hydrogen atoms on methyl groups bonded to a carbonyl carbon give signals near δ 2.0 –2.3 (see figures 20.27 and 20.29), and hydrogen atoms on methyl groups bonded to oxygen give signals near δ 3.7–3.9 (see figure 20.27). Table 20.9 lists the average chemical shift for most of the types of hydrogen atoms we deal with in this text. Notice that most of the values shown fall within a rather narrow range from 0 to 12 δ units (ppm). In fact, although the table shows a variety of functional groups and hydrogen atoms bonded to them, we can use the rules of thumb in figure 20.31 to remember the chemical shifts of most types of hydrogen atom.

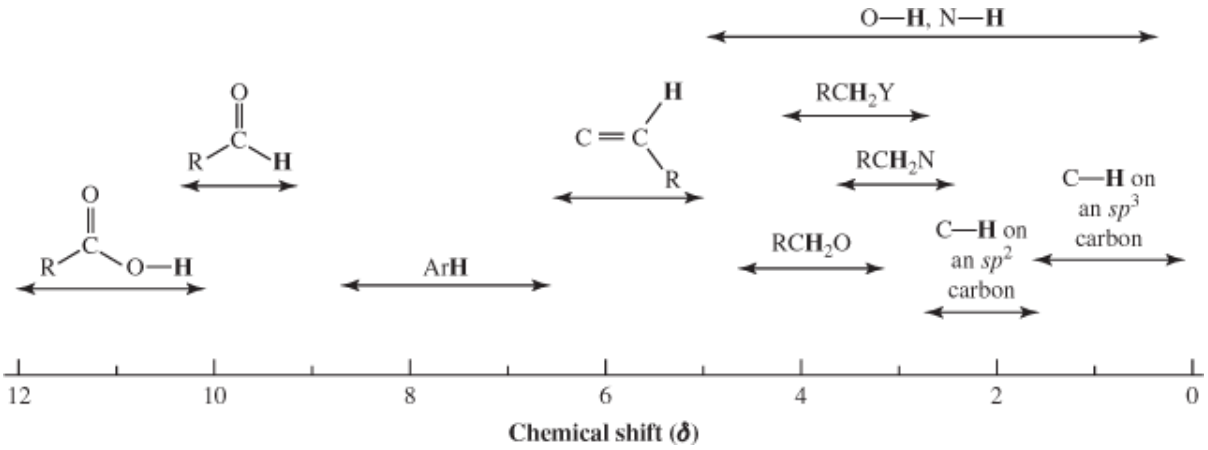


FIGURE 20.31 A simple correlation chart for ^{1}H-NMR chemical shifts. Where the range is labelled RC**H**$_2$Y (Y = halogen, N or O), shifts for methyl and methine hydrogen atoms, R$_2$C**H**Y, also fall within this range (with the methyl being at slightly lower chemical shift and the methine at slightly higher chemical shift).

TABLE 20.9 Average values of chemical shifts of representative types of hydrogen atoms

Type of hydrogen[a]	Chemical shift (δ)[b]
(C**H**^{3})^{4}Si	(by definition)
RC**H**^{3}	0.8–1.0
RC**H**^{2}R	1.2–1.4
R^{3}C**H**	1.4 -1.7
R^{2}C═CRC**H**R$_2$	1.6–2.6

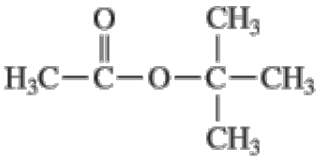
RC≡C**H**	2.0–3.0
Ar**CH**$_3$	2.2–2.5
ArCM**H**$_2$R	2.3–2.8
RO**H**	0.5–6.0
RC**H**$_2$OH	3.4–4.0
R$_2$N**H**	0.5–5.0
R$_2$N**H**	0.5–5.0
RC(=O)C**H**$_3$	2.0–2.3
RC(=O)C**H**$_2$R	2.2–2.6
RC(=O)OC**H**$_3$	3.7–3.9
RC(=O)OC**H**$_2$R	4.1–4.7
RC**H**$_2$I	3.1–3.3
RC**H**$_2$Br	3.4–3.6
RC**H**^{2}Cl	3.6–3.8
RC**H**^{2}F	4.4–4.5
Ar**OH**	4.5–10
R$_2$C=C**H**^{2}	4.6–5.0
R2C=C**H**R	5.0–5.7
Ar**H**	6.5–8.5
RC(=O)**H**	9.5–10.1
RC(=O)O**H**	10–12

(a) R = alkyl group, Ar = aryl group.
(b) Values are approximate. Other atoms within the molecule may cause the signal to appear outside these ranges.

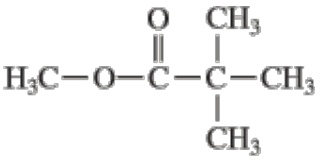
WORKED EXAMPLE 20.13

Identifying Isomers Using Chemical Shift Data

The following are two constitutional isomers with the molecular formula $C_6H_{12}O_2$.



isomer 1



isomer 2

(a) Predict the number of signals in the ^{1}H-NMR spectrum of each isomer.

(b) Predict the ratio of areas of the signals in each spectrum.

(c) Show how these isomers may be distinguished on the basis of chemical shift.

Analysis

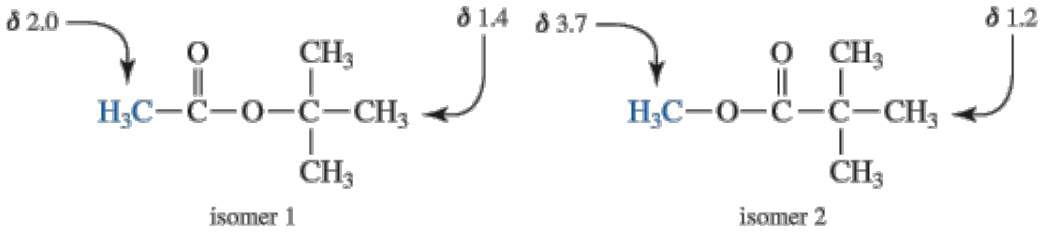
First identify the types of different hydrogen atoms and then the numbers of each type. Now carefully examine the two structures and identify the key differences. If there are any hydrogen atoms in very different environments, then the signals due to these hydrogen atoms will be most important in distinguishing between the two structures.

Solution

(a) Each compound contains a set of nine equivalent methyl hydrogen atoms and a set of three equivalent methyl hydrogen atoms.

(b) The ^{1}H-NMR spectrum of each consists of two signals in the ratio 9 : 3 or 3 : 1.

(c) The two constitutional isomers can be distinguished by the chemical shift of the single —CH_3 group (shown in blue for each compound). Using our rules of thumb in figure 20.31, we find that the hydrogen atoms of CH_3O are less shielded (appear further downfield) than the hydrogen atoms of $CH_3C{=}O$. Table 20.9 gives approximate values for each chemical shift. Experimental values are as follows:

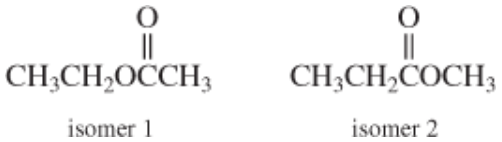


Is our answer reasonable?

Check the correlation tables to ensure that the chemical shifts are correct.

PRACTICE EXERCISE 20.12

(a) The following are two constitutional isomers with molecular formula $C_4H_8O_2$.

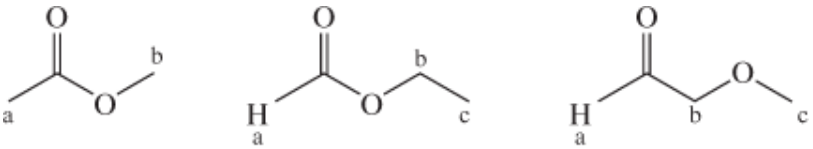


i. Predict the number of signals in the ^{1}H-NMR spectrum of each isomer.

ii. Predict the ratio of areas of the signals in each spectrum.

iii. Show how these isomers may be distinguished on the basis of chemical shift.

(b) Consider the compounds in worked example 20.7. We have already determined the number of signals as shown below.



i. Predict the ratio of areas of the signals in each spectrum.

ii. Show how these isomers may be distinguished on the basis of chemical shift.

Signal Splitting and the (*n* + 1) Rule

We have now seen three kinds of information that can be derived from an examination of a ^{1}H-NMR spectrum:

1. From the number of signals, we can determine the minimum number of sets of equivalent hydrogen atoms.
2. By integrating over signal areas, we can determine the relative numbers of hydrogen atoms giving rise to each signal.
3. From the chemical shift of each signal, we can derive information about the types of hydrogen atoms in each set.

We can derive a fourth kind of information from the **splitting pattern** of each signal. Consider the ^{1}H-NMR spectrum of 1,1,2-trichloroethane (figure 20.32), a solvent for waxes and natural resins. This molecule contains two 2° hydrogen atoms and one 3° hydrogen atom, and, according to what we have learned so far, we predict two signals with relative areas 2 : 1, corresponding to the two hydrogen atoms of the —CH_2Cl group and the one hydrogen atom of the —$CHCl_2$ group. You see from the spectrum, however, that there are in fact five peaks. How can this be when we predict only two signals? The answer is that a hydrogen atom's resonance frequency can be affected by the tiny magnetic fields of other hydrogen atoms close by. Those fields cause the signal to be split into numerous peaks. A signal may be split into two peaks (called a **doublet**, d), three peaks (a **triplet**, t), four peaks (a **quartet**, q) and so on. A signal that has not been split is referred to as a **singlet** (s) and those with **complex splitting patterns** are termed **multiplets** (m). In general, signals are split if there are hydrogen atoms on adjacent carbon atoms. Signal splitting when there are more than three bonds between the hydrogen atoms, as in H—C—C—C—H, are uncommon, except when π bonds are involved (for example, in aromatic rings).

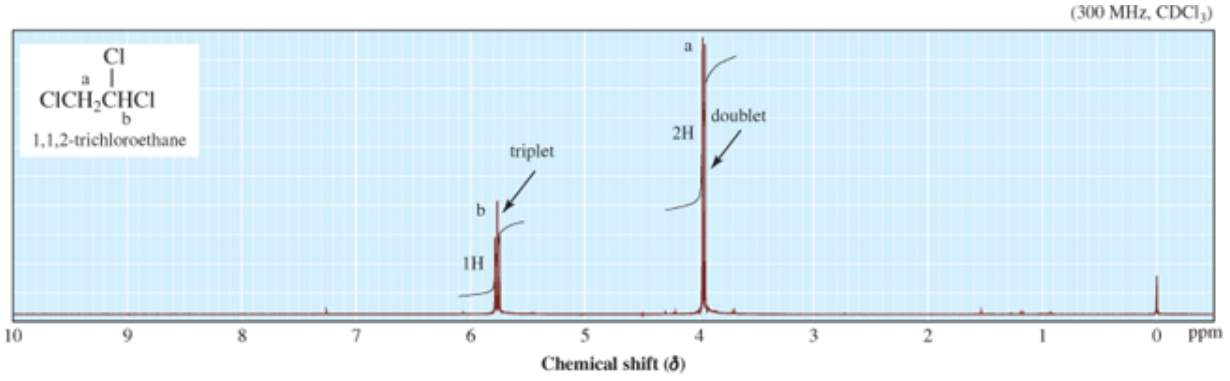


FIGURE 20.32 ^{1}H-NMR spectrum of 1,1,2-trichloroethane.

The signal at δ 4.0 in the ^{1}H-NMR spectrum of 1,1,2-trichloroethane is due to the hydrogen atoms of the —CH_2Cl group, and the signal at δ 5.8 is due to the single hydrogen of the —$CHCl_2$ group.

We say that the CH_2 signal at δ 4.0 is split into a doublet and that the CH signal at δ 5.8 is split into a triplet. In this phenomenon, called **signal splitting**, the ^{1}H-NMR signal from one set of hydrogen atoms is split by the influence of neighbouring hydrogen atoms that are equivalent to each other but not equivalent to the hydrogen atom(s) giving rise to the signal. The degree of signal splitting can be predicted on the basis of the **(*n* + 1) rule**, where *n* is the number of hydrogen atoms equivalent to each other on adjacent carbon atoms. Note that, if the signal due to H_a is split by H_b on an adjacent carbon atom, then the signal due to H_b is also split by H_a. No signal splitting is observed between equivalent neighbouring hydrogen atoms. For example, the spectrum of 1,2-dichloroethane has only one signal (a

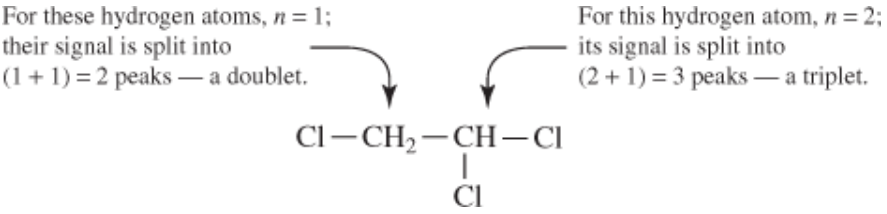
singlet) at δ 3.7.

Pascal's triangle can be used to describe the splitting pattern (also called the **multiplicity**) and the peak intensities within split signals, as shown in table 20.10.

TABLE 20.10 Multiplicity and relative intensities of peaks in split signals

Number of equivalent hydrogen atoms causing splitting	Multiplicity	Relative peak intensities
1	doublet	1 : 1
2	triplet	1 : 2 : 1
3	quartet	1 : 3 : 3 : 1
4	quintet	1 : 4 : 6 : 4 : 1
5	sextet	1 : 5 : 10 : 10 : 5 : 1
6	septet	1 : 6 : 15 : 20 : 15 : 6 : 1

Let us apply the (n + 1) rule to the analysis of the spectrum of 1,1,2-trichloroethane (figure 20.32). The two hydrogen atoms of the —CH_2Cl group have one neighbouring hydrogen (n = 1), so their signal is split into a doublet (1 + 1 = 2). The single hydrogen atom of the —$CHCl_2$ group has a set of two equivalent neighbouring hydrogen atoms (n = 2), so its signal is split into a triplet (2 + 1 = 3).



Let us now consider the splitting pattern in 1-chloropropane (figure 20.33). The two hydrogen atoms on C(1) have two neighbouring equivalent hydrogen atoms on the adjacent carbon atom and so the signal (δ 3.5) for these hydrogen atoms is split into a triplet (2 + 1). Similarly, the signal due to the three hydrogen atoms on C(3) (δ 1.1) is split into a triplet. The two hydrogen atoms on C(2) are flanked on one side by a set of two hydrogen atoms on C(1), and on the other side by a set of three hydrogen atoms on C(3). Because the sets of hydrogen atoms on C(1) and C(3) are not equivalent to each other, they can cause the signal for the CH_2 group on C(2) to be split into a complex pattern, which we will refer to simply as a multiplet. If the magnitude of the splitting between the hydrogen atoms of C(1) and C(2) is equal to that between C(2) and C(3), then we can describe the signal as a sextet. The (n + 1) rule can be used in cases where the coupling between the observed hydrogen atom(s) and adjacent nonequivalent hydrogen atoms is equal.

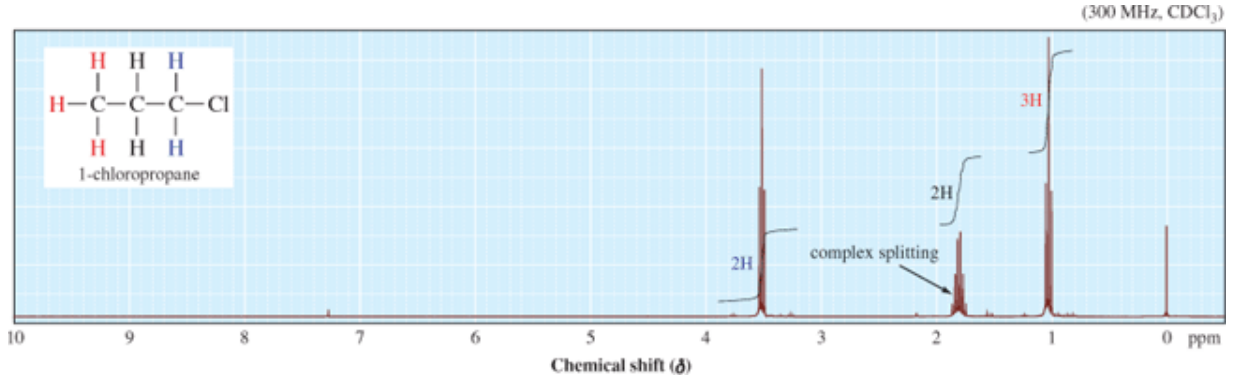


FIGURE 20.33 ^{1}H-NMR spectrum of 1-chloropropane.

WORKED EXAMPLE 20.14

Splitting Patterns

Predict the number of signals and the splitting pattern of each signal in the ^{1}H-NMR spectrum of each of the following compounds.

(a) $CH_3CCH_2CH_3$ (O)

(b) $CH_3CH_2CCH_2CH_3$ (O)

(c) $CH_3CCH(CH_3)_2$ (O)

Analysis

First identify the different types of hydrogen atoms. Now consider the number of hydrogen atoms on the neighbouring carbon atom. Applying the (n + 1) rule will give the splitting pattern.

Solution

The sets of equivalent hydrogen atoms in each molecule are colour coded below. In molecule (a), the signal for the red methyl group is unsplit (a singlet) because the group is too far (> 3 bonds) from any other hydrogen atoms. The blue —CH_2— group has three equivalent neighbouring hydrogen atoms (n = 3) so it shows a signal split into a quartet (3 + 1 = 4). The green methyl group has two equivalent neighbouring hydrogen atoms (n = 2) so its signal is split into a triplet. The integration ratios for these signals would be 3 : 2 : 3.

Molecules (b) and (c) can be analysed in the same way. Thus, molecule (b) shows a triplet and a quartet in a 3 : 2 ratio (remember that the two CH_2 groups are equivalent, as are the two CH_3 groups). Molecule (c) shows a singlet, a septet (6 + 1 = 7) and a doublet in the ratio 3 : 1 : 6.

(a) singlet, quartet, triplet — $CH_3-C(=O)-CH_2-CH_3$

(b) singlet, septet, doublet — $CH_3-C(=O)-CH(CH_3)_2$

(c) triplet, quartet, quartet, triplet — $CH_3-CH_2-C(=O)-CH_2-CH_3$

Is our answer reasonable?

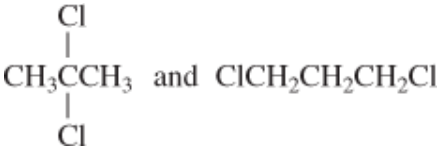
Check that you have considered only the hydrogen atoms on neighbouring atoms.

PRACTICE EXERCISE 20.13

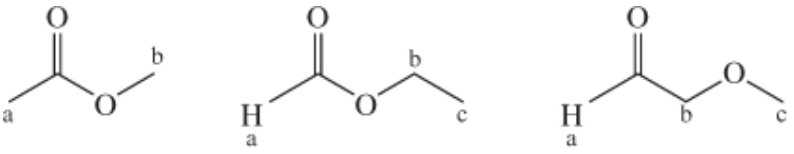
(a) The following are pairs of constitutional isomers. Predict the number of signals and the splitting pattern of each signal in the ^{1}H-NMR spectrum of each isomer.

i. $CH_3OCH_2CCH_3$ (O) and $CH_3CH_2COCH_3$ (O)

ii.



(b) Determine the multiplicities for each type of hydrogen atom in the esters from worked example 20.7 (p. 881). Although these compounds can be distinguished without considering multiplicity, it is a useful check that your initial analysis is correct.

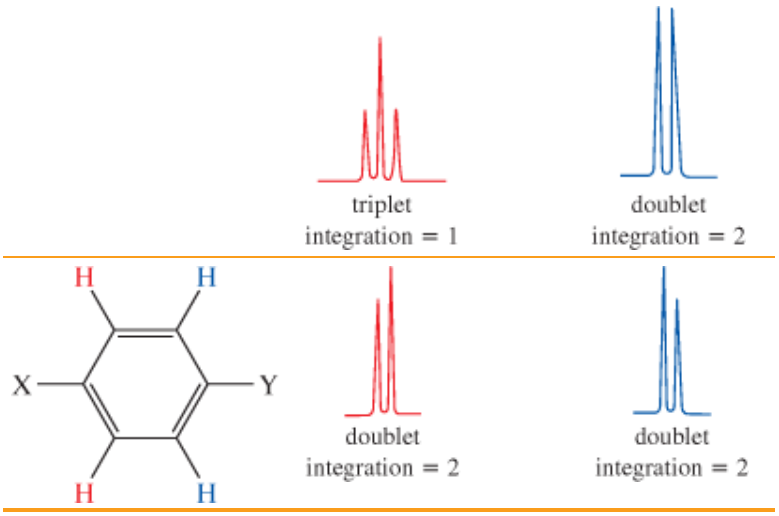


Splitting patterns give valuable information about the number of hydrogen atoms on neighbouring carbon atoms. For example, a triplet indicates that there are two equivalent hydrogen atoms on neighbouring carbon atoms and a quartet that there are three equivalent neighbouring hydrogen atoms.

A word of caution: Students often confuse information obtained from integration with that from multiplicity. *Integration values indicate the number of hydrogen atoms giving rise to a signal. Multiplicity indicates the number of equivalent hydrogen atoms on adjacent carbon atoms.* Table 20.11 shows some common splitting patterns and the corresponding structural units.

TABLE 20.11 Characteristic splitting patterns for common organic groups

Group	Splitting patterns	
X — CH_2CH_3 ethyl group	quartet, integration = 2	triplet, integration = 3
X — $CH_2(CH_3)_2$ isopropyl group	septet, integration = 1	doublet, integration = 6
X_2CHCH_3	quartet, integration = 1	doublet, integration = 3
X — CH_2CH_2 – Y	triplet, integration = 2	triplet, integration = 2
X_2CHCH_2 — X		



X is different from Y. It is assumed that the hydrogen atoms in the groups shown are not coupled to other hydrogen atoms.

^{13}C-NMR Spectroscopy

Nuclei of ^{12}C, the most abundant (98.89%) natural isotope of carbon, do not have a nuclear spin and so are not detected by NMR spectroscopy. Nuclei of ^{13}C (natural abundance 1.11%), however, do have nuclear spin and so are detected by NMR spectroscopy in the same manner as hydrogen atoms are detected.

In the most common mode for recording a ^{13}C spectrum, a proton decoupled spectrum, all ^{13}C signals appear as singlets. The ^{13}C-NMR spectrum of citric acid (figure 20.34), a compound used to increase the solubility in water of many pharmaceutical drugs, consists of four singlets. Notice that, as in ^{1}H-NMR, equivalent carbon atoms generate only one signal.

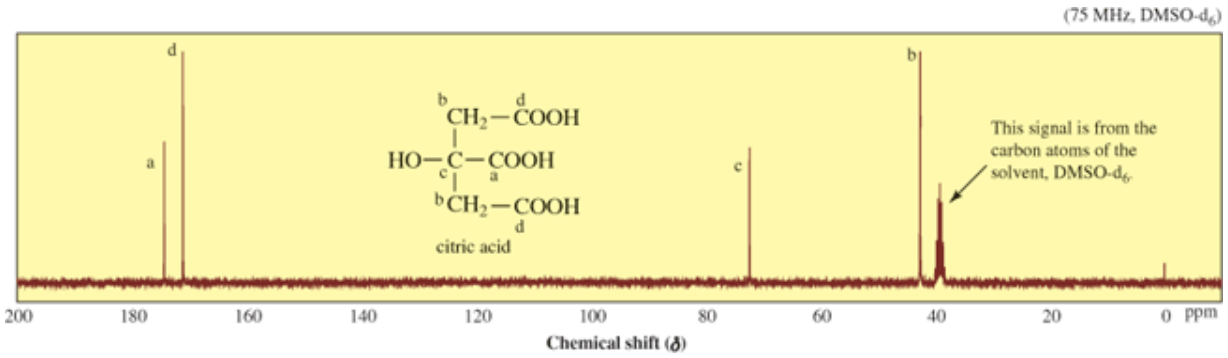


FIGURE 20.34 The ^{13}C-NMR spectrum of citric acid.

Figure 20.35 is a simple correlation chart for remembering the ^{13}C-NMR chemical shifts of various carbon atoms. If you compare this with figure 20.31, a correlation chart for ^{1}H-NMR chemical shifts, you will notice that signals for the C atoms fall in approximately the same relative region of the spectrum as their corresponding H atoms in the various functional groups. Table 20.12 shows approximate chemical shifts in ^{13}C-NMR spectroscopy.

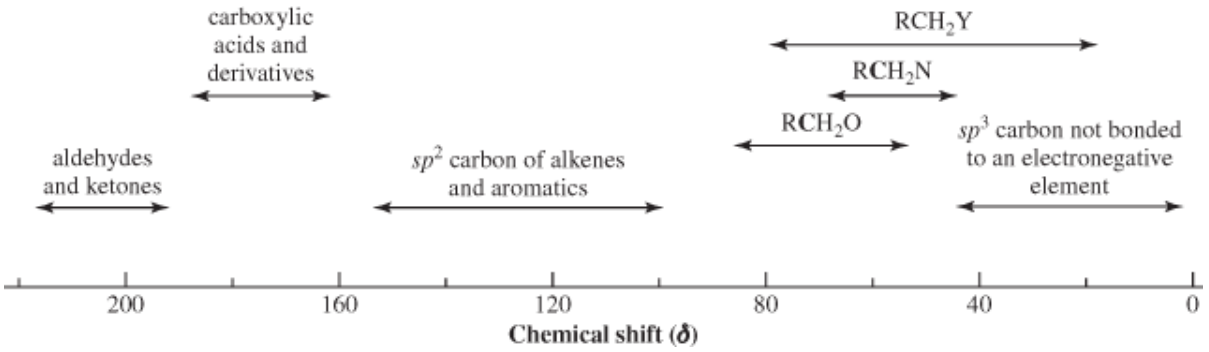


FIGURE 20.35 Carbon chemical shifts for common functional groups.

Notice how much broader the range of chemical shifts is for ^{13}C-NMR spectroscopy than for ^{1}H-NMR spectroscopy. Whereas most chemical shifts for ^{1}H-NMR spectroscopy fall within a rather narrow range of 0 -12 ppm, those for ^{13}C-NMR spectroscopy cover 0–210 ppm. Because of this expanded scale, it is very unusual to find any two nonequivalent carbon atoms in the same molecule with identical chemical shifts. Most commonly, each different type of carbon atom within a molecule has a distinct signal that is clearly resolved from all other signals. Notice further that the chemical shift of carbonyl carbon atoms is quite distinct from the chemical shifts of sp^3 hybridised carbon atoms and other types of sp^2 hybridised carbon atoms. The presence or absence of a carbonyl carbon atom is quite easy to recognise in a ^{13}C-NMR spectrum.

A great advantage of ^{13}C-NMR spectroscopy is that it is generally possible to count the number of different types of carbon atoms in a molecule. However, because of the particular manner in which ^{13}C-NMR spectra are obtained, integrating signal areas is often unreliable, and it is generally not possible to determine the number of carbon atoms of each type on the basis of the signal areas.

WORKED EXAMPLE 20.15

^{13}C-NMR spectra

Predict the number of signals in the ^{13}C-NMR spectrum of each of the following compounds.

(a) 

(b) 

(c) 

Analysis

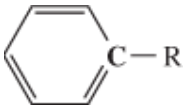
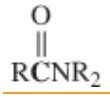
Check for symmetry. If there is no symmetry, the number of signals will equal the number of carbon atoms. If there is symmetry, the number of signals will be less than the number of carbon atoms. Count the number of nonequivalent carbon atoms.

Solution

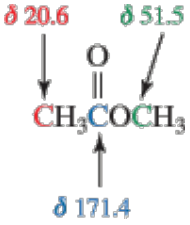
The diagram below shows the number of signals in each spectrum, along with the chemical shift of each, colour coded to the carbon atom responsible for that signal. The chemical shifts of the carbonyl carbon atoms are quite distinctive (table 20.12) and are δ 171.4, 208.9, and 212.0 in these examples.

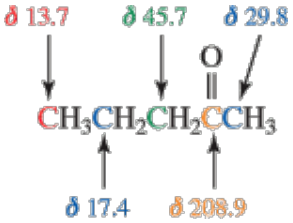
TABLE 20.12 ^{13}C-NMR chemical shifts

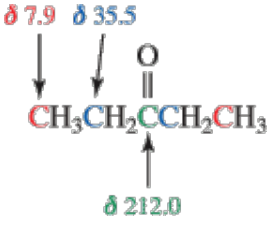
Type of carbon	Chemical shift (δ)[a]

RCH_3	
RCH_2R	15–55
R_3CH	20–60
RCH_2I	0–40
RCH_2Br	25–65
RCH_2Cl	35–80
R_3COH	40–80
R_3COR	40–80
$RC{\equiv}CR$	65–85
$R_2C{=}CR_2$	100–150
	110–160
	160–180
	165–180
	175–185
	180–210

(a) Values are approximate. Other atoms within the molecule may cause the signal to appear outside these ranges.

(a) 

(b) 

(c) 

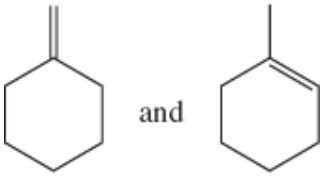
Is our answer reasonable?

Have you identified every carbon atom (this is particularly important when condensed structures or line structures are used)? Check also that you have not overlooked any symmetry.

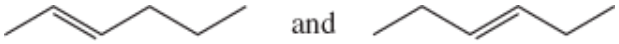
PRACTICE EXERCISE 20.14

Explain how to distinguish between the members of each of the following pairs of constitutional isomers on the basis of the number of signals in the ^{13}C-NMR spectrum of each isomer.

(a)



(b)



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20.6 Interpreting NMR Spectra

Interpreting NMR spectroscopic data is a skill that is best acquired through practice and exposure to examples. In this section, we will see specific examples of NMR spectra for characteristic functional groups. Familiarising yourself with them will help you to master the technique of spectral interpretation.

Alkanes

Because all hydrogen atoms in alkanes are in similar chemical environments, ^{1}H-NMR chemical shifts of their hydrogen atoms fall within a narrow range of δ 0.8 -1.7, so signals often overlap. Chemical shifts for alkane carbon atoms in ^{13}C-NMR spectroscopy fall within the wider range of δ 0 - 60. Notice how it is relatively easy to distinguish all the signals in the ^{13}C-NMR spectrum of 2,2,4-trimethylpentane (common name isooctane, figure 20.36), a major component in petrol, compared with the signals in the ^{1}H-NMR spectrum of 2,2,4-trimethylpentane (figure 20.37). In the ^{13}C-NMR spectrum, we can see all five signals; in the ^{1}H-NMR spectrum, we expect to see four signals but, in fact, we see only three. The reason is that nonequivalent hydrogen atoms often have similar chemical shifts, which lead to an overlap of signals. Note that, in the ^{13}C-NMR spectrum below, the three closely spaced peaks at δ 77 are due to the solvent $CDCl_3$. In fact, a signal due to the solvent is observed in all ^{13}C-NMR spectra, except those run in D_2O.

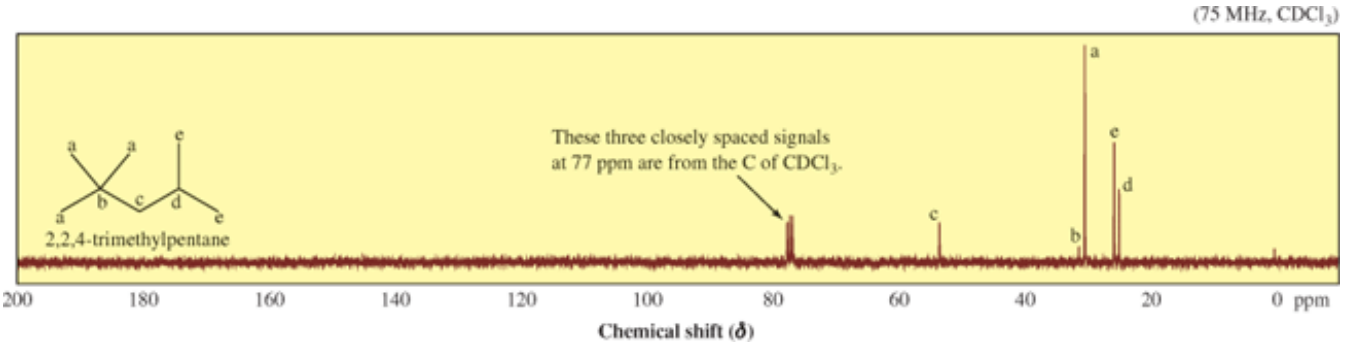


FIGURE 20.36 ^{13}C-NMR spectrum of 2,2,4-trimethylpentane, showing all five signals.

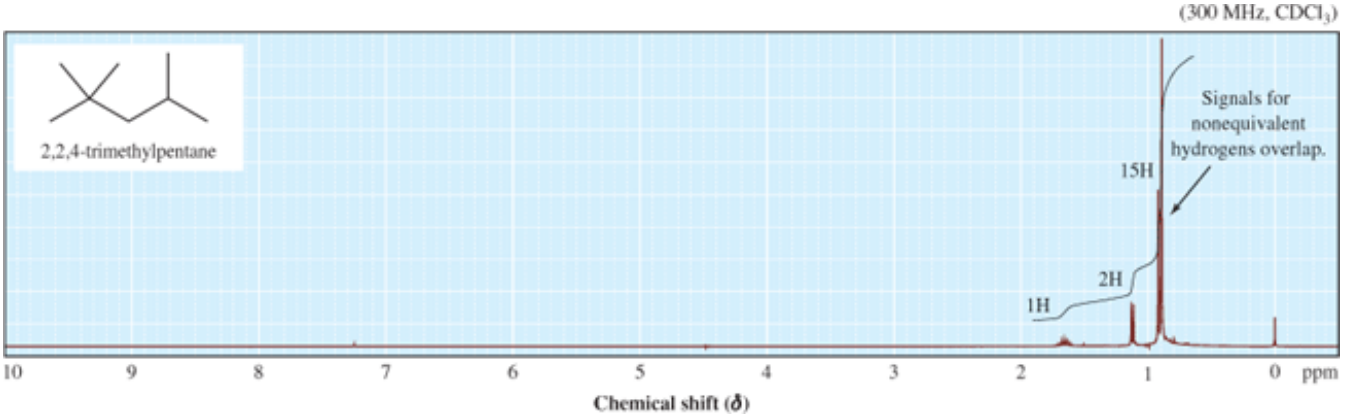


FIGURE 20.37 ^{1}H-NMR spectrum of 2,2,4-trimethylpentane, showing only three signals. Two sets of nonequivalent hydrogen atoms produce signals at δ 0.9, giving an integration ratio of 1 : 2 : 15 for the peaks at δ 1.7, 1.1 and 0.9, respectively.

Alkenes

The ^{1}H-NMR chemical shifts of vinylic hydrogen atoms (hydrogen atoms on a carbon atom of a carbon–

carbon double bond) are larger than those of alkane hydrogen atoms and typically fall into the range δ 4.6 – 5.7. Figure 20.38 shows a ^{1}H-NMR spectrum of 1-methylcyclohexene. The signal for the one vinylic hydrogen atom appears at δ 5.4 split into a triplet by the two hydrogen atoms of the neighbouring —CH_2— group of the ring.

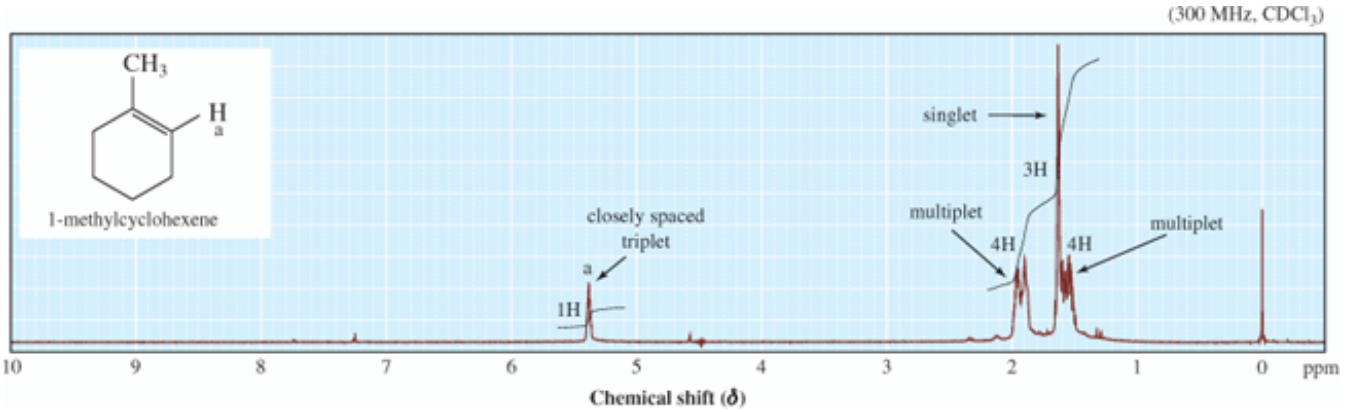


FIGURE 20.38 1H-NMR spectrum of 1-methylcyclohexene.

The sp^2 hybridised carbons of alkenes come into resonance in ^{13}C-NMR spectroscopy in the range δ 100 -150 (table 20.12), which is considerably downfield from resonances of sp^3 hybridised carbons.

Alcohols

The chemical shift of a hydroxyl hydrogen atom in a ^{1}H-NMR spectrum is variable and depends on the purity of the sample, the solvent, the concentration and the temperature. Normally, the shift appears in the range δ 3.0 - 4.5, but, depending on experimental conditions, it may have a chemical shift as low as δ 0.5. Hydrogen atoms on the carbon atom bearing the —OH group are deshielded by the electron-withdrawing inductive effect of the oxygen atom, and their absorptions typically appear in the range δ 3.4 - 4.0. Figure 20.39 shows a ^{1}H-NMR spectrum of 2,2-dimethyl-propan-1-ol. The spectrum consists of three signals. The hydroxyl hydrogen atom appears at δ 2.2 as a slightly broad singlet. The signal of the hydrogen atoms on the carbon atom bearing the hydroxyl group in 2,2-dimethylpropan-1-ol appears as a singlet at δ 3.3.

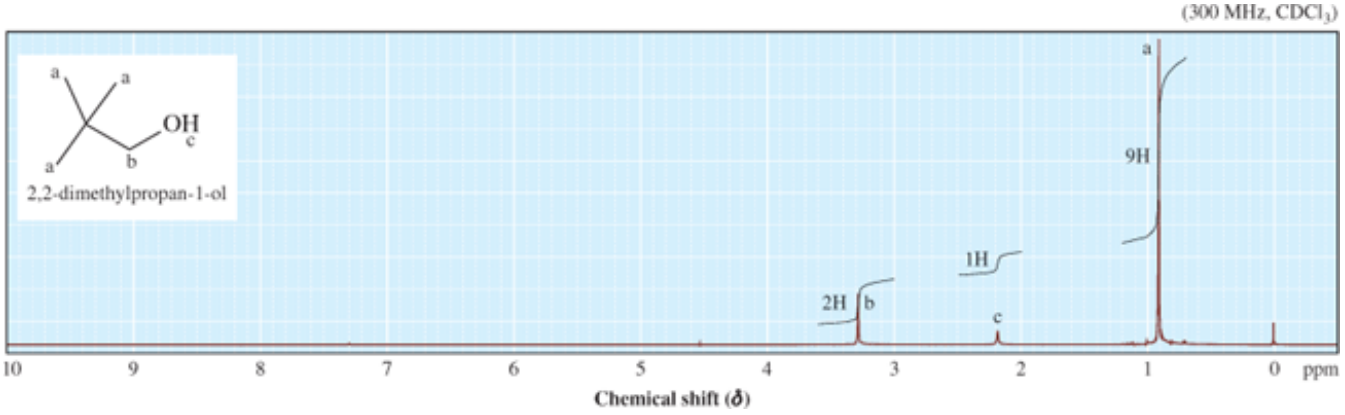
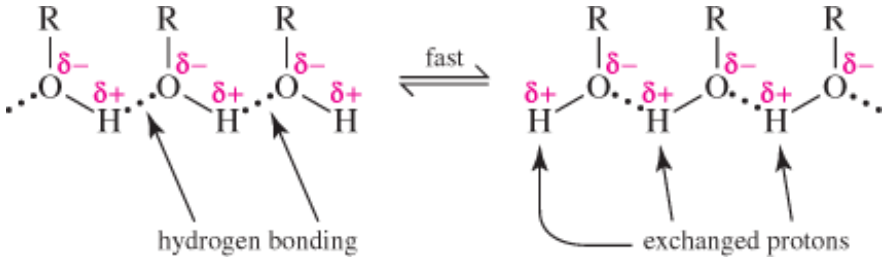


FIGURE 20.39 ^{1}H-NMR spectrum of 2,2-dimethylpropan-1-ol.

Signal splitting between the hydrogen atom on the—OH group and its neighbours on the adjacent —CH_2— group is not seen in the ^{1}H-NMR spectrum of 2,2-dimethylpropan-1-ol. The reason is that traces of acid, base or other impurities in the NMR solvent or the sample catalyse the transfer of the hydroxyl proton from the oxygen atom of one alcohol molecule to that of another alcohol molecule.



Signals from alcohol hydrogen atoms typically appear as broad singlets, as shown in the ^{1}H-NMR spectrum of 3,3-dimethylbutan-1-ol (figure 20.40).

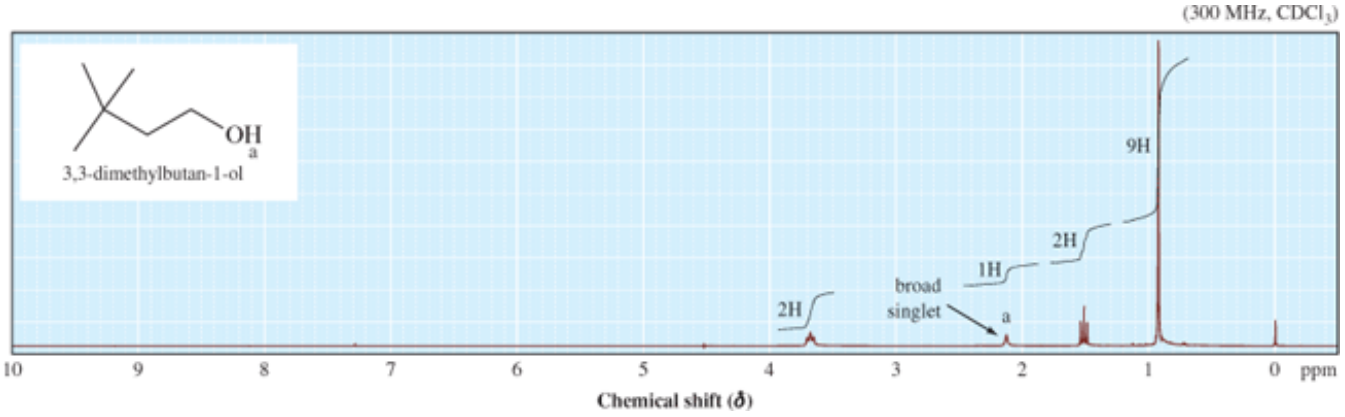


FIGURE 20.40 ^{1}H-NMR spectrum of 3,3-dimethylbutan-1-ol, showing the broad hydroxyl signal at δ 2.1.

Benzene and its Derivatives

All six hydrogen atoms of benzene are equivalent, and their signal appears in its ^{1}H-NMR spectrum as a sharp singlet at δ 7.3. Hydrogen atoms bonded to a substituted benzene ring appear in the region δ 6.5–8.5. Few other types of hydrogen atoms give signals in this region; thus, aromatic hydrogen atoms are quite easily identifiable by their distinctive chemical shifts.

Recall that vinylic hydrogen atoms appear at δ 4.6–5.7. Hence, aromatic hydrogen atoms absorb radiation of even higher frequency than vinylic hydrogen atoms.

The ^{1}H-NMR spectrum of toluene (figure 20.41) shows a singlet at δ 2.3 for the three hydrogen atoms of the methyl group and a closely spaced multiplet at δ 7.3 for the five hydrogen atoms of the aromatic ring. The hydrogen atoms of an aromatic ring can produce quite complex signals as seen in the spectrum of ethyl benzoate (figure 20.42) with a multiplet at δ 8.1 (integrating for two hydrogen atoms) and a multiplet at δ 7.5 (integrating for three hydrogen atoms). The spectrum also shows the typical triplet (δ 1.4) and quartet (δ 4.4) pair of signals characteristic of an ethoxy group.

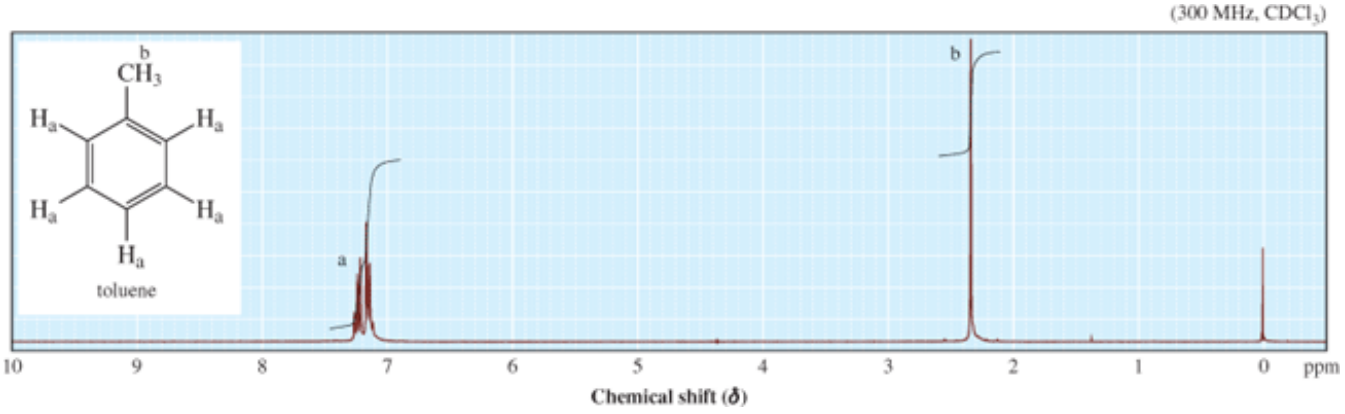


FIGURE 20.41 ^{1}H-NMR spectrum of toluene.

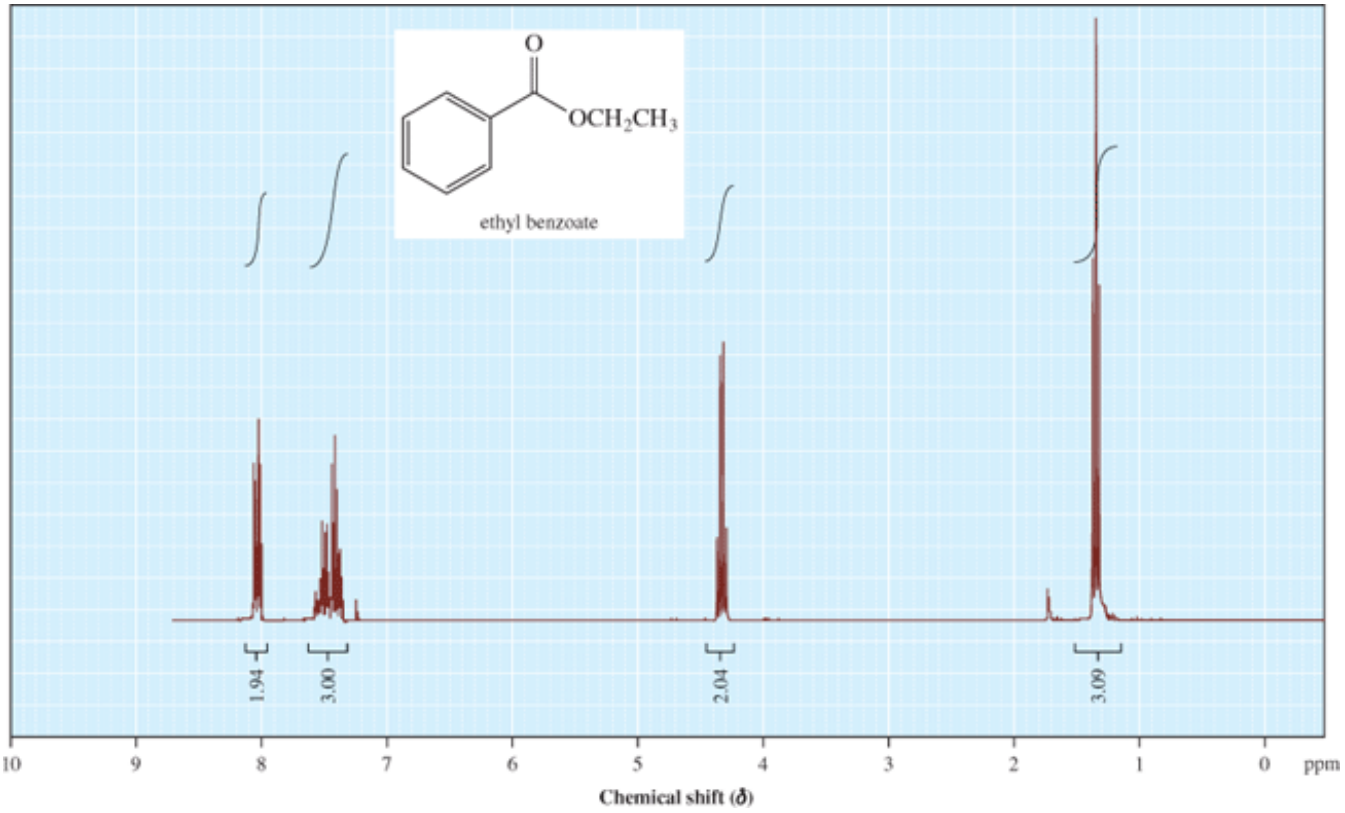


FIGURE 20.42 ^{1}H-NMR spectrum of ethyl benzoate.

In ^{13}C-NMR spectroscopy, carbon atoms of aromatic rings appear in the range δ 110 -160. Benzene, for example, shows a single signal at δ 128. Because ^{13}C signals for alkene carbon atoms appear in the same range, it is generally not possible to establish the presence of an aromatic ring by ^{13}C-NMR spectroscopy alone. However, ^{13}C-NMR spectroscopy is particularly useful in establishing substitution patterns of aromatic rings. The ^{13}C-NMR spectrum of 2-chlorotoluene (figure 20.43) shows six signals in the aromatic region; the compound's more symmetric isomer 4-chlorotoluene (figure 20.44) shows only four signals in the aromatic region. Thus, to distinguish between these constitutional isomers, just count the signals. Notice in the ^{13}C-NMR spectra below that the signal intensities are not proportional to the number of equivalent carbon atoms giving rise to that signal, so integrating signal areas is often unreliable. This is a consequence of the way in which ^{13}C nuclei return to their lower energy states. Typically, quaternary (4°) carbon atoms (those not bonded to a hydrogen atom) give signals of low intensity.

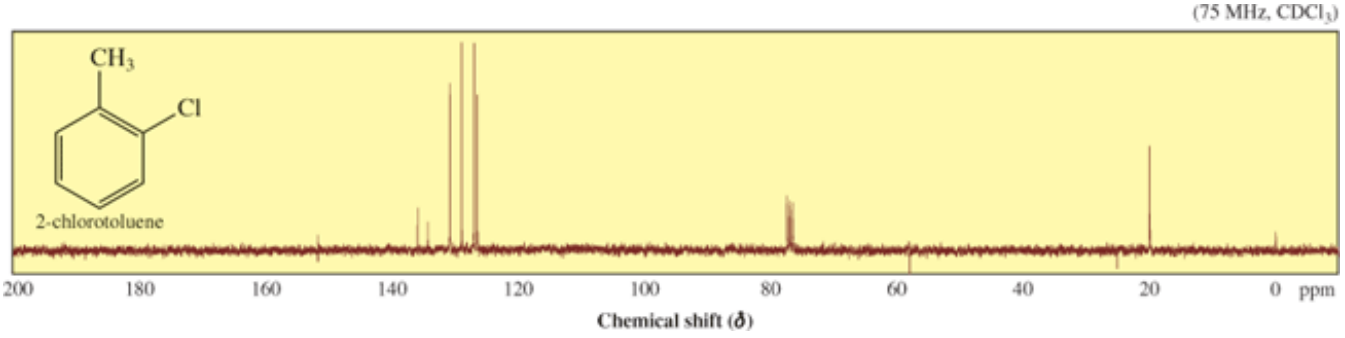


FIGURE 20.43 ^{13}C-NMR spectrum of 2-chlorotoluene.

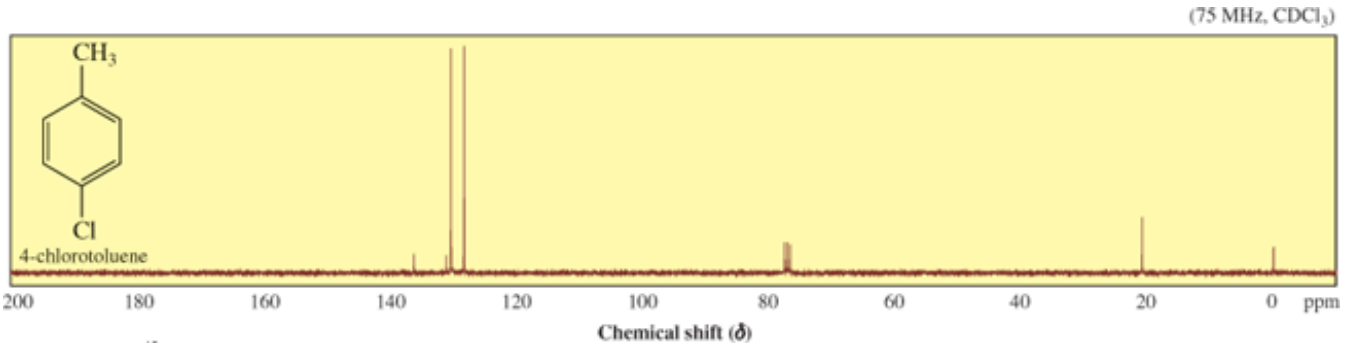
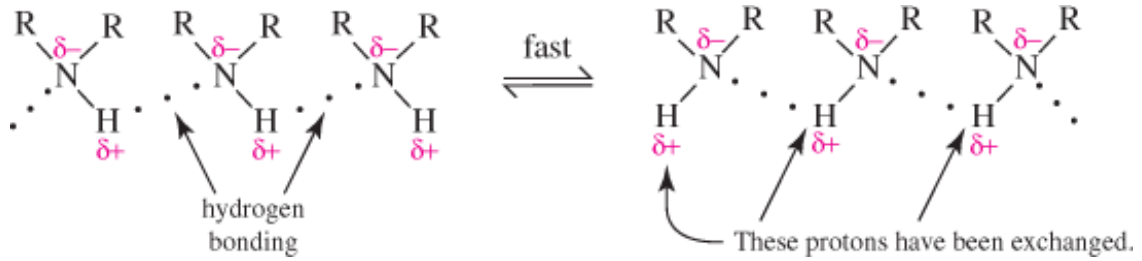


FIGURE 20.44 ^{13}C-NMR spectrum of 4-chlorotoluene.

Amines

The chemical shifts of amine hydrogen atoms, like those of hydroxyl hydrogen atoms, are variable and may be found in the region δ 0.5–5.0, depending on the solvent, the concentration and the temperature. Furthermore, signal splitting is not generally observed between amine hydrogen atoms and hydrogen atoms on an adjacent α-carbon atom due to rapid intermolecular exchange of the N—H hydrogen atoms.



Thus, amine hydrogen atoms generally appear as singlets. The NH_2 hydrogen atoms in benzylamine, $C_6H_5CH_2NH_2$, for example, appear as a singlet at δ 1.4 (figure 20.45).

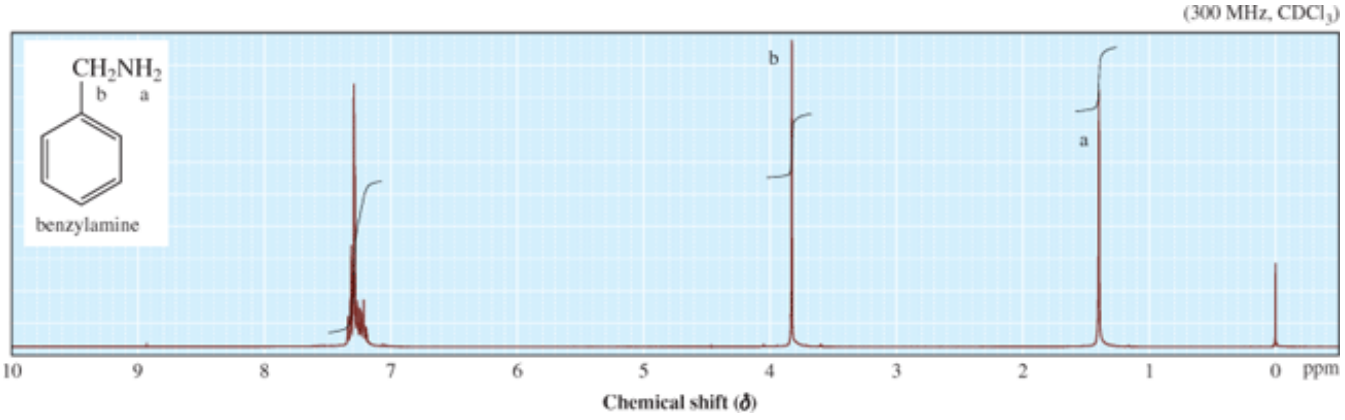


FIGURE 20.45 ^{1}H-NMR spectrum of benzylamine.

Aldehydes and Ketones

^{1}H-NMR spectroscopy is an important tool for identifying aldehydes and for distinguishing between aldehydes and other carbonyl-containing compounds. Just as the signal of a vinylic hydrogen atom has a higher chemical shift (relative to one on an sp^3 hybridised carbon atom), the signal of an aldehyde hydrogen atom also has a higher chemical shift (relative to one on an sp^3 hybridised carbon atom), typically to δ 9.5–10.1. Signal splitting between this hydrogen atom and those on the adjacent α-carbon atom is slight; consequently, the aldehyde hydrogen signal often appears as a closely spaced doublet or triplet. In the spectrum of butanal, for example, the triplet signal for the aldehyde hydrogen atom at δ 9.8 is so closely spaced that it looks almost like a singlet (figure 20.46).

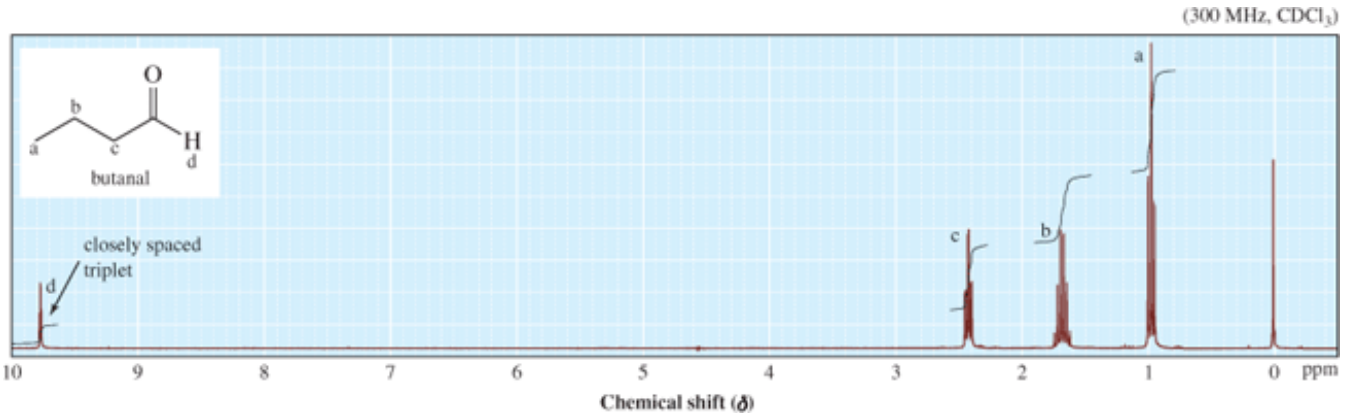


FIGURE 20.46 ^{1}H-NMR spectrum of butanal.

Just as the signal for an aldehyde hydrogen atom is only weakly split by the adjacent nonequivalent α-hydrogen atoms, the α-hydrogen atoms are weakly split by the aldehyde hydrogen atom. Hydrogen atoms on an α-carbon atom of an aldehyde or ketone typically appear around δ 2.1–2.6. The carbonyl carbon atoms of aldehydes and ketones are readily identifiable in 13C-NMR spectroscopy by the position of their signal between δ 180 and 210.

Carboxylic Acids

The hydrogen atom of the carboxyl group gives a signal in the range δ 10–12. The chemical shift of a carboxyl hydrogen atom is so large — even larger than the chemical shift of an aldehyde hydrogen atom (δ 9.5–10.1)— that it serves to distinguish carboxyl hydrogen atoms from most other types of hydrogen atoms. The signal of the carboxyl hydrogen of 2-methylpropanoic acid, labelled ‘c’ on the ^{1}H-NMR spectrum in figure 20.47, has been offset by δ 2.4. (Add 2.4 to the position at which the signal appears on the spectrum.) The chemical shift of this hydrogen is δ 12.0.

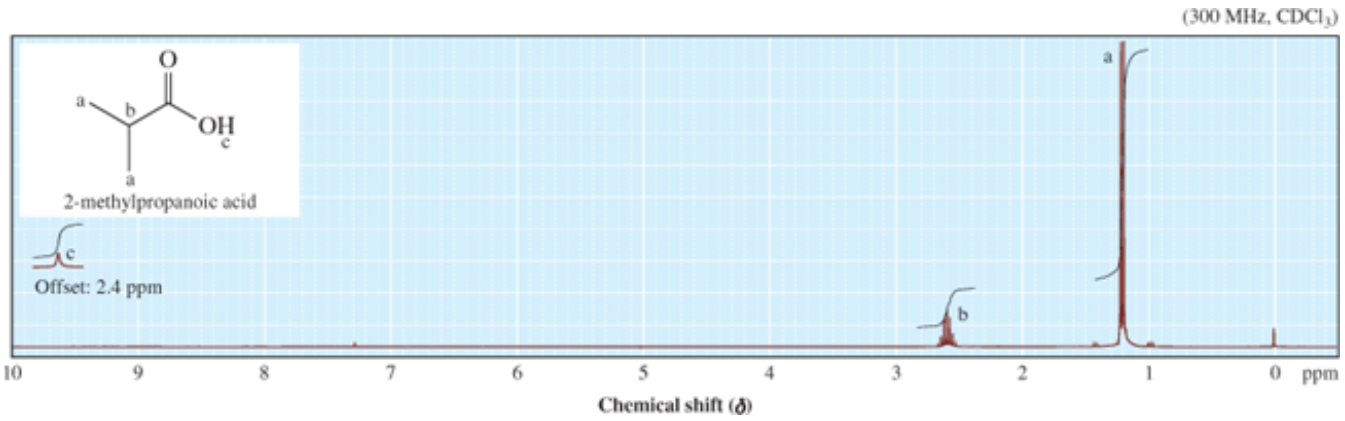
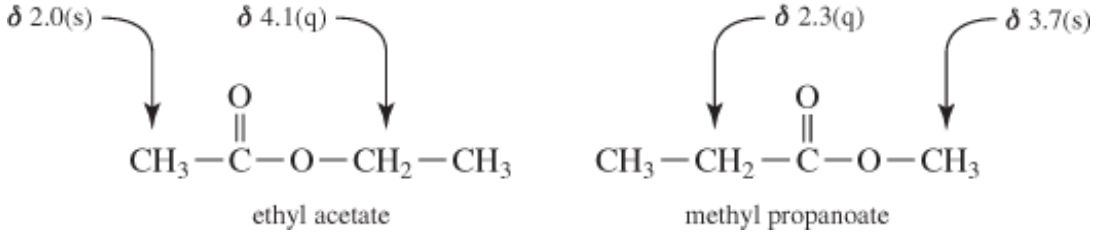


FIGURE 20.47 ^{1}H-NMR spectrum of 2-methylpropanoic acid (isobutyric acid).

Esters

Hydrogen atoms on the α-carbon atom of the carbonyl group of an ester are slightly deshielded and give signals at δ 2.1–2.6. Hydrogen atoms on the carbon atom bonded to the ester oxygen atom are more strongly deshielded and give signals at δ 3.7–4.7. It is thus possible to distinguish between ethyl acetate and its constitutional isomer, methyl propanoate, by the chemical shifts of either the singlet (s) —CH_3 absorption (compare δ 2.0 with 3.7) or the quartet (q) —CH_2— absorption (compare δ 4.1 with 2.3):



Solving NMR Problems

One of the first steps in determining the molecular structure of a compound is to establish the compound's molecular formula. In the past, this was most commonly done by elemental analysis, as described in chapter 3. More commonly today, we determine molecular mass and molecular formula by *mass spectrometry*. In the examples that follow, we assume that the molecular formula of any unknown compound has already been determined and we proceed from there, using spectral analysis to determine a structural formula.

The following steps may prove helpful as a systematic approach to solving ^{1}H-NMR spectral problems:

Step 1: *Molecular formula and index of hydrogen deficiency.* Examine the molecular formula, calculate the index of hydrogen deficiency (section 20.1), and deduce any information you can about the presence or absence of rings or π bonds.

Step 2: *Number of signals.* Count the number of signals to determine the minimum number of sets of equivalent hydrogen atoms in the compound.

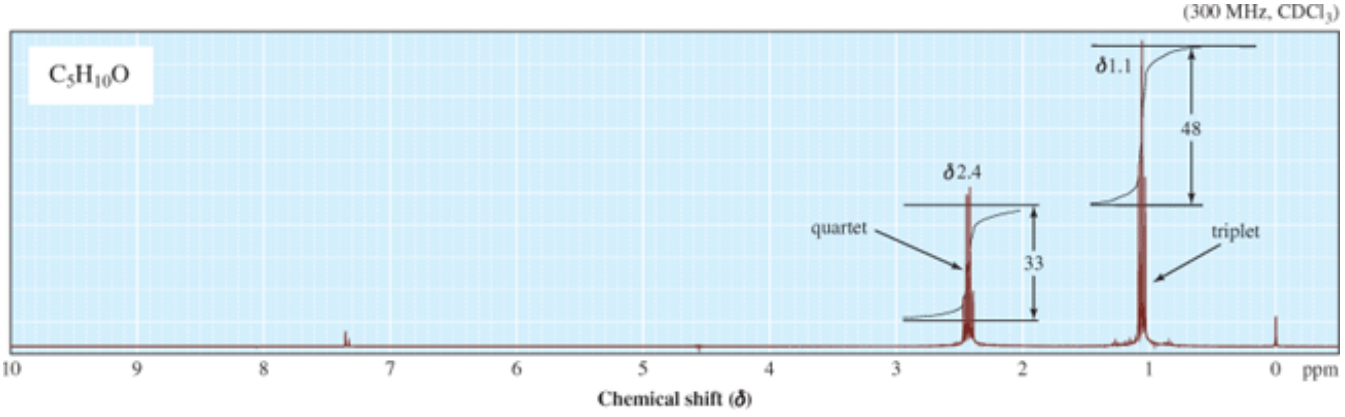
Step 3: *Integration.* Use signal integration and the molecular formula to determine the number of hydrogen atoms in each set.

Step 4: *Pattern of chemical shifts.* Examine the NMR spectrum for signals characteristic of the most common types of equivalent hydrogen atoms. (See the general rules of thumb for ^{1}H-NMR chemical shifts in section 20.5, p. 891.) Keep in mind that the ranges are broad and that hydrogen atoms of each type may be shifted outside the range, depending on details of the molecular structure in question.

Step 5: *Splitting pattern.* Examine splitting patterns for information about the number of nonequivalent neighbouring hydrogen atoms.

Step 6: *Structural formula.* Write a structural formula consistent with the information learned in steps 1–5.

Spectral problem 1: The compound is a colourless liquid with molecular formula $C_5H_{10}O$.



Analysis of spectral problem 1:

Step 1: *Molecular formula and index of hydrogen deficiency.* The reference compound is $C_5H_{12}O$ so the index of hydrogen deficiency is 1 and the molecule contains either one ring or one π bond.

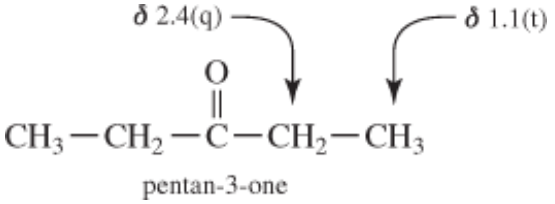
Step 2: *Number of signals.* There are two signals (a triplet and a quartet) so there are two sets of equivalent hydrogen atoms.

Step 3: *Integration.* By signal integration, we calculate that the number of hydrogen atoms giving rise to each signal is in the ratio 3 : 2. Because there are 10 hydrogen atoms, we conclude that the signal assignments are δ 1.1 (6H) and δ 2.4 (4H).

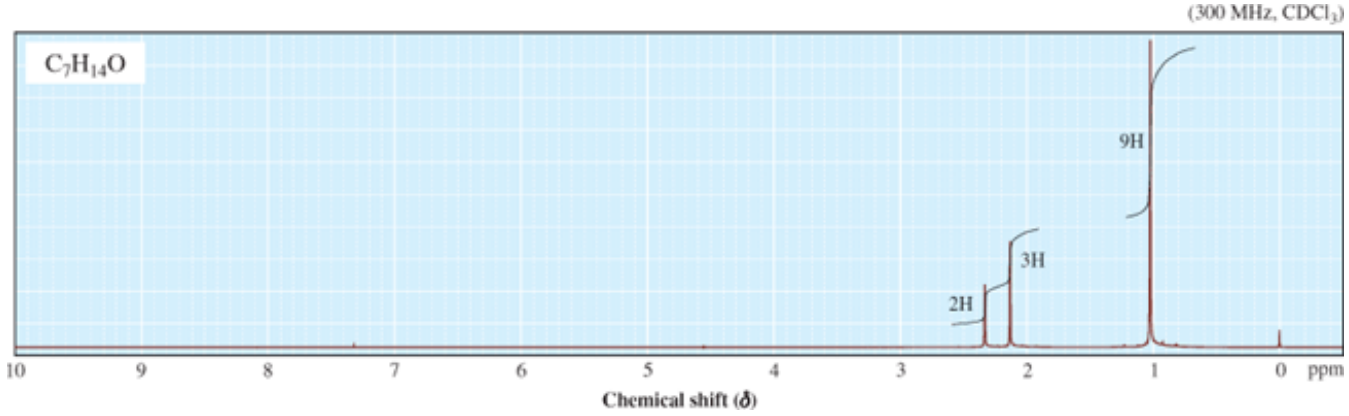
Step 4: *Pattern of chemical shifts.* The signal at δ 1.1 is in the alkyl region and, based on its chemical shift, most probably represents a methyl group (two methyl groups based on integration data on the previous page). No signal occurs at δ 4.6 to 5.7, so there are no vinylic hydrogen atoms. (If there is a carbon–carbon double bond in the molecule, there are no hydrogen atoms on it; that is, it is tetrasubstituted.) The signal at δ 2.4 is in the region for hydrogen atoms on the α-carbon atom of the carbonyl group (δ 2.1–2.6).

Step 5: *Splitting pattern.* The methyl signal at δ 1.1 is split into a triplet (t), so it must have two equivalent neighbouring hydrogen atoms, indicating —CH_2CH_3. The signal at δ 2.4 is split into a quartet (q), so it must have three equivalent neighbouring hydrogen atoms, which is also consistent with —CH_2CH_3. Consequently, an ethyl group accounts for these two signals. No other signals occur in the spectrum; therefore, there are no other types of hydrogen atoms in the molecule.

Step 6: *Structural formula.* So far we have learned that there are two signals with an integration of 6H and 4H (steps 2 and 3) and that these belong to two equivalent ethyl groups (steps 4 and 5). This accounts for all the hydrogen atoms in the formula and four of the carbon atoms; this leaves one carbon atom and one oxygen atom. Step 1 gave IHD = 1, so the remaining carbon and oxygen atoms must be a carbonyl group. Putting this information together we arrive at the following structural formula. Note that the chemical shift of the methylene group (—CH_2—) at δ 2.4 is consistent with an alkyl group adjacent to a carbonyl group.



Spectral problem 2: The compound is a colourless liquid with molecular formula $C_7H_{14}O$.



Analysis of spectral problem 2:

Step 1: *Molecular formula and index of hydrogen deficiency.* The index of hydrogen deficiency is 1, so the compound contains one ring or one π bond.

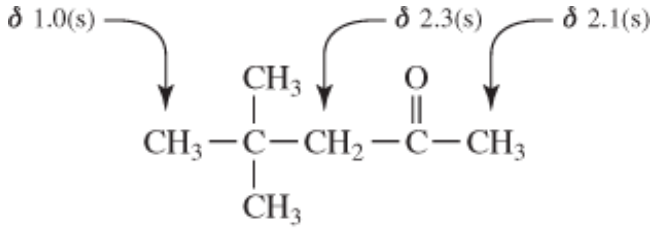
Step 1: *Number of signals.* There are three signals and therefore three sets of equivalent hydrogen atoms.

Step 1: *Integration.* By signal integration, we calculate that the number of hydrogen atoms giving rise to each signal is in the ratio 2 : 3 : 9, reading from left to right.

Step 1: *Pattern of chemical shifts.* The singlet at δ 1.0 is characteristic of a methyl group adjacent to an sp^3 hybridised carbon atom (three methyl groups based on the integration). The sing-lets at δ 2.1 and 2.3 are characteristic of alkyl groups adjacent to a carbonyl group.

Step 1: *Splitting pattern.* All signals are singlets (s), which means that none of the hydrogen atoms are within three bonds of each other.

Step 1: *Structural formula.* Summarising the data above, we have three equivalent methyl groups (δ 1.0): another methyl group (δ 2.1) adjacent to a carbonyl group, and a methylene group (δ 2.3) also adjacent to a carbonyl group. We also have a carbonyl group as deduced from the IHD, molecular formula and the chemical shift of the methyl and methylene groups. This accounts for six carbon atoms, 14 hydrogen atoms and one oxygen atom. By comparison with the molecular formula, we know that we must also have a carbon atom not bonded to any hydrogen atoms. Now, to put this information together, let's start by considering the carbonyl group and the two attached groups, giving us —$CH_2C(O)CH_3$. The only possible arrangement for the remaining quaternary carbon atom and three methyl groups is —$C(CH_3)_3$. Therefore, we get the compound 4,4-dimethylpentan-2-one.



4,4-dimethylpentan-2-one

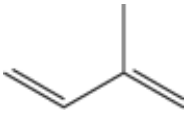
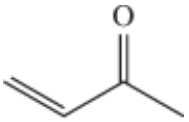
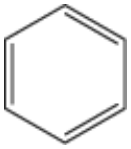
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20.7 Other Tools for Determining Structure

This chapter has focused on the tools most commonly used by chemists. However, there are other useful techniques including UV/visible spectroscopy, X-ray crystallography and electron spin resonance.

UV/visible spectroscopy is used in the study of compounds that absorb light in the ultra-violet–visible region of the spectrum (λ = 200–800 nm; see section 4.2, p. 112). The technique is applicable to organic compounds with conjugated π bonds (a sequence of four or more sp^2 hybridised atoms) and to coordination compounds of transition metals with partially filled *d* orbitals. UV/visible spectroscopy is a useful tool for studying the coordination chemistry of metals, as changes in coordination geometry and ligand donor atom can have marked effects on the spectrum. The colours and the theory of UV/visible spectroscopy of coordination compounds have been described in detail in section 13.4. As a general rule, for organic substances, the wavelength of maximum absorption (λ_{max}) increases with an increase in the extent of conjugation (see table 20.13 for some examples).

TABLE 20.13 Wavelength of maximum ultraviolet absorption of selected conjugated molecules

Molecule	Structure	λ_{max} (nm)
2-methylbuta-1,3-diene		220
but-3-en-2-one		219
octa-2,4,6-triene		263
benzene		254

The spectra obtained have few absorption bands and generally lack fine detail. Consequently this technique is now rarely used to determine the structure of organic compounds. However, UV/visible spectroscopy is used widely in detectors for the analysis of liquid and gas samples as it can detect very low concentrations of analyte and provides quantitative data. The quantification is possible by applying the **Beer–Lambert law** (commonly known as Beer's law), which relates the absorbance to the concentration of the analyte and the sample cell pathlength:

$$A = \varepsilon bc$$

where ε is the molar absorptivity (L mol^{-1} cm^{-1}), *b* is the pathlength of the cell (cm), and *c* is the concentration of the sample (mol L^{-1}).

WORKED EXAMPLE 20.16

Application of the Beer–Lambert Law

The molar absorptivity of vanillin at a wavelength of 231 nm is 14 200 L mol^{-1} cm^{-1}. A sample of vanillin was found to have an absorbance of 0.764 L mol^{-1} cm^{-1} at a wavelength of 231 nm when passing through a cell with a pathlength of 1.00 cm. What is the concentration of vanillin in this sample?

Analysis and solution

Before we start, it is good to check the data you are provided with and whether it is all required to solve the problem. Note that the wavelength of light is not part of the Beer–Lambert law, so this is not required to determine the concentration. It is provided because the value of the molar absorptivity is dependent on the wavelength of light absorbed. As the concentration is required, the Beer–Lambert law can be rewritten in terms of concentration:

$$c = \frac{A}{\varepsilon b}$$

Now substituting into the equation we get:

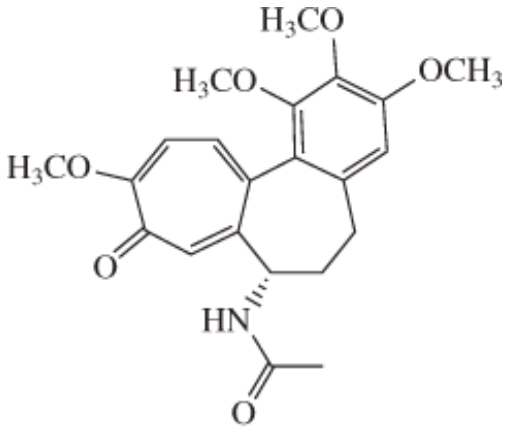
$$c = \frac{0.764}{14\,200} \times 1.00 = 5.38 \times 10^{-5}\text{M}$$

Is your answer reasonable?

A simple way to check your answer is to determine the absorbance using the value of the concentration you have determined.

PRACTICE EXERCISE 20.15

Colchicine is a natural product used in the treatment of gout. It has a molar absorptivity of 29 200 L mol^{-1} cm^{-1} at a wavelength of 231 nm. What is the concentration of a colchicine sample that has an absorbance of 0.845 L mol^{-1} cm^{-1} at a wavelength of 231 nm and cell pathlength of 5.00 cm?



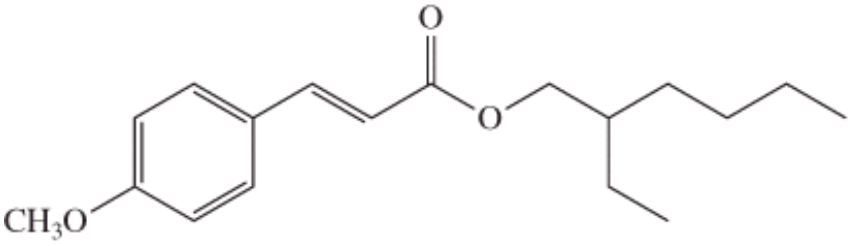
colchicine

An important application of UV-absorbing compounds is in sunscreens to protect against skin cancer (figure 20.48). Octyl methoxycinnamate and 4-methylbenzylidine camphor, which both absorb UVB radiation (290 –320 nm), are the UV absorbers most commonly used in sunscreens.

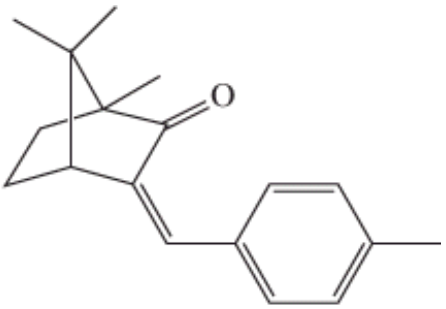




FIGURE 20.48 UV-absorbing compounds are used in sunscreens.



octyl methoxycinnamate
(2-ethylhexyl 4-methoxycinnamate)



4-methylbenzylidene camphor

X-ray crystallography is the study of crystal structures through X-ray diffraction techniques and is a powerful way of obtaining detailed information on structure and bonding within a crystal. When a beam of X-rays passes through a crystal, the beam is diffracted in a manner that is dependent on the size and position of the atoms within the crystal (see chapter 7, p. 278). Analysis of the diffraction pattern allows the determination of the three-dimensional structure of the compound, including bond lengths and bond angles. Each year, X-ray crystallography is used to determine the structure of thousands of inorganic, organic, organometallic and biological compounds. It is the most important technique available for the determination of the 3-D structure of proteins and other large biomolecules. However, this technique is limited to crystalline samples of suitable quality and size. Growing appropriate crystals, particularly of biomolecules, can be a significant challenge in itself.

Electron spin resonance (ESR) also known as **electron paramagnetic resonance (EPR)** is a type of magnetic resonance that is useful for the study of free radicals, paramagnetic species (see section 13.1, p. 544) and other substances containing unpaired electrons. It is arguably the most important technique for studying structure in free radicals and plays an important part in under-standing reaction mechanisms.

chemistry Research

Looking for Molecules in Space

Tim Schmidt and Scott Kable, University of Sydney

In the laser spectroscopy laboratories at the University of Sydney, researchers Tim Schmidt and Scott Kable are looking for molecules in space. Because interstellar molecules are so very far away, the only way to identify them is by analysing the light that they emit and absorb.

Tim and Scott collaborate with Rob Sharp from the Anglo-Australian Observatory to acquire spectra of astrophysical objects such as dust clouds and nebulae (figure 20.49). By using a background star as a light source, they are able to measure absorption spectra of diffuse interstellar clouds using a spectrometer attached to the telescope. Most of the absorption spectra observed in the visible range are due to unidentified molecules. The researchers hope that, by recreating the same spectra in a laboratory setting, they can identify these molecules, which are absorbing light many light-years away.

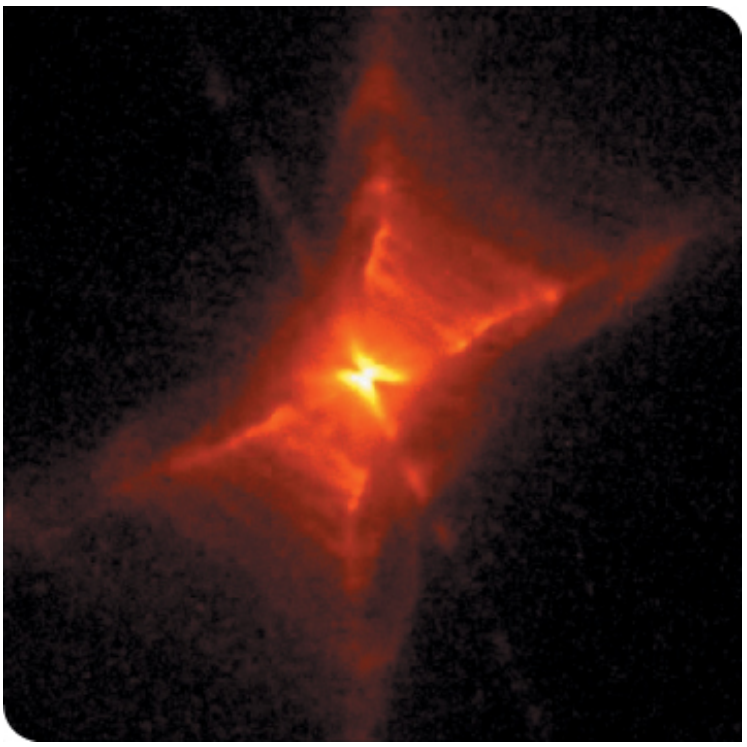


FIGURE 20.49 The Red Rectangle is a source of unidentified molecular emission bands. Some of these bands are close to the unidentified diffuse interstellar bands. Tim Schmidt and Rob Sharp are studying the carbon cluster C_2 in the Red Rectangle to learn more about its photophysical environment.

The carbon clusters C_2 and C_3 are readily observed in interstellar spectra. By recreating interstellar conditions of low temperature and high vacuum in the laboratory, Tim and Scott can make these inter-stellar molecules in a hydrocarbon discharge and study them using a technique known as laser-induced fluorescence. In this technique, the sample is irradiated with laser light which is varied over a range of wavelengths. Fluorescence is observed at the wavelength where the sample absorbs light. Absorption spectra are difficult to acquire for these molecules, but such fluorescence gives similar information as a function of laser wavelength. Using spectroscopic techniques developed by astronomers such as Rob Sharp, the Sydney researchers can also analyse the emitted light. The result is a two-dimensional fluorescence map (figure 20.50). By looking between the C_2 and C_3 features, they have been able to locate spectra of hitherto unobserved species. One new discovery of great chemical interest was the phenylpropargyl radical, C_9H_9. This is the most conspicuously fluorescent species in an electrical discharge containing benzene, hinting at its importance in the chemistry of planetary atmospheres, combustion and the interstellar medium.

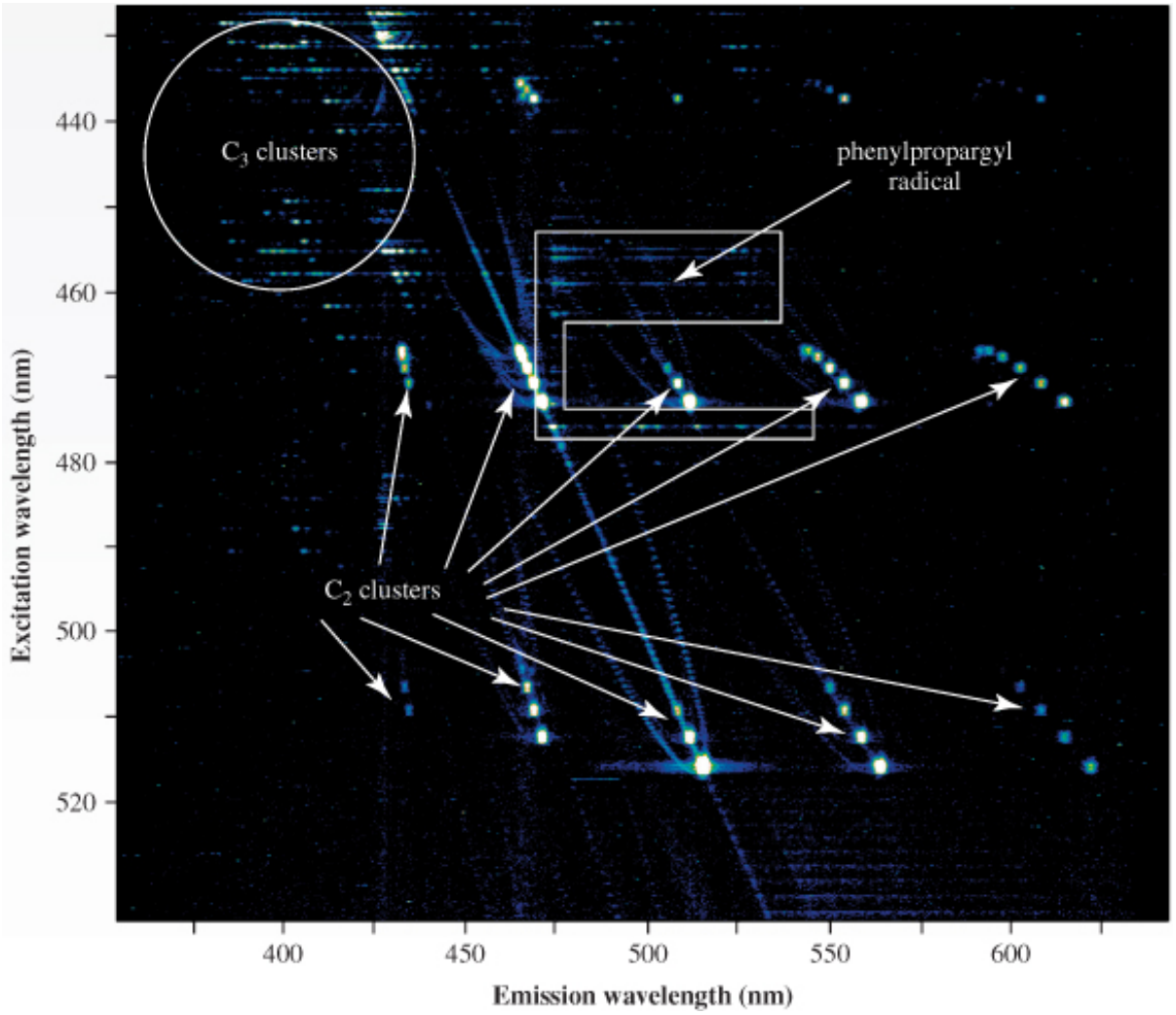


FIGURE 20.50 A two-dimensional fluorescence spectrum of a benzene discharge showing C_2, C_3 and the recently identified phenylpropargyl radical.

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SUMMARY

Tools for Determining Structure

The index of hydrogen deficiency is the sum of the number of rings and π bonds in a molecule. It can be determined by comparing the number of hydrogen atoms in the molecular formula of a compound of unknown structure with the number of hydrogen atoms in a reference compound with the same number of carbon atoms and with no rings or π bonds.

Mass Spectrometry

Mass spectrometry is a technique that allows us to determine the mass of molecules and fragments of molecules. In mass spectrometry, a sample is ionised by bombardment with a stream of high-energy electrons to produce a molecular ion (an ion generated by removal of an electron from the molecule) and fragment ions. The molecular ion is a radicalcation, because it has one unpaired electron and is positively charged, and has the same mass as the parent molecule. High resolution mass spectrometry is a process that measures the mass to charge ratio of ions (including the molecular ion) with a high degree of precision (usually to four decimal places), allowing the determination of a molecular formula. Relative abundances of isotopes may be used to identify elements present in a molecule.

Infrared Spectroscopy

Electromagnetic radiation can be described in terms of its wavelength (λ) and frequency (ν). Frequency is reported in s^{-1}. An alternative way to describe electromagnetic radiation is in terms of its energy, where $E = h\nu$. Molecular spectroscopy is the experimental process of measuring the frequencies of radiation that are absorbed or emitted by a substance and correlating these patterns with details of molecular structure. Interactions of molecules with infrared radiation excite covalent bonds to higher vibrational energy levels.

The vibrational infrared spectrum extends from 4000 to 400 cm^{-1}. Radiation in this region is referred to by its wavenumber ($\tilde{\nu}$) in reciprocal centimetres (cm^{-1}). To be infrared active, a bond must be polar; the more polar it is, the stronger is its absorption of IR radiation. There are $3n$ - 6 fundamental vibrations for a nonlinear molecule containing n atoms. The simplest vibrations that give rise to the absorption of infrared radiation are stretching and bending vibrations. Stretching may be symmetrical or asymmetrical.

Interpreting Infrared Spectra

Functional groups within molecules have characteristic vibrational frequencies, and these are often listed on correlation tables. The intensity of a signal is referred to as strong (s), medium (m) or weak (w). Stretching vibrations for most functional groups appear in the region from 3650 to 1000 cm^{-1}. The region from 1000 to 450 cm^{-1} is called the fingerprint region.

Nuclear Magnetic Resonance Spectroscopy

The interaction of molecules with radio-frequency radiation gives us information about nuclear spin energy levels. Nuclei of ^{1}H and ^{13}C, isotopes of the two elements most common to organic compounds, have a spin and behave like tiny bar magnets. When placed in a powerful magnetic field, the nuclear spins of these elements become aligned either with the applied field or against it. Nuclear spins aligned with the applied field are in the lower energy state; those aligned against the applied field are in the higher energy state. Resonance is the absorption of electromagnetic radiation by a nucleus and the resulting flip of its nuclear spin from a lower energy spin state to a higher energy spin state. An NMR spectrometer records such a resonance as a signal.

Interpreting NMR Spectra

In a ^{1}H-NMR spectrum, a resonance signal is reported by how far it is shifted from the resonance signal of the 12 equivalent hydrogen atoms in tetramethylsilane (TMS). A resonance signal in a ^{13}C-NMR spectrum is reported by how far it is shifted from the resonance signal of the four equivalent carbon atoms in TMS. A chemical shift (δ) is the frequency shift from TMS, divided by the operating frequency of the spectrometer.

Equivalent hydrogen atoms within a molecule have identical chemical shifts. The area of a ^{1}H-NMR signal is proportional to the number of equivalent hydrogen atoms giving rise to that signal. In signal splitting, the ^{1}H-NMR signal from one hydrogen atom or set of equivalent hydrogen atoms is split by the influence of hydrogen atoms on adjacent carbon atoms that are equivalent to each other but not to the atoms giving rise to the signal. According to the (n + 1) rule, if a hydrogen atom has n hydrogen atoms that are not equivalent to it, but are equivalent to each other, on adjacent carbon atom(s), its ^{1}H-NMR signal is split into (n + 1) peaks. Complex splitting patterns occur when a hydrogen atom is flanked by two or more sets of hydrogen atoms and those sets are nonequivalent. Splitting patterns are commonly referred to as singlets (s), doublets (d), triplets (t), quartets (q), quintets and multiplets (m).

In 13C-NMR spectra, all the ^{13}C signals appear as singlets. The number of singlets almost always corresponds to the number of nonequivalent carbon atoms within a molecule. The area of a 13C-NMR signal is *not* proportional to the number of equivalent *t* carbon atoms giving rise to that signal.

Other Tools for Determining Structure

UV/visible spectroscopy is used in the study of compounds that absorb light in the ultraviolet–visible region of the spectrum (λ = 200 - 800 nm). X-ray crystallography is the study of crystal structures through X-ray diffraction techniques. Electron spin resonance (ESR), also known as electron paramagnetic resonance (EPR), is a type of magnetic resonance that is useful for the study of free radicals, paramagnetic species and other substances containing unpaired electrons.

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KEY CONCEPTS AND EQUATIONS

Index of hydrogen deficiency *(section 20.1)*

The sum of the number of rings and π bonds in a molecule.

(n + 1) rule *(section 20.5)*

According to this rule for determining splitting patterns in NMR spectroscopy, if a hydrogen atom has n hydrogen atoms that are not equivalent to it, but equivalent to each other, on the same or adjacent atom(s), then the ^{1}H-NMR signal of the hydrogen atom is split into (n + 1) peaks.

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REVIEW QUESTIONS

Tools for Determining Structure

20.1 Complete the following table.

Class of compound	Molecular formula	Index of hydrogen deficiency	Reason for hydrogen deficiency
alkane	C_nH_{2n+2}	0	(reference hydrocarbon)
alkene	C_nH_{2n}	1	one π bond
alkyne			
alkadiene			
cycloalkane			
cycloalkene			

20.2 Calculate the index of hydrogen deficiency of each of the following compounds.

(a) aspirin, $C_9H_8O_4$

(b) urea, CH_4N_2O

(c) ascorbic acid (vitamin C), $C_6H_8O_6$

(d) cholesterol, $C_{27}H_{46}O$

(e) pyridine, C_5H_5N

(f) trichloroacetic acid, C_2HCl_3O

Mass Spectrometry

20.3 What information can we gain from mass spectrometry?

20.4 What is a molecular ion?

20.5 What does *m*/*z* stand for?

20.6 In the mass spectrum of decane, the peak due to the molecular ion $(M)^+$ is at $m/z = 142$. This, however, is not the peak with the highest *m*/*z* value. There is a peak at $m/z = 143$ with an intensity of approximately 10% that of the $(M)^+$ peak. This peak is referred to as the $(M + 1)^+$ peak. What is the source of this peak?

20.7 In the mass spectrum of chlorobenzene, there is a peak at $m/z = 112$ $(M)^+$ and another at $m/z = 114$ $(M + 2)^+$. Explain the occurrence of these two peaks.

20.8 You are provided with the mass spectrum of a compound that contains one of the following halogens: fluorine, chlorine or bromine. Using your knowledge of isotopes, explain how you could identify the halogen present in the compound.

20.9 What mass spectrometry technique can be used to determine the molecular formula of a compound?

20.10 Determine the accurate mass of each of the following compounds.

(a) hexan-3-ol

(b) 4-aminobutanal

(c) bromobenzene

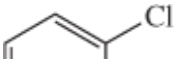
(d) chloroacetic acid

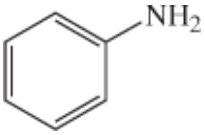
(e) phenol

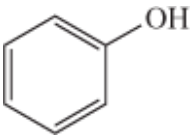
(f) bromobenzene

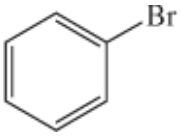
(g) cholesterol, $C_{27}H_{46}O$

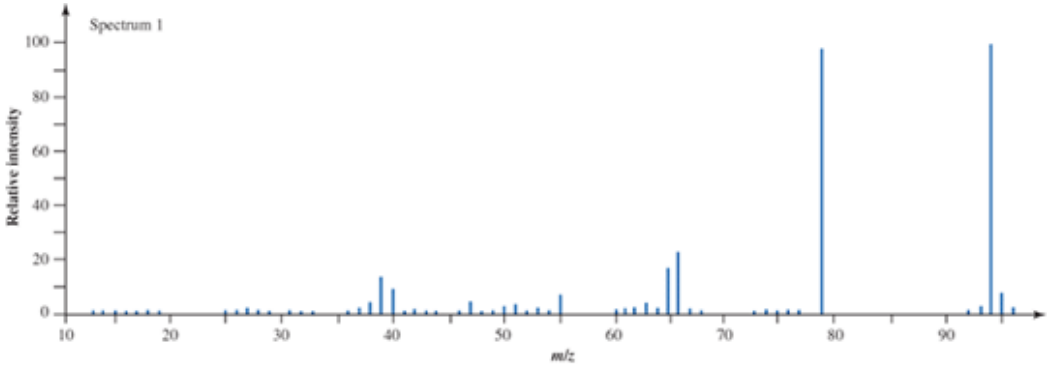
20.11 Match each of the following compounds with the appropriate spectrum.

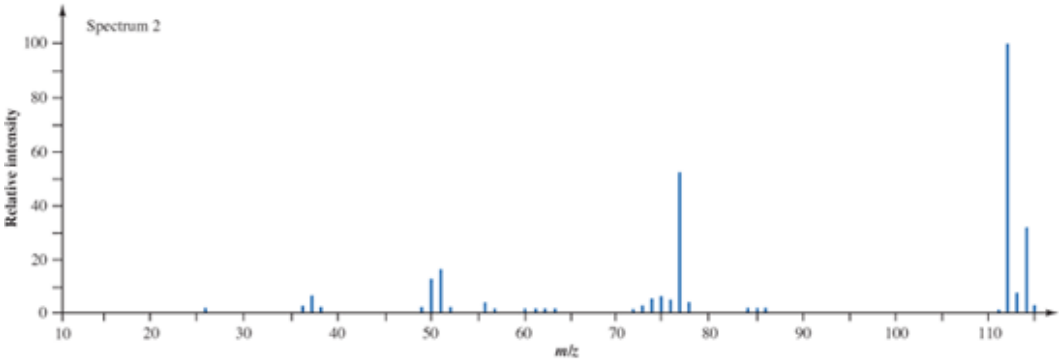
(a) 

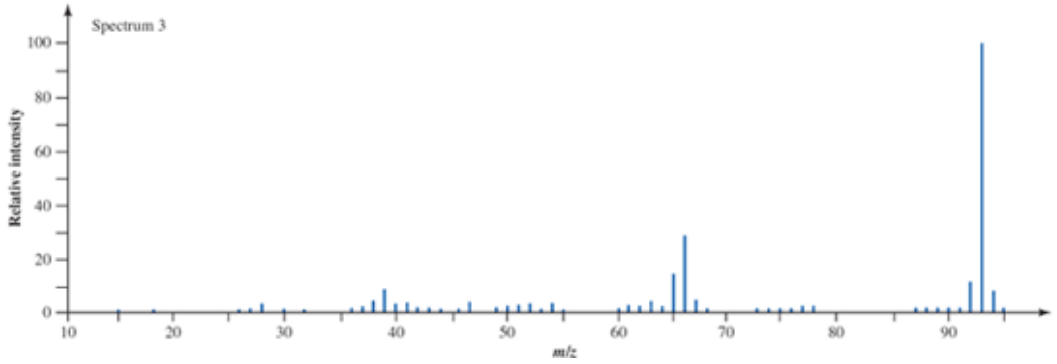
(b) 
NH2

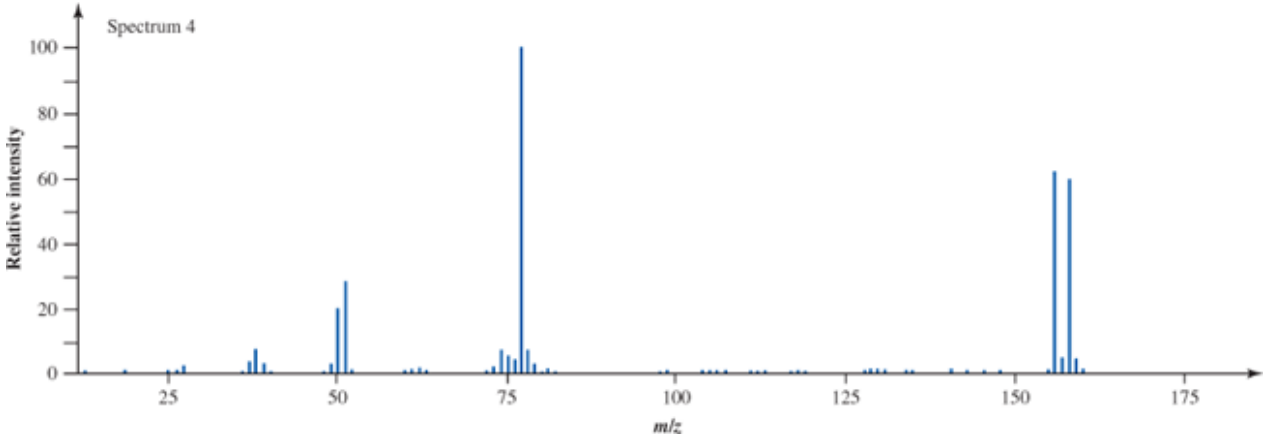
(c) 
OH

(d) 
Br


Spectrum 1
Relative intensity
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
m/z







Infrared Spectroscopy

20.12 What information can we gain from infrared spectroscopy?

20.13 Which region of the electromagnetic spectrum, IR or UV, contains photons of higher energy?

20.14 Which region of the electromagnetic spectrum, radio or visible, is characterised by waves of shorter wavelength?

20.15 Arrange the following regions of the electromagnetic spectrum in order of decreasing wavelength: microwaves, visible light, ultraviolet light, infrared radiation, X-rays.

20.16 Which has a lower characteristic stretching frequency, a C—C or a C—O bond? Explain briefly.

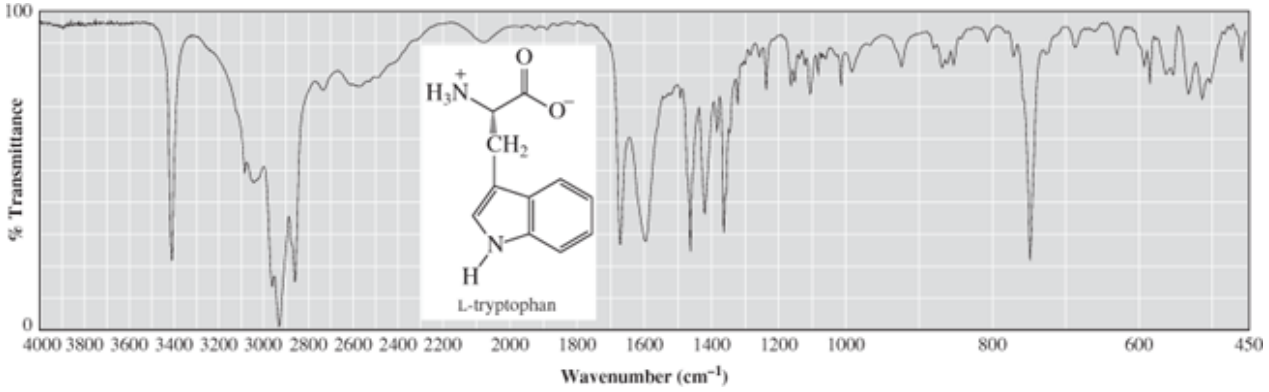
20.17 Which has a lower characteristic stretching frequency, a C═O bond or a C —O bond? Explain briefly.

20.18 How could IR spectroscopy be used to distinguish between the compounds $(CH_3)_3N$ and $CH_3NHCH_2CH_3$?

20.19 Predict the position of the C═O stretching absorption in acetate ion, $CH_3CO_2^-$, relative to that in acetic acid, CH_3CO_2H.

Interpreting Infrared Spectra

20.20 The following is the IR spectrum of L-tryptophan, a naturally occurring amino acid that is abundant in foods such as turkey.



For many years, the L-tryptophan in turkey was believed to make people drowsy after Christmas dinner. Scientists now know that consuming L-tryptophan makes you drowsy only if the compound is taken on an empty stomach. Therefore, it is unlikely that your Christmas turkey is the cause of drowsiness. Notice that L-tryptophan contains one stereocentre. Its enantiomer, D-tryptophan, does not occur in nature, but can be synthesised in the laboratory. What would the IR spectrum of D-tryptophan look like?

20.21 The sex attractant of the codling moth has the molecular formula $C_{13}H_{24}O$. It gives an IR spectrum with a broad signal between 3200 and 3600 cm^{-1} and two signals between 1600 and 1700 cm^{-1}.

(a) Determine the index of hydrogen deficiency for this compound.

(b) What functional groups are present in this compound?

Nuclear Magnetic Resonance Spectroscopy

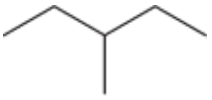
20.22 What is used as the reference in NMR spectroscopy; its signal is assigned $\delta = 0$ in ^{1}H and ^{13}C NMR spectroscopy?

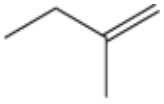
20.23 What form of electromagnetic radiation is used in NMR spectroscopy?

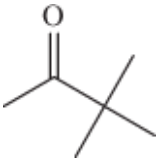
20.24 Predict the number of signals expected, their splitting and their relative areas in the ^{1}H-NMR spectrum of 1,2-dichloroethane, $ClCH_2CH_2Cl$.

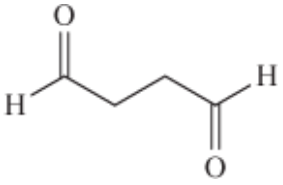
20.25 How many distinct carbon signals are expected in the ^{13}C-NMR spectrum of 5-methylhexan-3-ol?

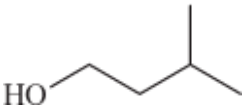
20.26 Determine the number of signals you would expect to see in the ^{1}H-NMR spectrum of each of the following compounds.

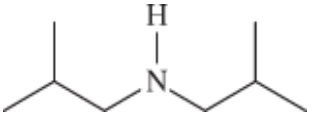
a 

b 

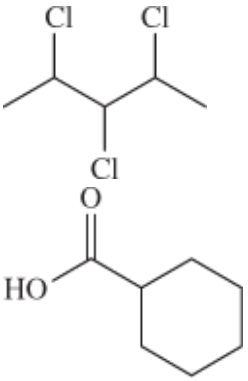
c 

d 

f 

g 

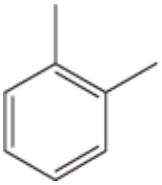
g

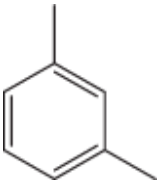
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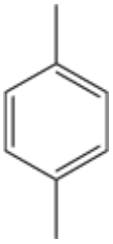
20.27 Determine the number of signals you would expect to see in the ^{13}C-NMR spectrum of each of the compounds in question 20.26.

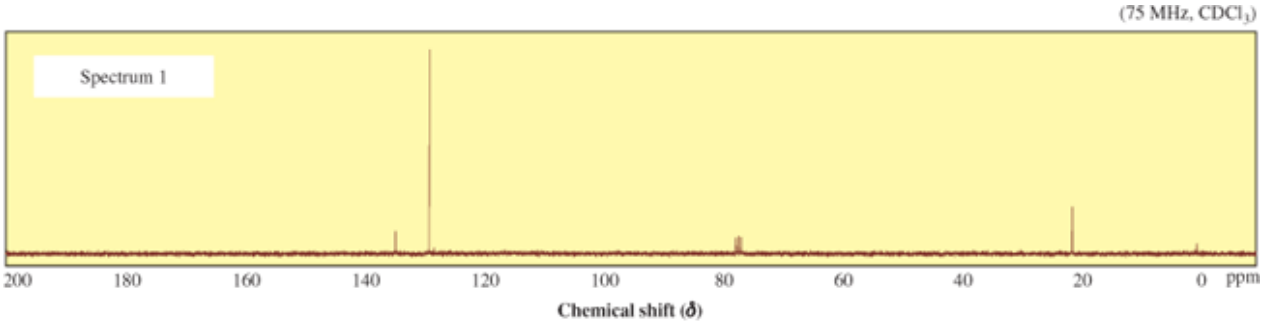
Interpreting NMR Spectra

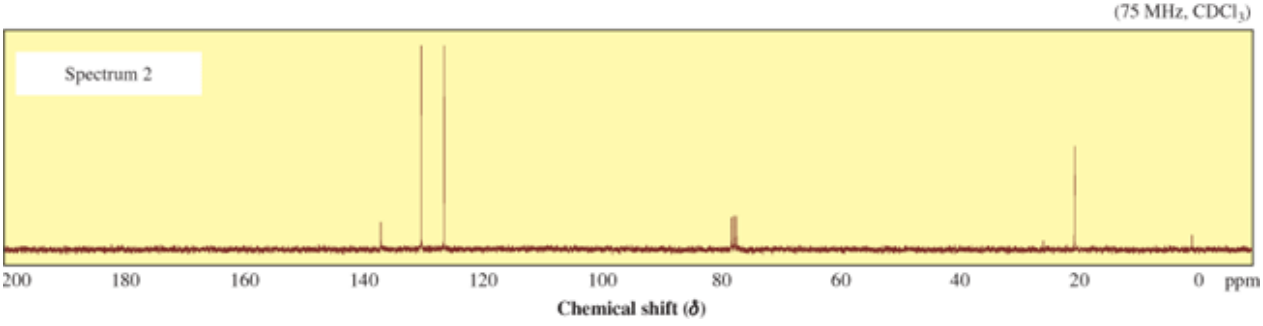
20.28 The following are structural formulae for the constitutional isomers of dimethylbenzene (*o*-xylene, *p*-xylene and *m*-xylene) and three sets of ^{13}C-NMR spectra. Assign each constitutional isomer to its correct spectrum.

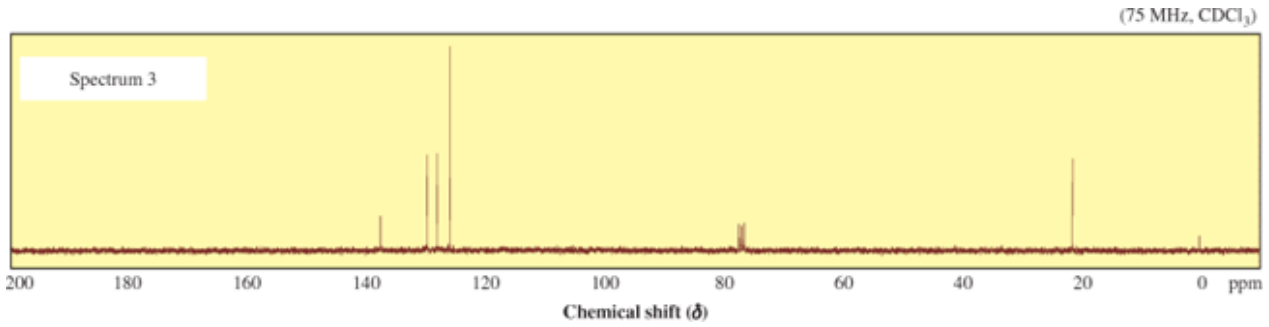
(a) 

(b) 

(c) 







Other Tools for Determining Structure

20.29 What is the most important analytical technique for determining the three-dimensional structure of proteins?

20.30 What structural feature is required for organic molecules to absorb UV light?

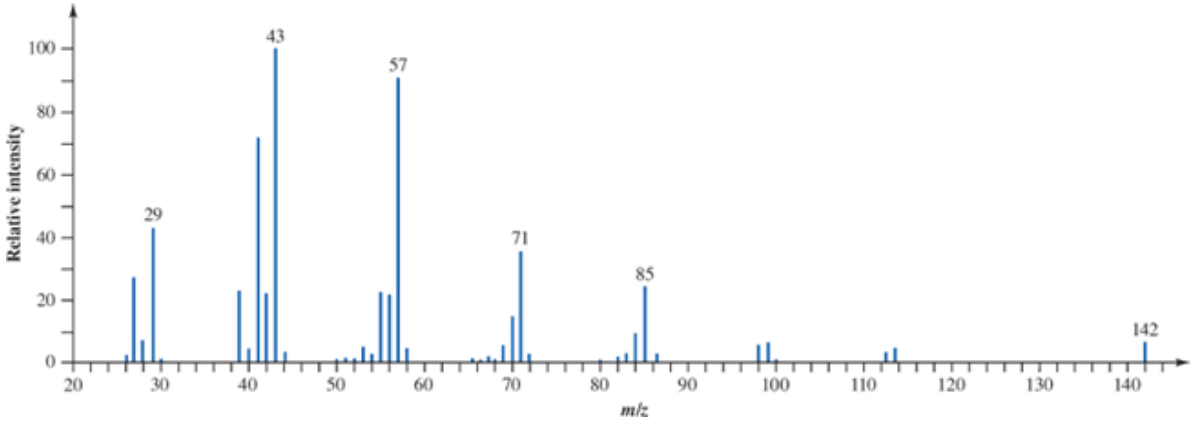
20.31 Determine the molar absorptivity of a compound that has an absorbance of 0.845 L mol^{-1} cm^{-1} (pathlength = 2 cm) for a solution with a concentration of 5.6×10^{-5} m.

20.32 Codeine phosphate has a molar absorptivity of 1570 L mol^{-1} cm^{-1} in water at 284 nm. Determine the concentration of a solution of codeine phosphate that has an absorbance of 0.82.

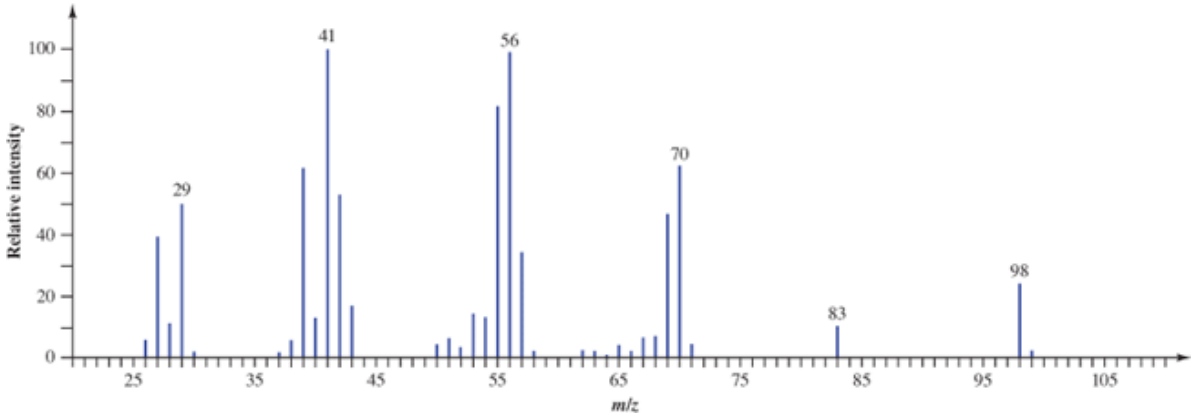
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REVIEW PROBLEMS

20.33 The mass spectrum below is that of an unbranched alkane. Which alkane produced this spectrum?



20.34 The mass spectrum below is that of a non-cyclic alkene. What is the molecular formula for the alkene that produced this spectrum?

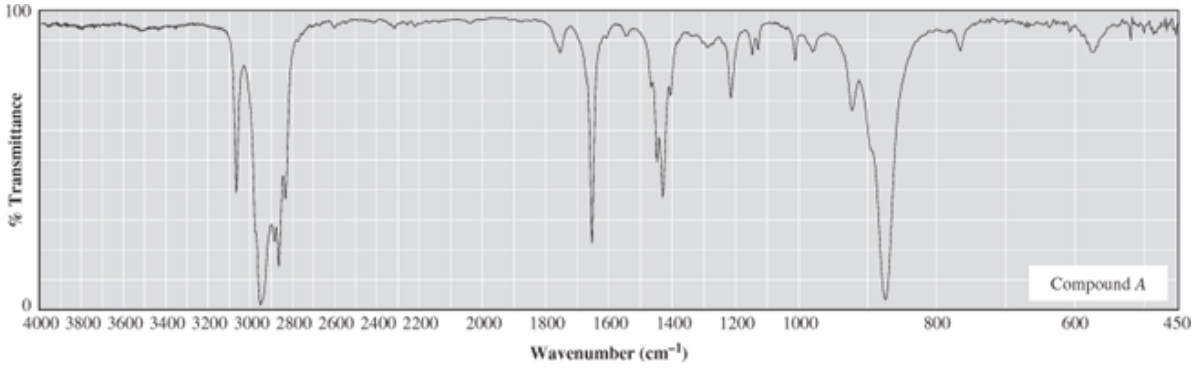


20.35 Compound *A*, with the molecular formula C_6H_{10}, reacts with H_2/Ni to give compound *B*, with the molecular formula C_6H_{12}. The IR spectrum of compound *A* is provided. From this information about compound *A*, determine:

(a) its index of hydrogen deficiency

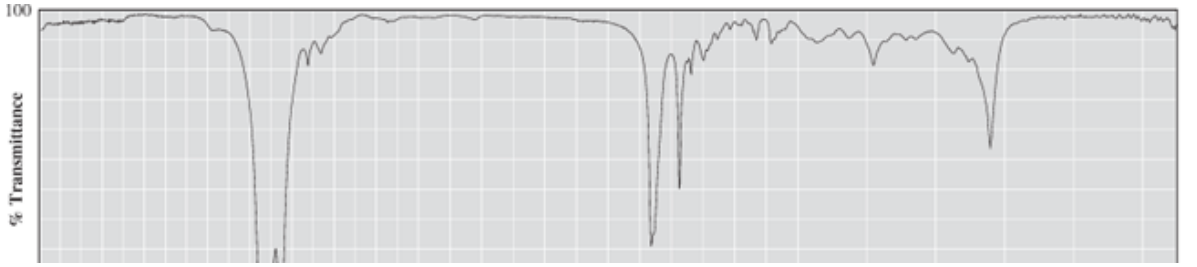
(b) the number of rings or π bonds (or both) in compound *A*

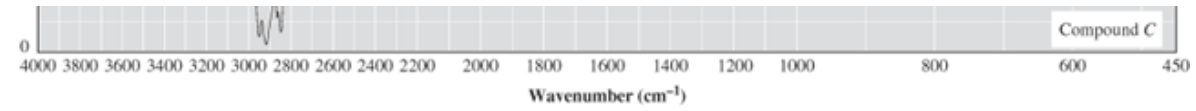
(c) the structural feature(s) that would account for the index of hydrogen deficiency of compound *A*.

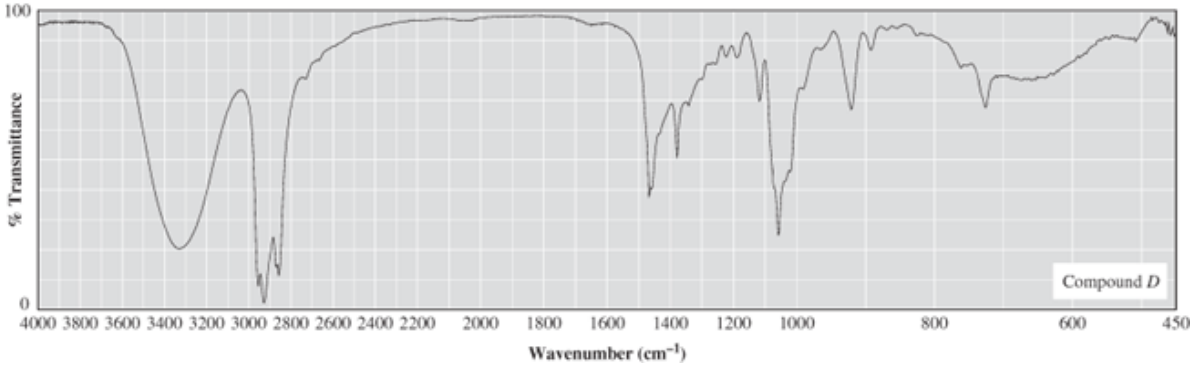


20.36 The following are infrared spectra of compounds *C* and *D*. One spectrum is of hexan-1-ol, the other of nonane.

Assign each compound to its correct spectrum.





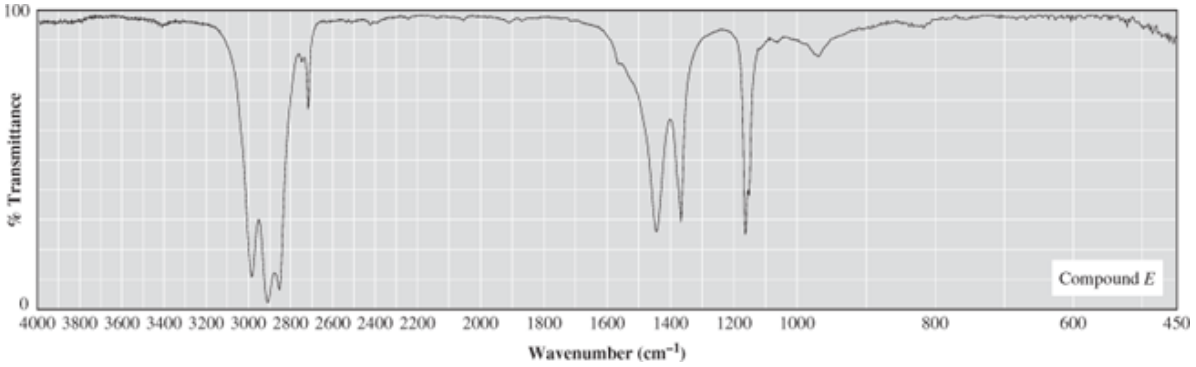


20.37 Compound *E*, with the molecular formula C_6H_{12}, reacts with H_2/Ni to give compound *F*, with the molecular formula C_6H_{14}. The IR spectrum of compound *E* is provided. From this information about compound *E*, determine:

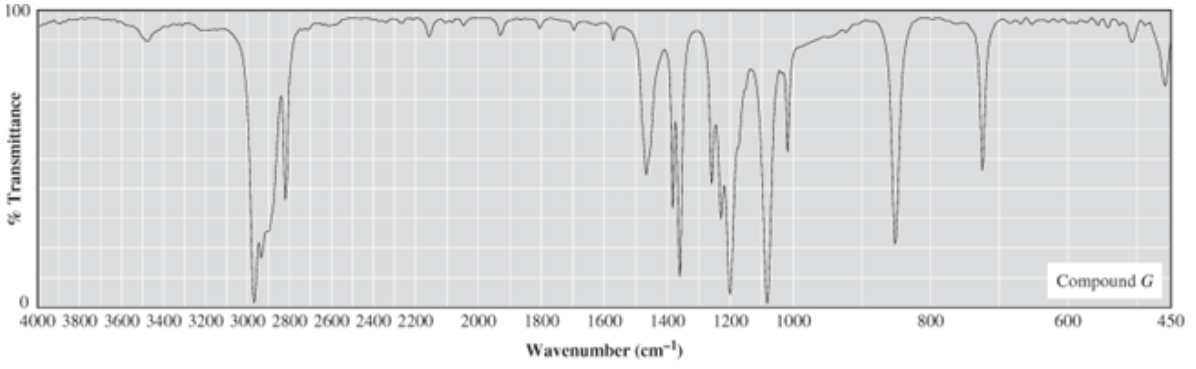
(a) its index of hydrogen deficiency

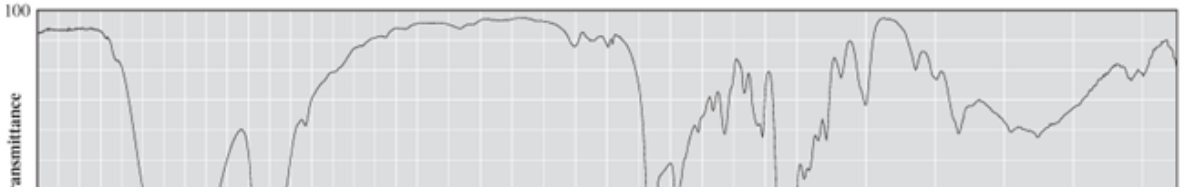
(b) the number of rings or π bonds (or both) in compound *E*

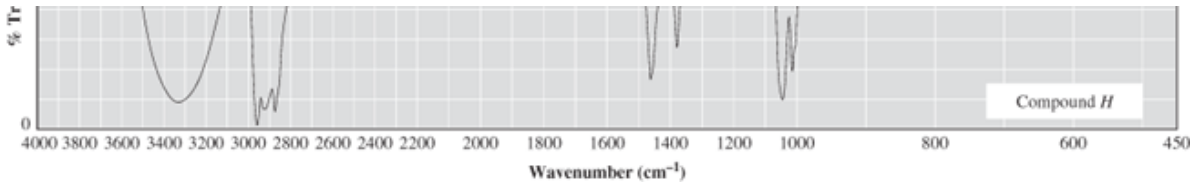
(c) the structural feature(s) that would account for the index of hydrogen deficiency of compound *E*.



20.38 The constitutional isomers 2-methylbutan-1-ol and *tert*-butyl methyl ether have the molecular formula $C_5H_{12}O$. Assign each compound to its correct infrared spectrum, *G* or *H*.







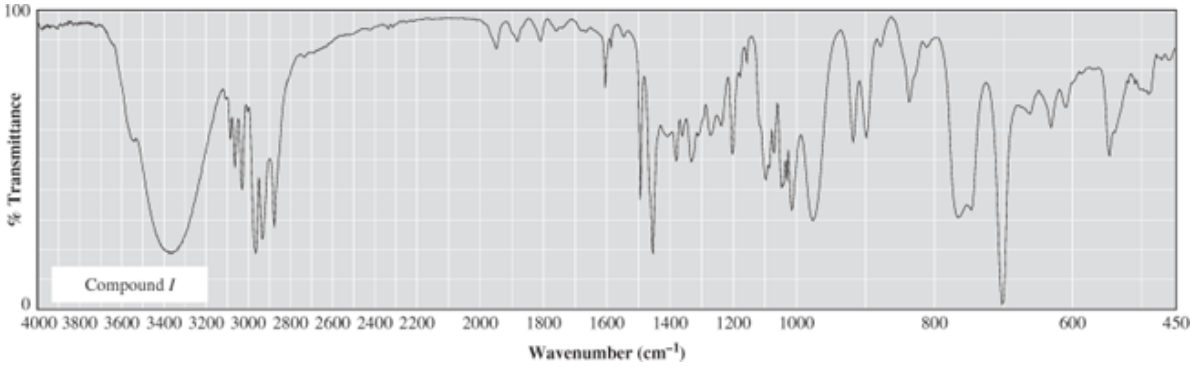
20.39 Examine the following IR spectrum and the molecular formula of compound *I*, $C_9H_{12}O$, and determine:

(a) its index of hydrogen deficiency

(b) the number of rings or π bonds (or both) in compound *I*

(c) which structural feature would account for its index of hydrogen deficiency

(d) which oxygen-containing functional group compound *I* contains.

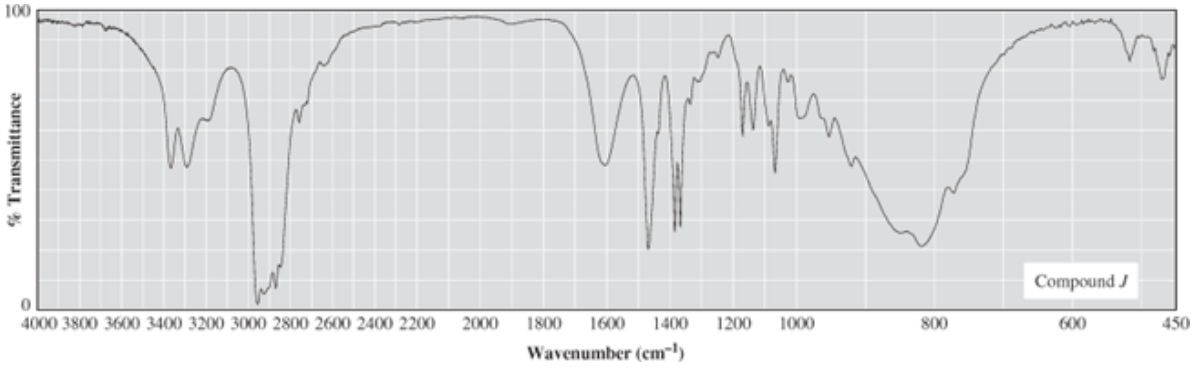


20.40 Examine the following IR spectrum and the molecular formula of compound *J*, $C_5H_{13}N$. Determine:

(a) its index of hydrogen deficiency

(b) the number of rings or π bonds (or both) in compound *J*

(c) the nitrogen-containing functional group(s) compound *J* might contain.

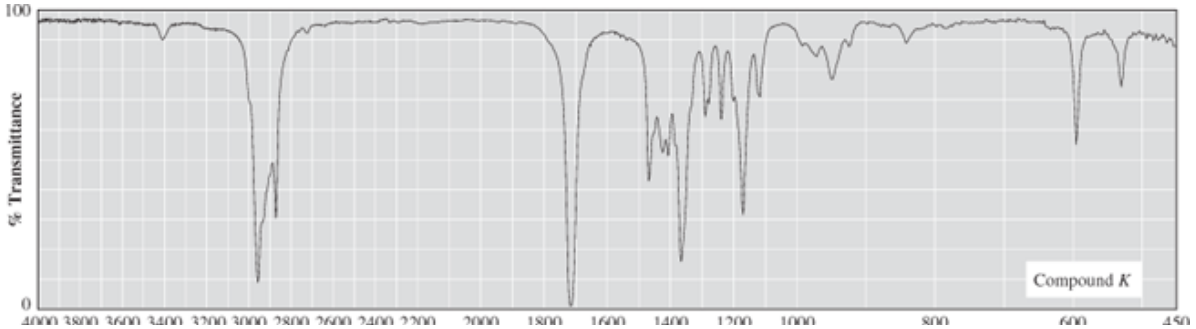


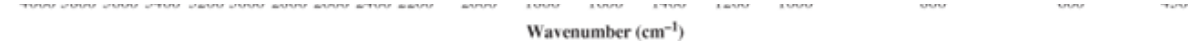
20.41 Examine the following IR spectrum and the molecular formula of compound *K*, $C_6H_{12}O$. Determine:

(a) its index of hydrogen deficiency

(b) the number of rings or π bonds (or both) in compound *K*

(c) which structural features would account for its index of hydrogen deficiency.



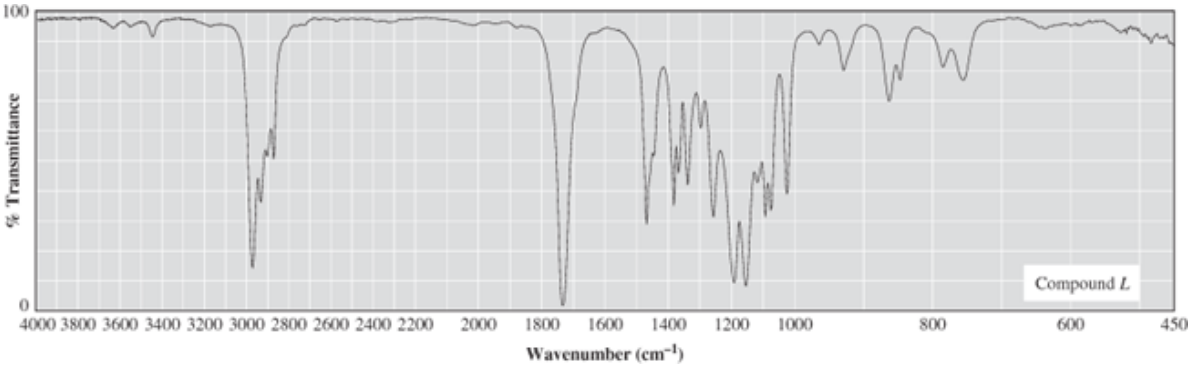


20.42 Examine the following IR spectrum and the molecular formula of compound *L*, $C_6H_{12}O_2$. Determine:

(a) its index of hydrogen deficiency

(b) the number of rings or π bonds (or both) in compound *L*

(c) the oxygen-containing functional group(s) compound *L* might contain.

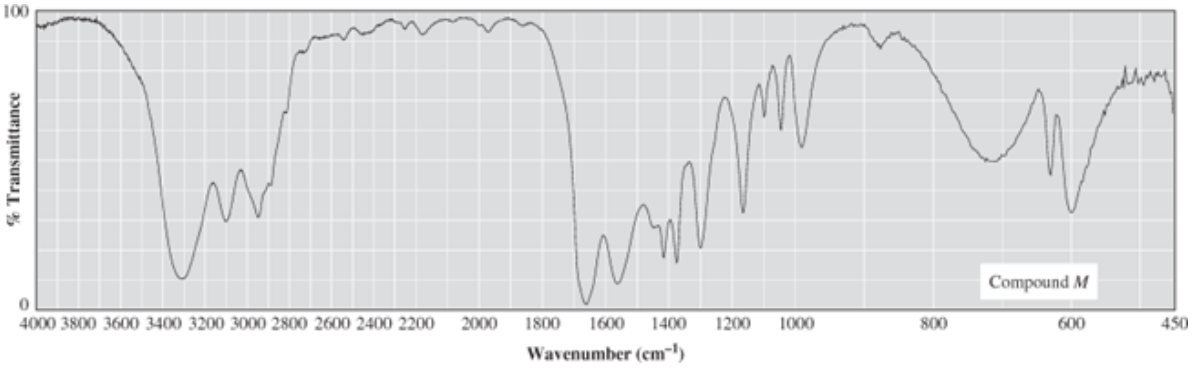


20.43 Examine the following IR spectrum and the molecular formula of compound *M*, C_3H_7NO. Determine:

(a) its index of hydrogen deficiency

(b) the number of rings or π bonds (or both) in compound *M*

(c) the oxygen- and nitrogen-containing functional group(s) in compound *M*.



20.44 Show how IR spectroscopy can be used to distinguish between the following compounds.

(a) butan-1-ol and diethyl ether

(b) butanoic acid and butan-1-ol

(c) butanoic acid and butanone

(d) butanal and but-1-ene

(e) butanone and butan-2-ol

(f) butane and (*Z*)-but-2-ene

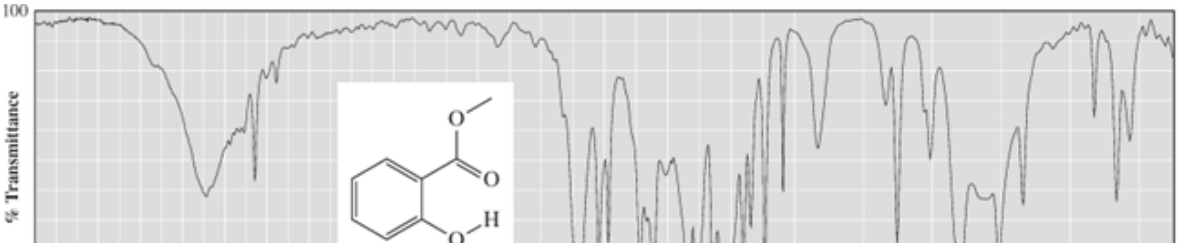
20.45 The following are an infrared spectrum and a structural formula for methyl salicylate, the fragrant component of oil of wintergreen. On this spectrum, locate the absorption peak(s) due to:

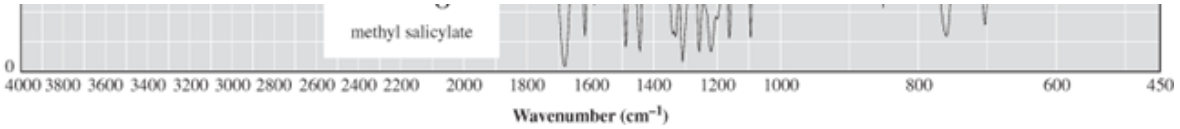
(a) O—H stretching of the hydrogen-bonded —OH group (very broad and of medium intensity)

(b) C—H stretching of the aromatic ring (sharp and of weak intensity)

(c) C═O stretching of the ester group (moderately sharp and of strong intensity)

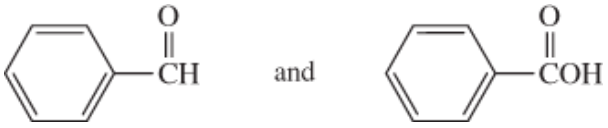
(d) C═C stretching of the aromatic ring (sharp and of medium intensity).



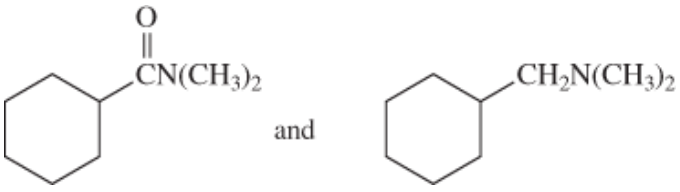


20.46 For each of the following pairs of compounds, list one major feature that appears in the IR spectrum of one compound but not the other. In your answer, state what type of bond vibration is responsible for the spectral feature you list, and give its approximate position in the IR spectrum.

(a)



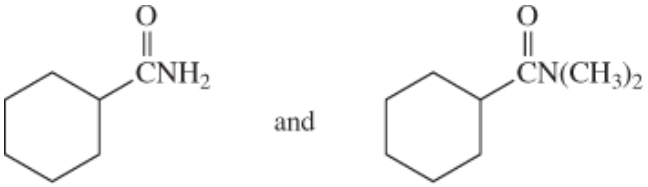
(b)



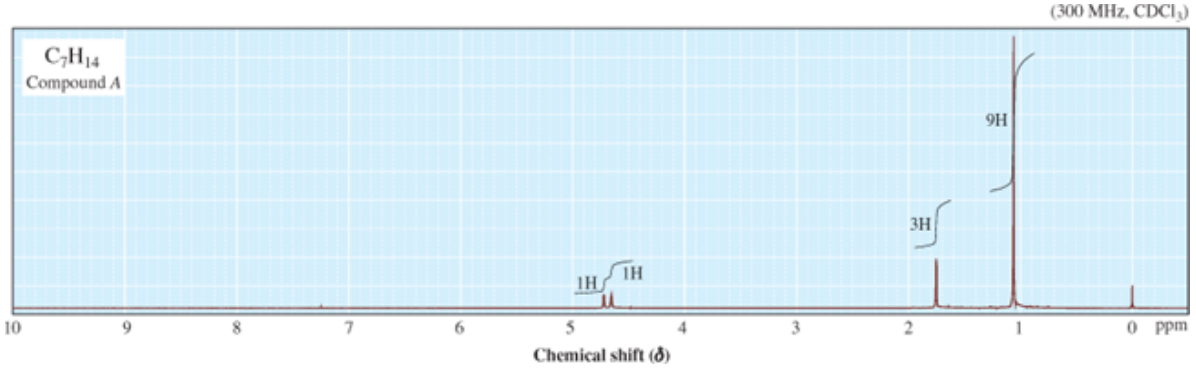
(c)



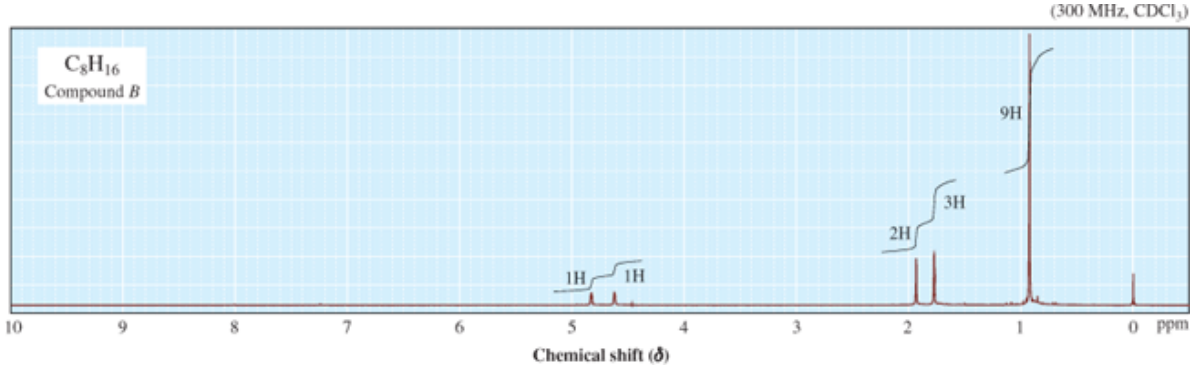
(d)



20.47 The following is a ^{1}H-NMR spectrum for compound *A*, with the molecular formula C_7H_{14}. Compound *A* decolourises a solution of bromine in dichloromethane, CH_2Cl_2. Propose a structural formula for compound *A*.

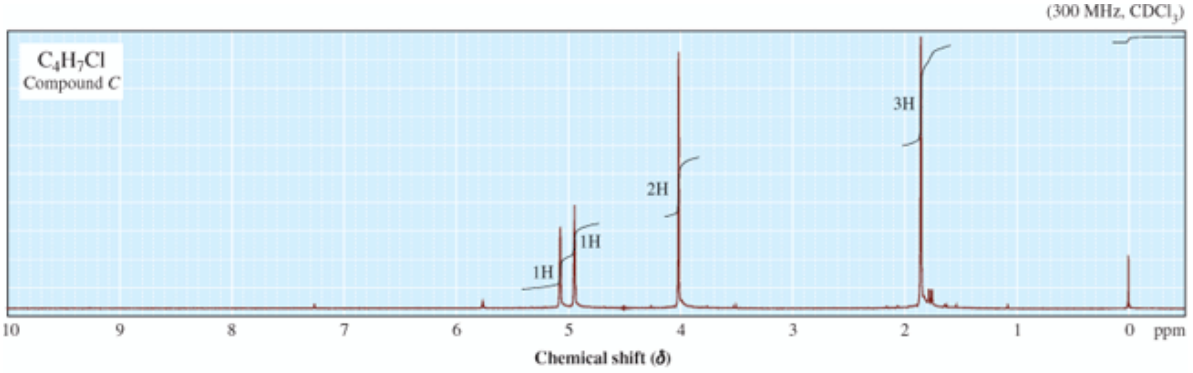


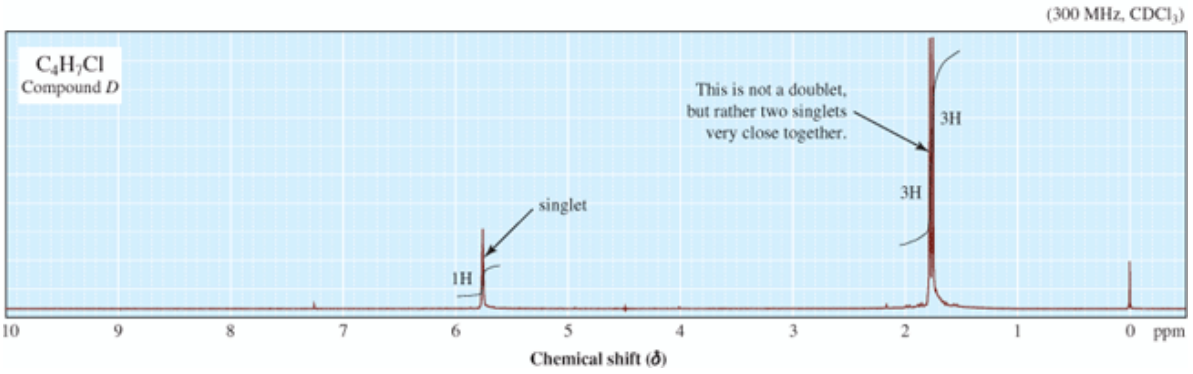
20.48 The following is a ^{1}H-NMR spectrum for compound *B*, with the molecular formula C_8H_{16}. Compound *B* decolourises a solution of Br_2 in CH_2Cl_2. Propose a structural formula for compound *B*.



20.49 The following are the ^{1}H-NMR spectra of compounds *C* and *D*, both with the molecular formula C_4H_7Cl. Each

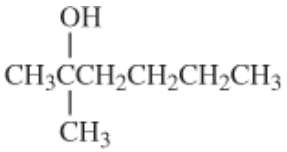
compound decolourises a solution of Br_2 in CH_2Cl_2. Propose structural formulae for compounds *C* and *D*.

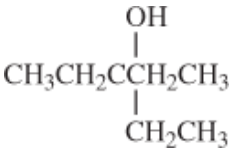




20.50 The following are the structural formulae of three alcohols with the molecular formula $C_7H_{16}O$ and three sets of ^{13}C-NMR spectral data. Assign each constitutional isomer to its correct spectral data.

(a) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$

(b)


(c)


Spectrum 1	Spectrum 2	Spectrum 3
δ = 74.7	δ = 71.0	δ = 62.9
30.5	43.7	32.8
7.7	29.2	31.9
	26.6	29.1
	23.3	25.8
	14.1	22.6
		14.1

20.51 Alcohol *E*, with the molecular formula $C_6H_{14}O$, undergoes acid-catalysed dehydration when it is warmed with phosphoric acid, giving compound *F*, with the molecular formula C_6H_{12}, as the major product. A ^{1}H-NMR spectrum of compound *E* shows peaks at δ 0.9 (t, 6H), 1.1 (s, 3H), 1.4 (s, 1H) and 1.5 (q, 4H). The ^{13}C-NMR spectrum of compound *E* shows peaks at δ 73.0, 33.7, 25.9 and 8.2. Propose structural formulae for compounds *E* and *F*.

compound *E* shows peaks at δ 75.6, 55.7, 25.9 and 8.2. Propose structural formulae for compounds *E* and *F*.

20.52 Compound *G*, $C_6H_{14}O$, does not react with sodium metal and does not discharge the colour of Br_2 in CCl_4. The ^{1}H-NMR spectrum of compound *G* consists of only two signals: a 12H doublet at δ 1.1 and a 2H septet at δ 3.6. Propose a structural formula for compound *G*.

20.53 Propose a structural formula for each of the following haloalkanes.

(a) $C_2H_4Br_2$; δ 2.5 (d, 3H) and 5.9 (q, 1H)

(b) $C_4H_8Cl_2$; δ 1.7 (d, 6H) and 2.2 (q, 4H)

(c) $C_5H_8Br_4$; δ 3.6 (s, 8H)

(d) C_4H_9Br; δ 1.1 (d, 6H), 1.9 (m, 1H), and 3.4 (d, 2H)

(e) $C_5H_{11}Br$; δ 1.1 (s, 9H) and 3.2 (s, 2H)

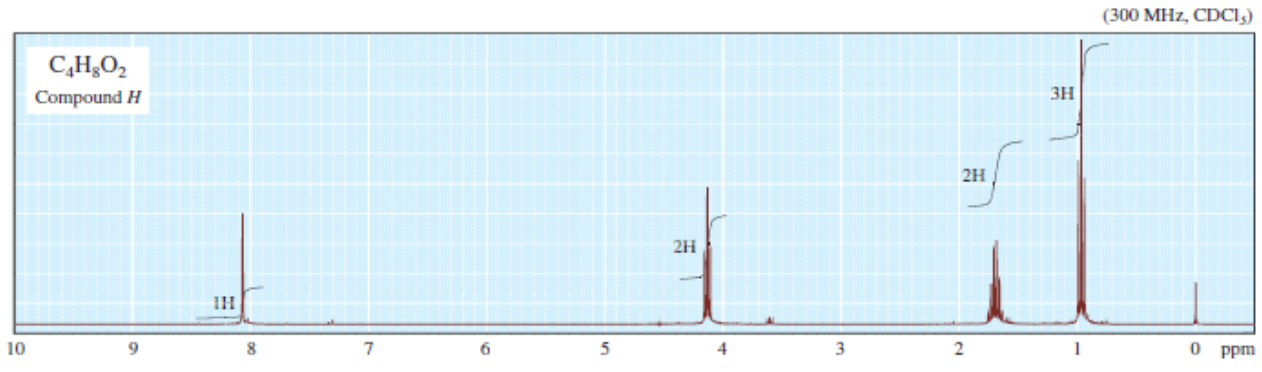
(f) $C_7H_{15}Cl$; δ 1.1 (s, 9H) and 1.6 (s, 6H)

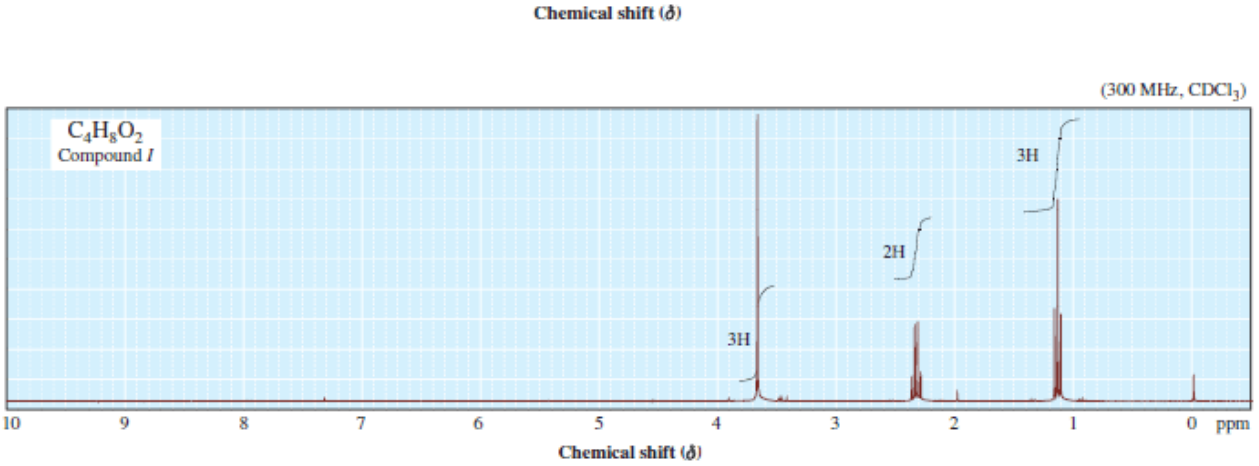
20.54 The following are structural formulae for esters (a), (b) and (c) and three ^{1}H-NMR spectra. Assign each compound to its correct spectrum and assign all signals to their corresponding hydrogen atoms.

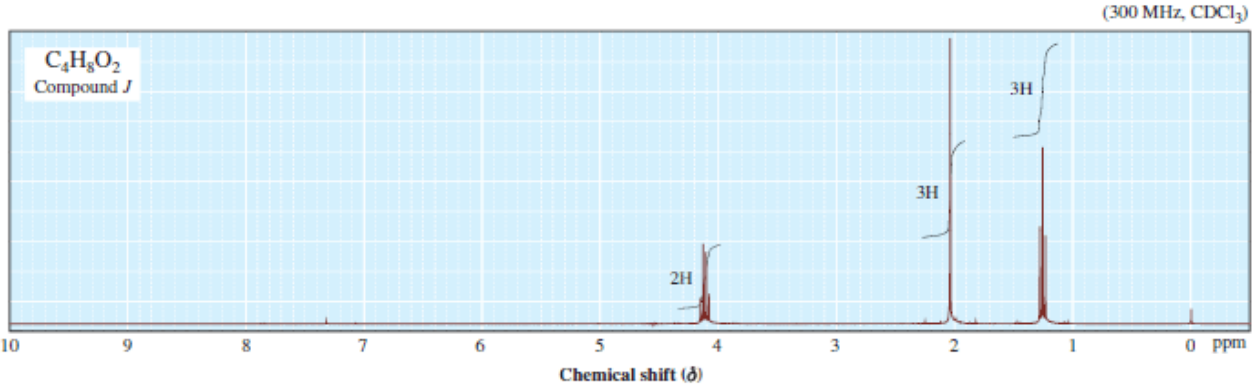
(a) $CH_3COCH_2CH_3$

(b) $HCOCH_2CH_2CH_3$

(c) $CH_3OCCH_2CH_3$

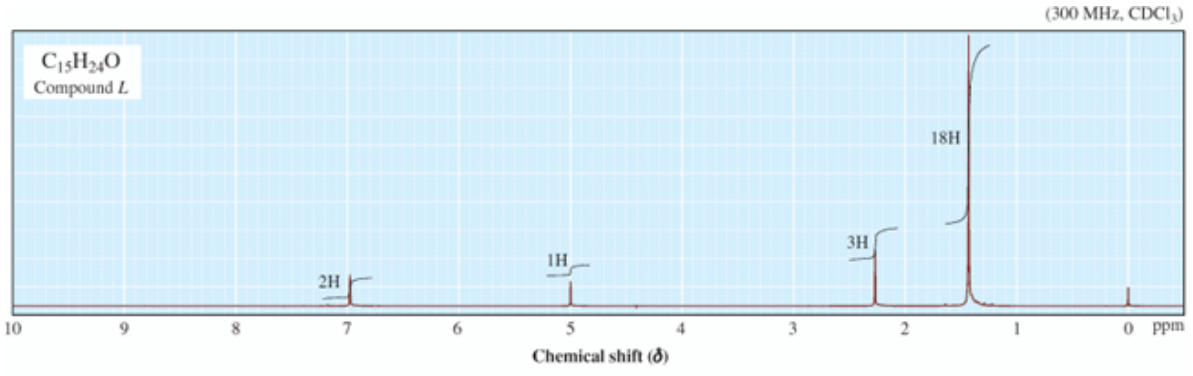




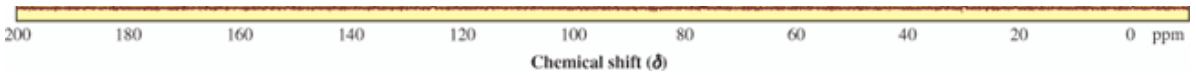


20.55 Compound *K*, $C_{10}H_{10}O_2$, is not soluble in water, 10% NaOH or 10% HCl. A ^{1}H-NMR spectrum of compound *K* shows signals at δ 2.6 (s, 6H) and 8.0 (s, 4H). A ^{13}C-NMR spectrum of compound *K* shows four signals. From this information, propose a structural formula for *K*.

20.56 Compound *L*, $C_{15}H_{24}O$, is used as an antioxidant in many commercial food products, synthetic rubbers and petroleum products. Propose a structural formula for compound *L* based on the following ^{1}H-NMR and ^{13}C-NMR spectra.



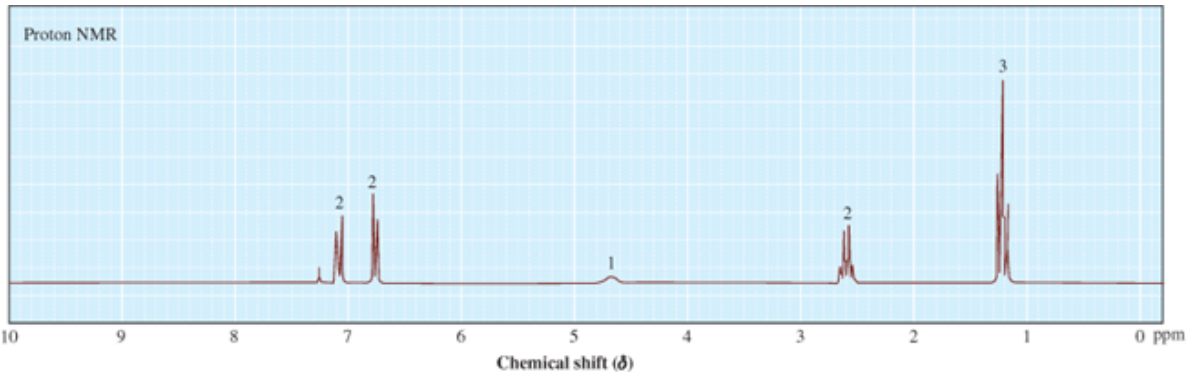




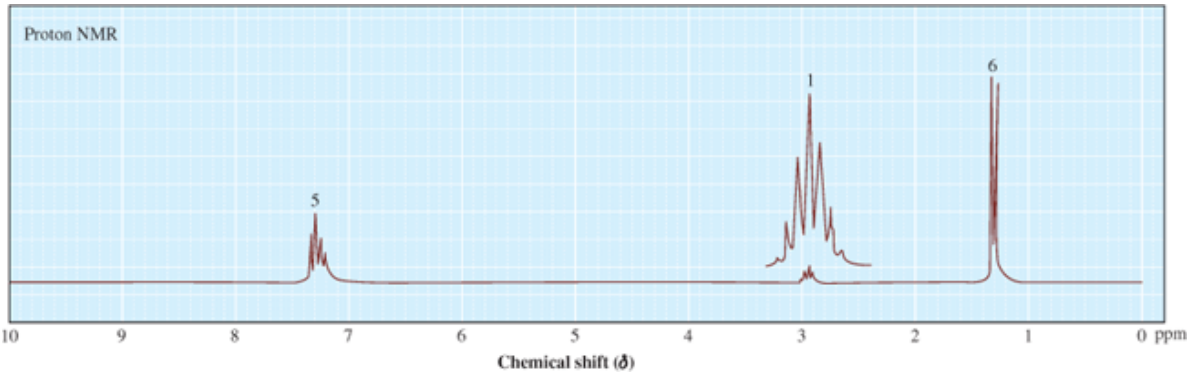
20.57 A compound with molecular formula C_8H_{18} exhibits a ^{1}H-NMR spectrum with only one signal and a ^{13}C-NMR spectrum with two signals. Propose a structure for this compound.

20.58 A compound with molecular formula C_9H_{18} exhibits a ^{1}H-NMR spectrum with only one signal and a ^{13}C-NMR spectrum with two signals. Deduce the structure of this compound.

20.59 A compound with molecular formula $C_8H_{10}O$ produces six signals in its ^{13}C-NMR spectrum and exhibits the following ^{1}H-NMR spectrum. Deduce the structure of the compound.



20.60 Deduce the structure of a compound with molecular formula C_9H_{12} that produces the following



20.61 Propose a structural formula for each of the following compounds, which all contain an aromatic ring.

(a) $C_9H_{10}O$; δ 1.2 (t, 3H), 3.0 (q, 2H) and 7.4 –8.0 (m, 5H)

(b) $C_{10}H_{12}O_2$; δ 2.2 (s, 3H), 2.9 (t, 2H), 4.3 (t, 2H) and 7.3 (s, 5H)

(c) $C_{10}H_{14}$; δ 1.2 (d, 6H), 2.3 (s, 3H), 2.9 (septet, 1H) and 7.0 (s, 4H)

(d) C_8H_9Br; δ 1.8 (d, 3H), 5.0 (q, 1H) and 7.3 (s, 5H)

20.62 Compound *M*, with the molecular formula $C_9H_{12}O$, readily undergoes acid-catalysed dehydration to give compound *N*, with the molecular formula C_9H_{10}. A ^{1}H-NMR spectrum of compound *M* shows signals at δ 0.9 (t, 3H), 1.8 (m, 2H), 2.3 (s, 1H), 4.6 (t, 1H) and 7.5 (m, 5H). From this information, propose structural formulae for compounds *M* and *N*.

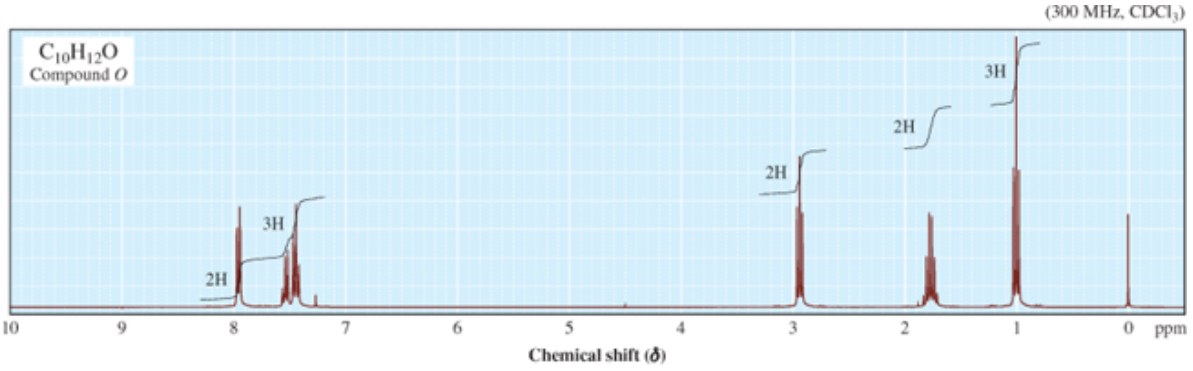
20.63 Propose a structural formula for each of the following ketones.

(a) C_4H_8O; δ 1.0 (t, 3H), 2.1 (s 3H) and 2.4 (q, 2H)

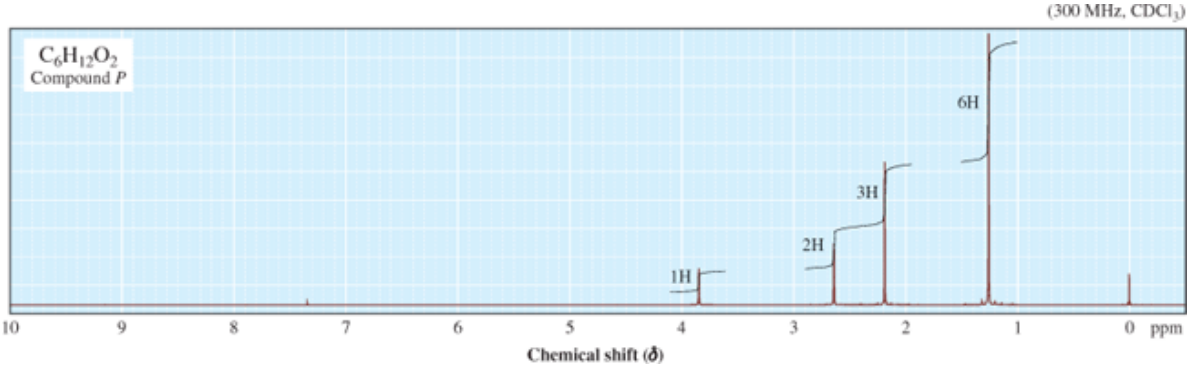
(b) $C_7H_{14}O$; δ 0.9 (t, 6H), 1.6 (sextet, 4H) and 2.4 (t, 4H)

20.64 Propose a structural formula for compound *O*, a ketone with the molecular formula $C_{10}H_{12}O$ and the ^{1}H-NMR

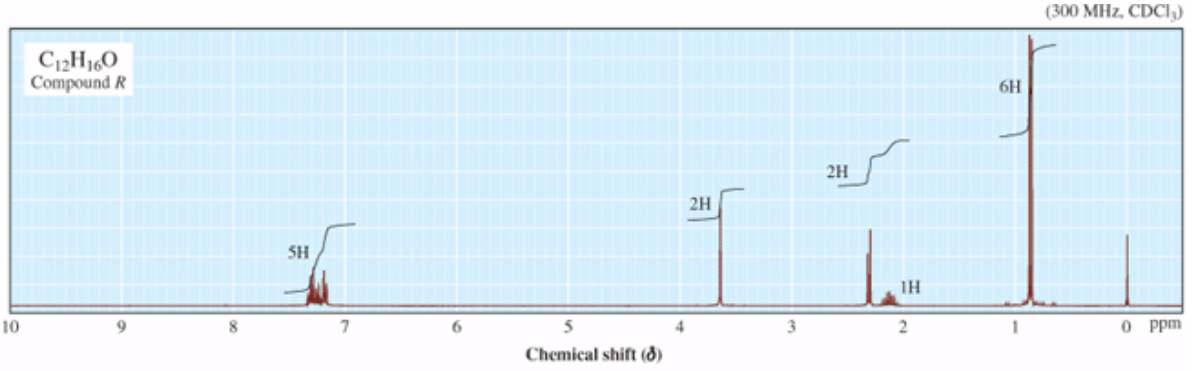
spectrum shown below.

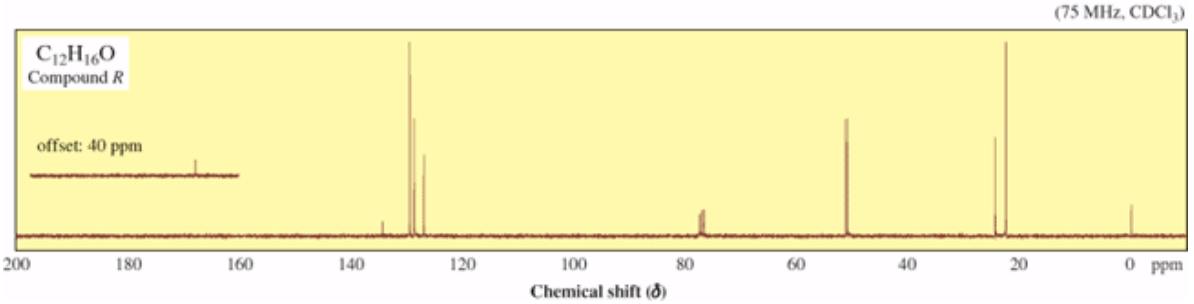


20.65 The following is a ^{1}H-NMR spectrum of compound *P*, with the molecular formula $C_6H_{12}O_2$. Compound *P* undergoes acid-catalysed dehydration to give compound *Q*, $C_6H_{10}O$. Propose structural formulae for compounds *P* and *Q*.



20.66 Propose a structural formula for compound *R*, with the molecular formula $C_{12}H_{16}O$. The following are its ^{1}H-NMR and ^{13}C-NMR spectra.





20.67 Propose a structural formula for each of the following carboxylic acids with the NMR signals given in the tables.

(a) $C_5H_{10}O_2$

^{1}H-NMR	^{13}C-NMR
0.9 (t, 3H)	180.7
1.4 (m, 2H)	33.9
1.6 (m, 2H)	26.8
2.4 (t, 2H)	22.2
12.0 (s, 1H)	13.7

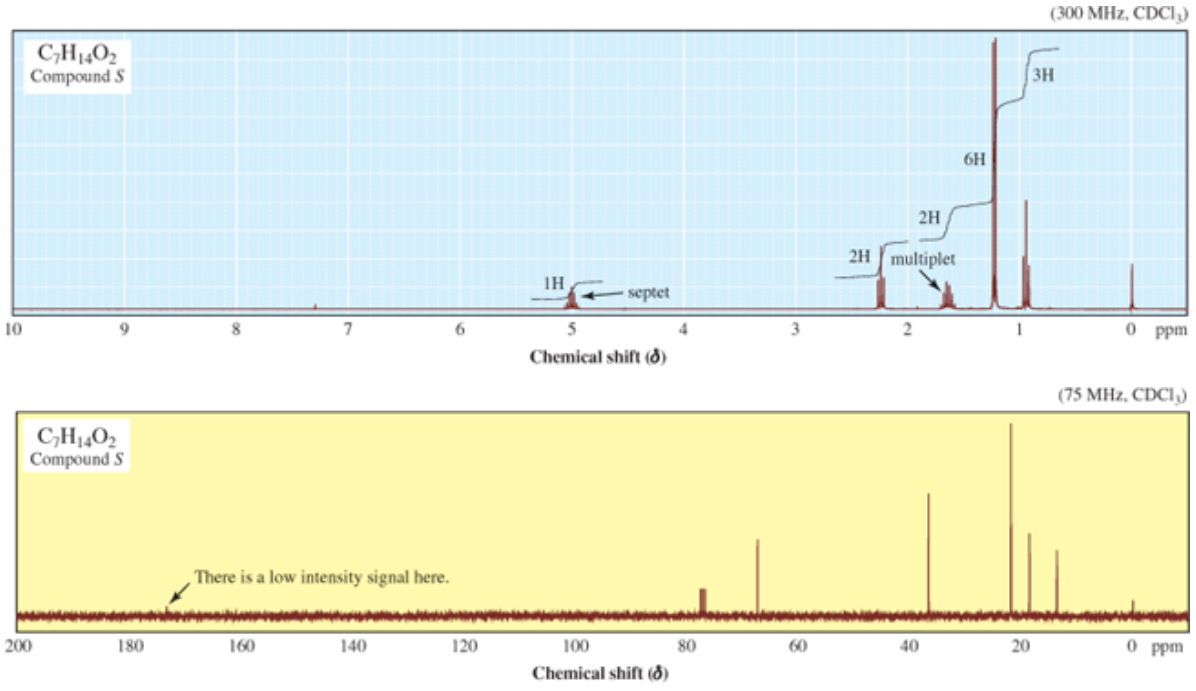
(b) $C_6H_{12}O_2$

^{1}H-NMR	^{13}C-NMR
1.1 (s, 9H)	179.3
2.2 (s, 2H)	46.8
12.1 (s, 1H)	30.6
	29.6

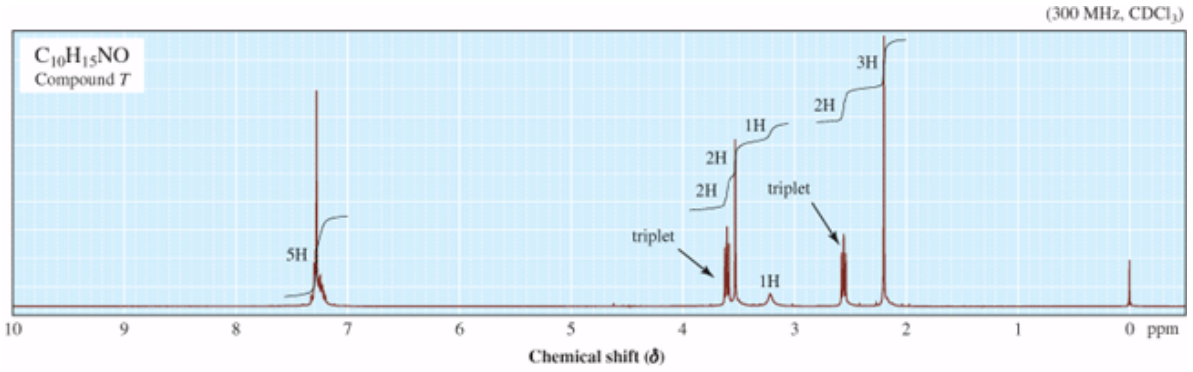
(c) $C_5H_8O_4$

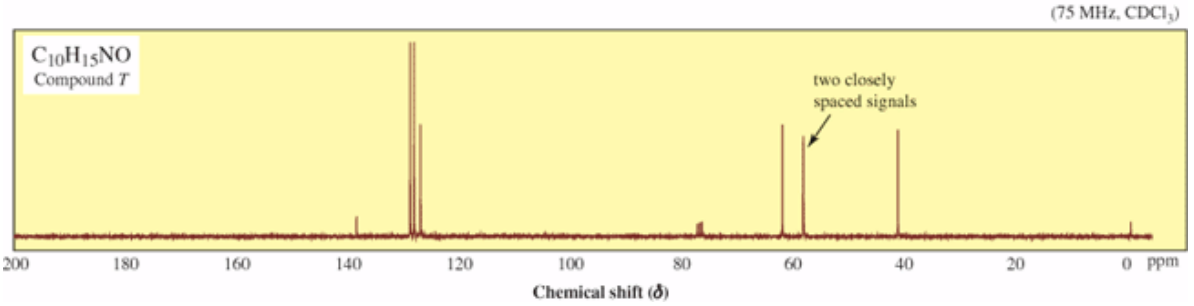
^{1}H-NMR	^{13}C-NMR
0.9 (t, 3H)	170.9
1.8 (m, 2H)	53.3
3.1 (t, 1H)	21.9
12.7 (s, 2H)	11.8

20.68 The following are ^{1}H-NMR and ^{13}C-NMR spectra of compound *S*, with the molecular formula $C_7H_{14}O_2$. Propose a structural formula for compound *S*.

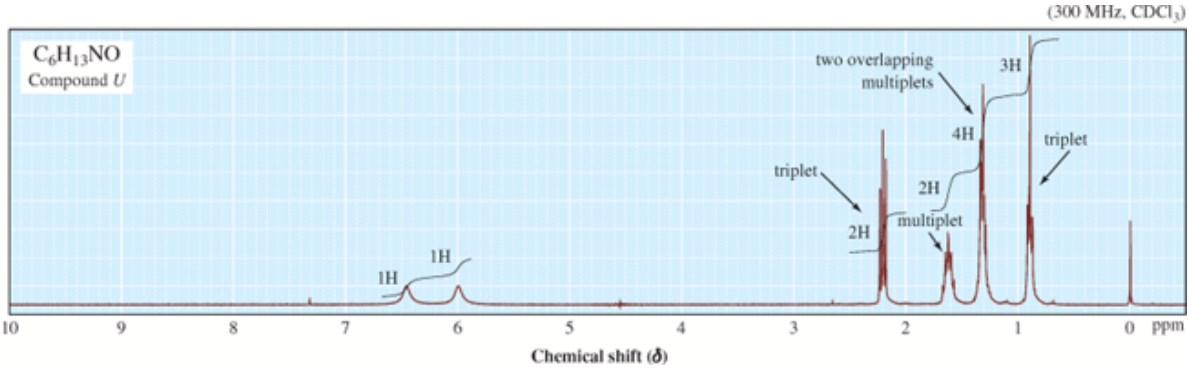


20.69 The following are ^{1}H-NMR and ^{13}C-NMR spectra of compound *T*, with the molecular formula $C_{10}H_{15}NO$. Propose a structural formula for this compound.

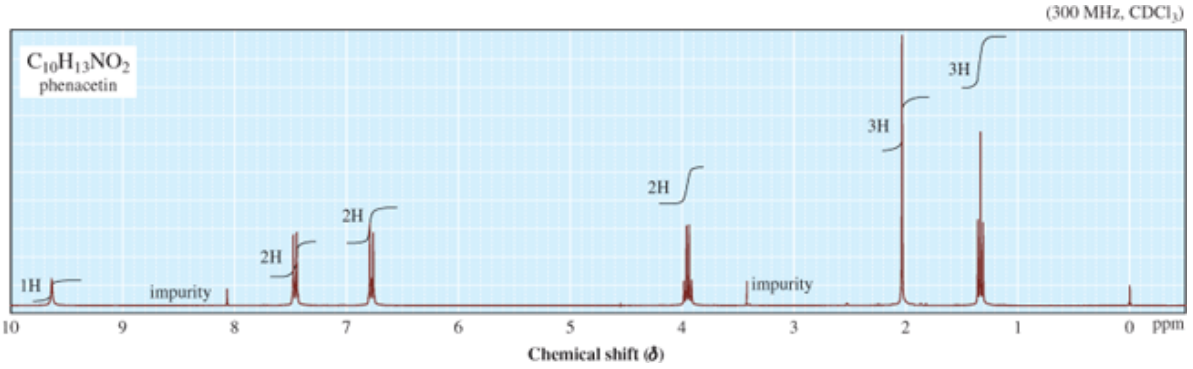




20.70 Propose a structural formula for amide *U*, with the molecular formula $C_6H_{13}NO$ and the ^{1}H-NMR spectrum shown below.

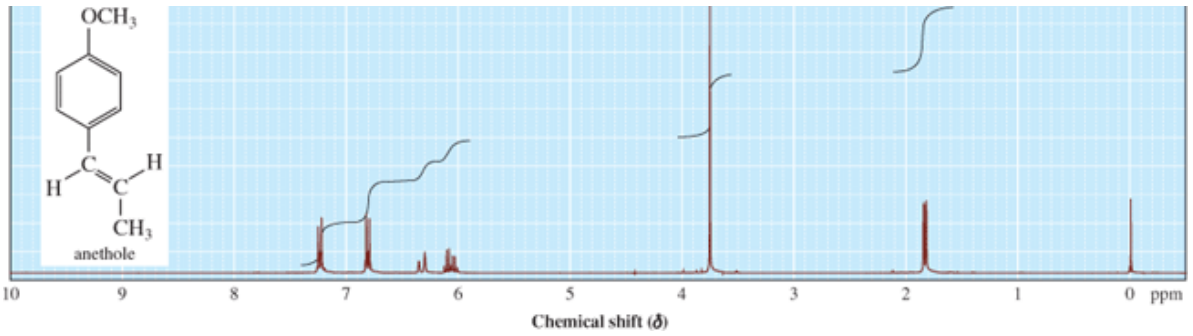


20.71 Propose a structural formula for the analgesic phenacetin, with the molecular formula $C_{10}H_{13}NO_2$, based on its ^{1}H-NMR spectrum.



20.72 The following is a ^{1}H-NMR spectrum and a structural formula for anethole, $C_{10}H_{12}O$, a natural fragrant product obtained from anise. Using the lines of integration, determine the number of protons giving rise to each signal. Show that this spectrum is consistent with the structure of anethole.

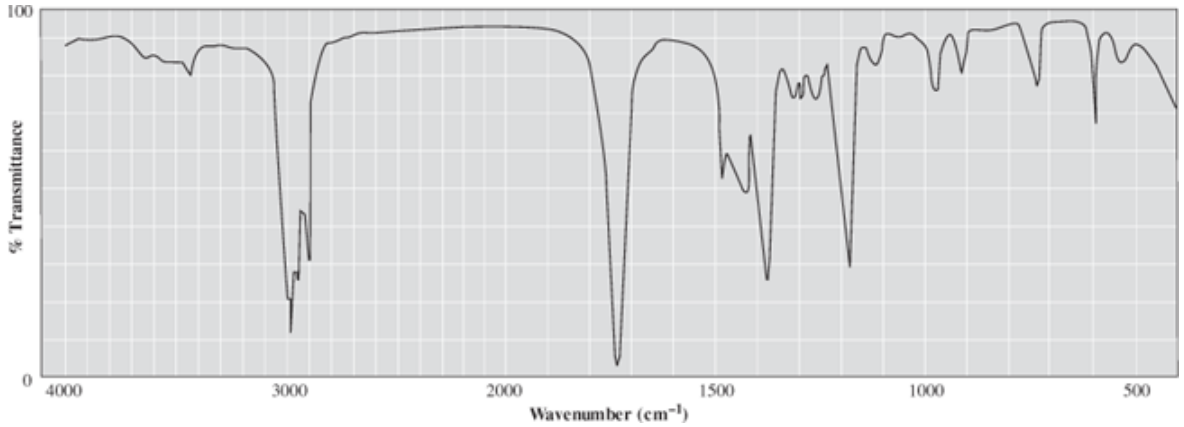


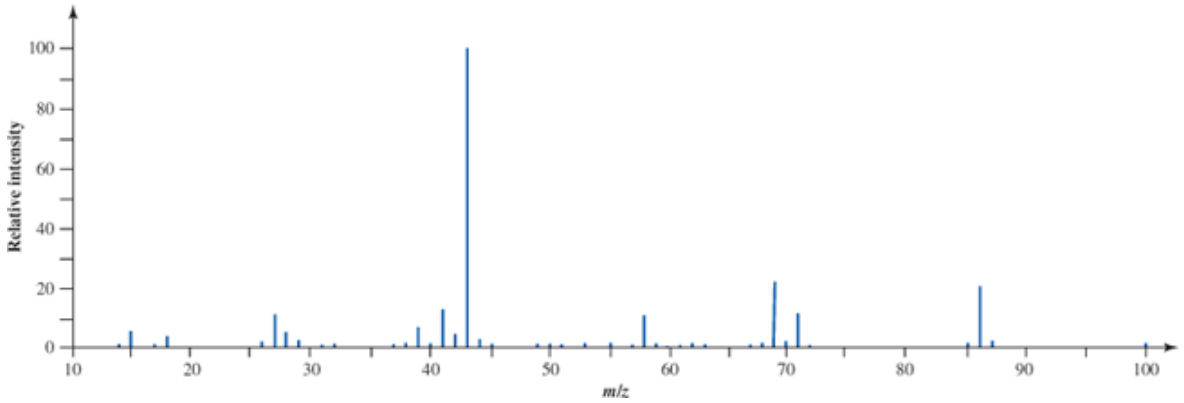


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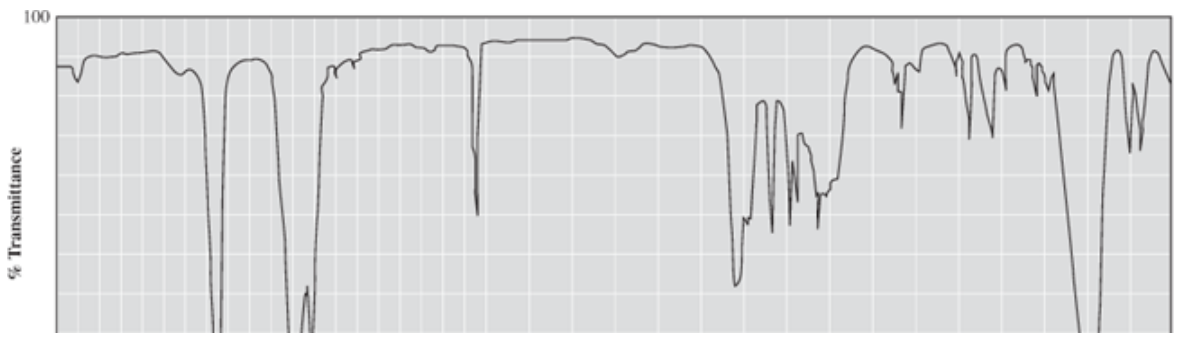
20.73 Limonene is a hydrocarbon found in the peels of lemons that contributes significantly to the smell of lemons. Limonene has a molecular ion peak at $m/z = 136$ in its mass spectrum, and it has two double bonds and one ring in its structure. What is the molecular formula of limonene?

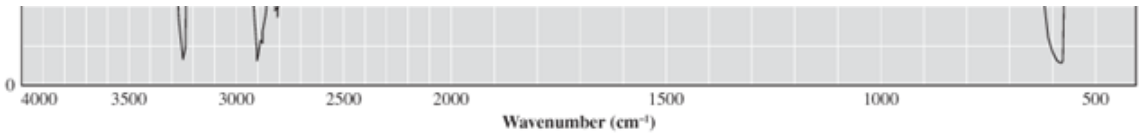
20.74 Following are the IR spectrum and mass spectrum of an unknown compound. Propose at least two possible structures for the unknown compound.

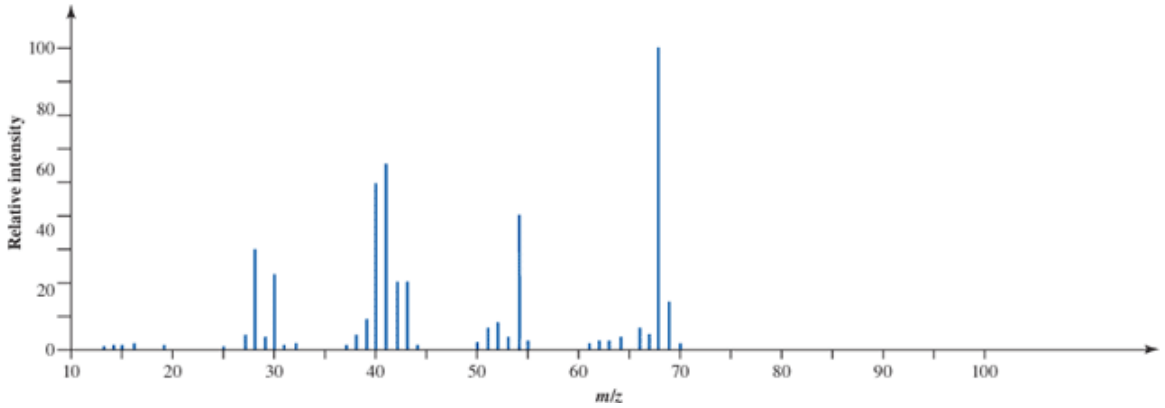




20.75 Following are the IR spectrum and mass spectrum of an unknown compound. Propose at least two possible structures for the unknown compound.







20.76 Propose a structural formula for each of the following esters with the NMR signals given.

(a) $C_6H_{12}O_2$

^{1}H-NMR	^{13}C-NMR
1.2 (d, 6H)	177.2
1.3 (t, 3H)	60.2
2.5 (m, 1H)	34.0
4.1 (q, 2H)	20.0
	14.3

(b) $C_7H_{12}O_4$

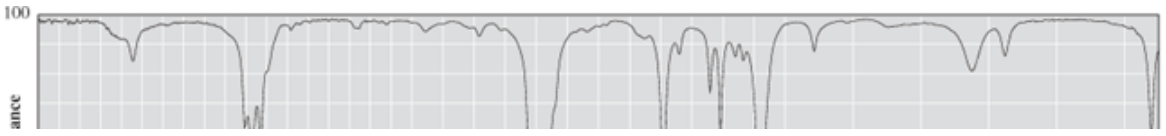
^{1}H-NMR	^{13}C-NMR
1.3 (t, 6H)	166.5
3.4 (s, 2H)	61.4
4.2 (q, 4H)	41.7
	14.1

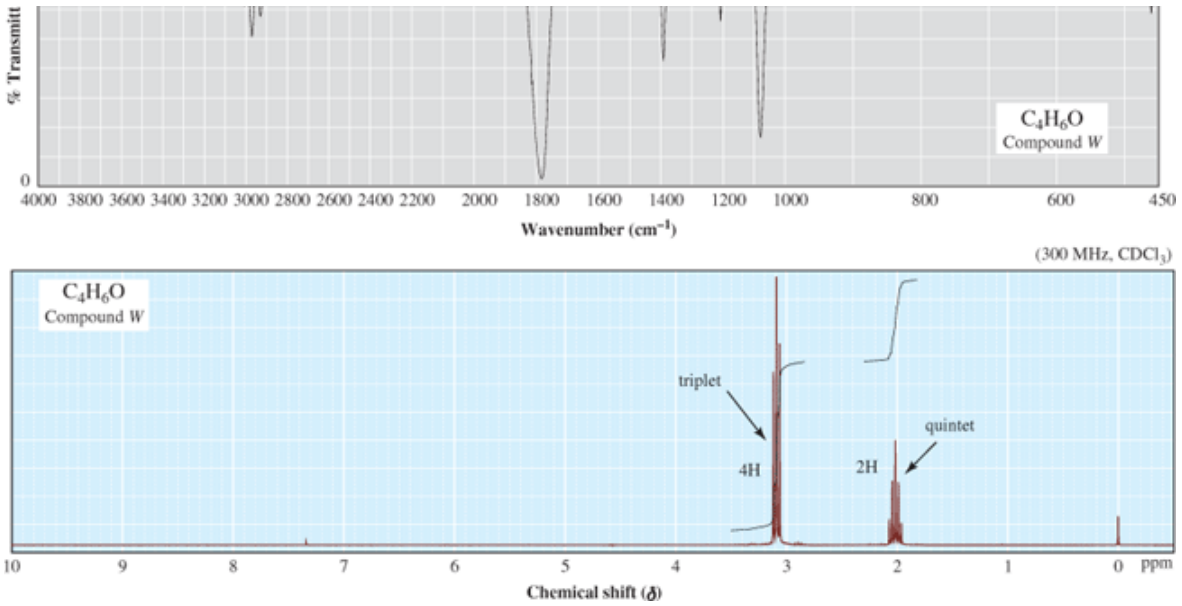
(c) $C_7H_{14}O_2$

^{1}H-NMR	^{13}C-NMR
0.9 (d, 6H)	171.2
1.5 (m, 2H)	63.1
1.7 (m, 1H)	37.3
2.1 (s, 3H)	25.1
4.1 (t, 2H)	22.5
	21.1

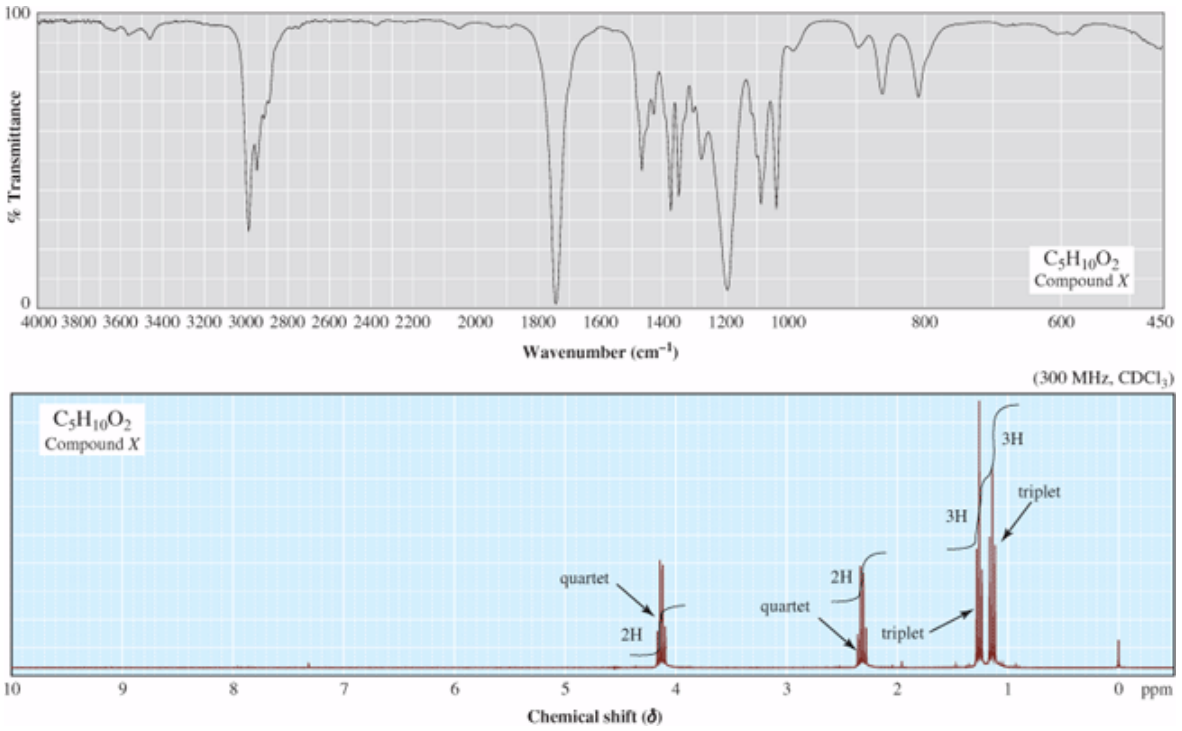
20.77 Compound *V* is an oily liquid with the molecular formula $C_8H_9NO_2$. It is insoluble in water and aqueous NaOH, but it dissolves in 10% HCl. When its solution in HCl is neutralised with NaOH, compound *V* is recovered unchanged. A ^{1}H-NMR spectrum of compound *V* shows signals at δ 3.8 (s, 3H), 4.2 (s, 2H), 7.6 (d, 2H) and 8.7 (d, 2H). Propose a structural formula for compound *V*.

20.78 Propose a structural formula for compound *W*, C_4H_6O, based on the following IR and ^{1}H-NMR spectra.

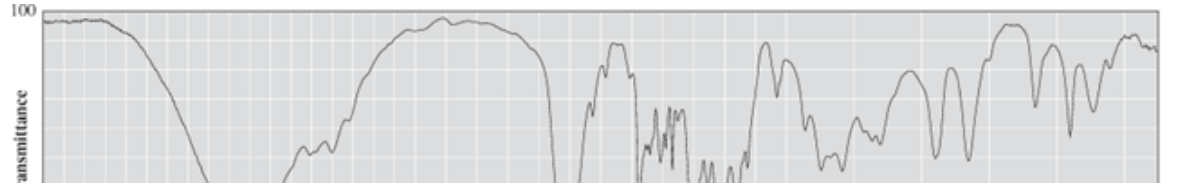


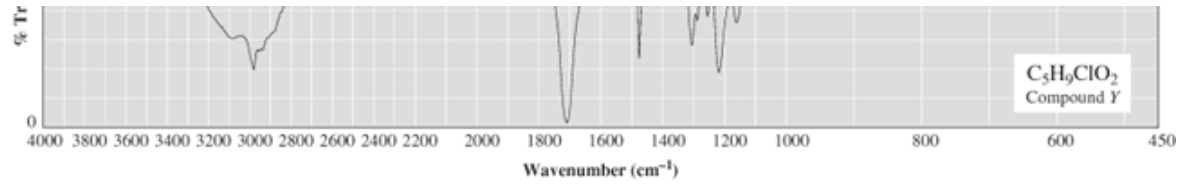


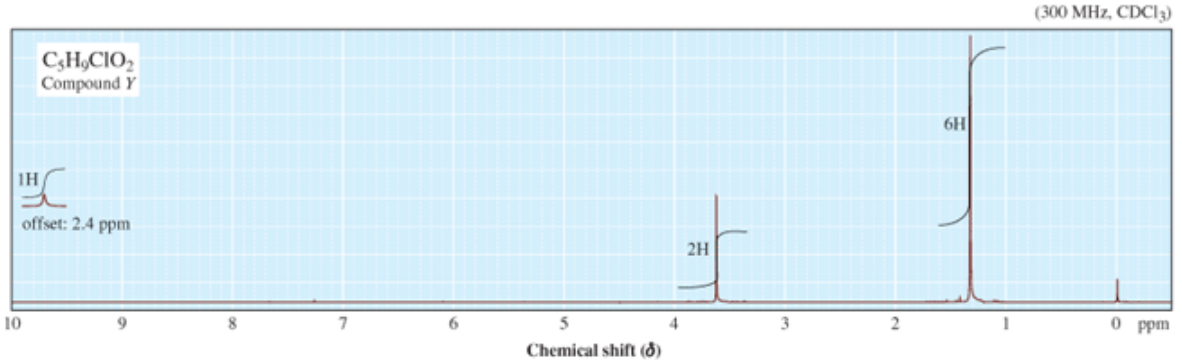
20.79 Propose a structural formula for compound *X*, $C_5H_{10}O_2$, based on the following IR and ^{1}H-NMR spectra.



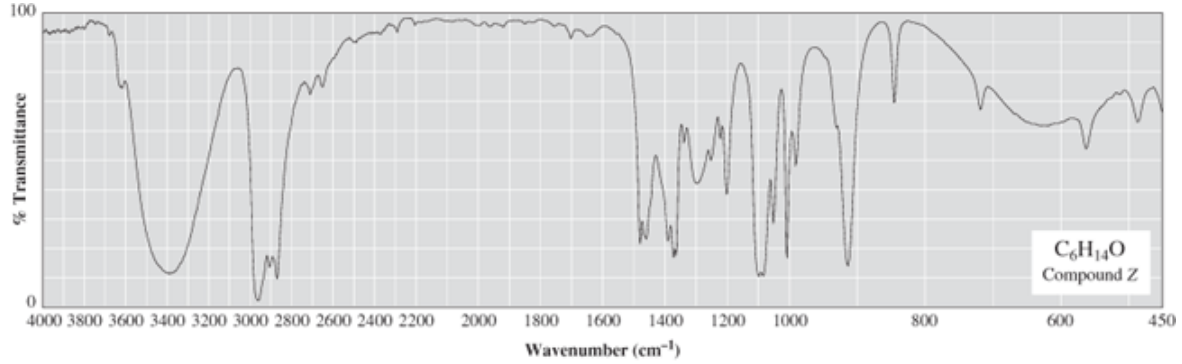
20.80 Propose a structural formula for compound *Y*, $C_5H_9ClO_2$, based on the following IR and spectra.

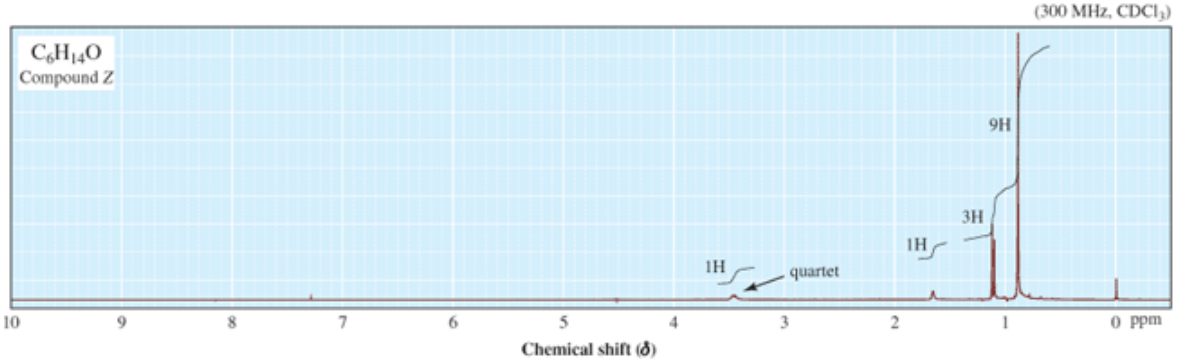




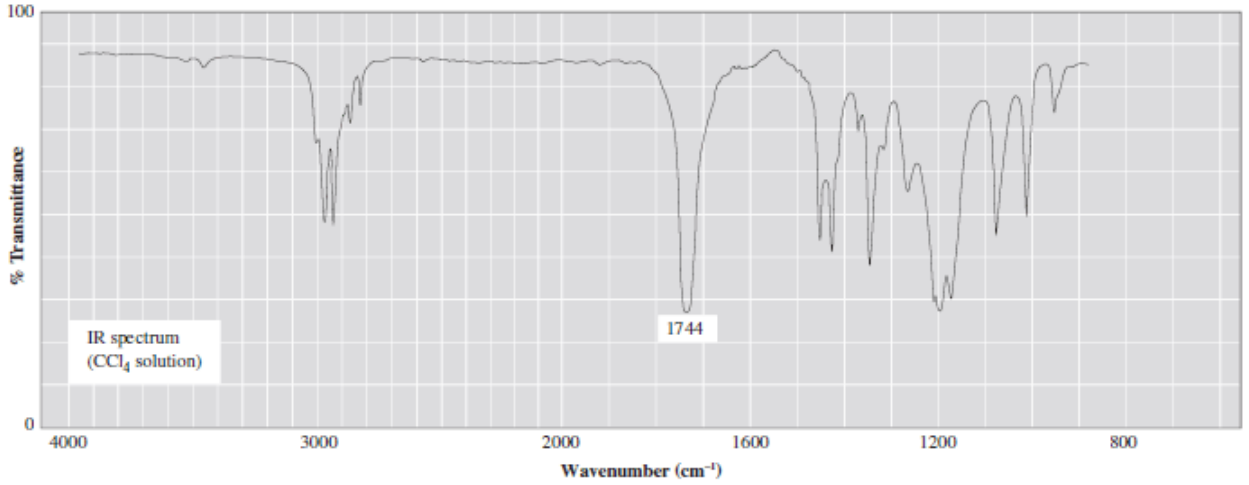


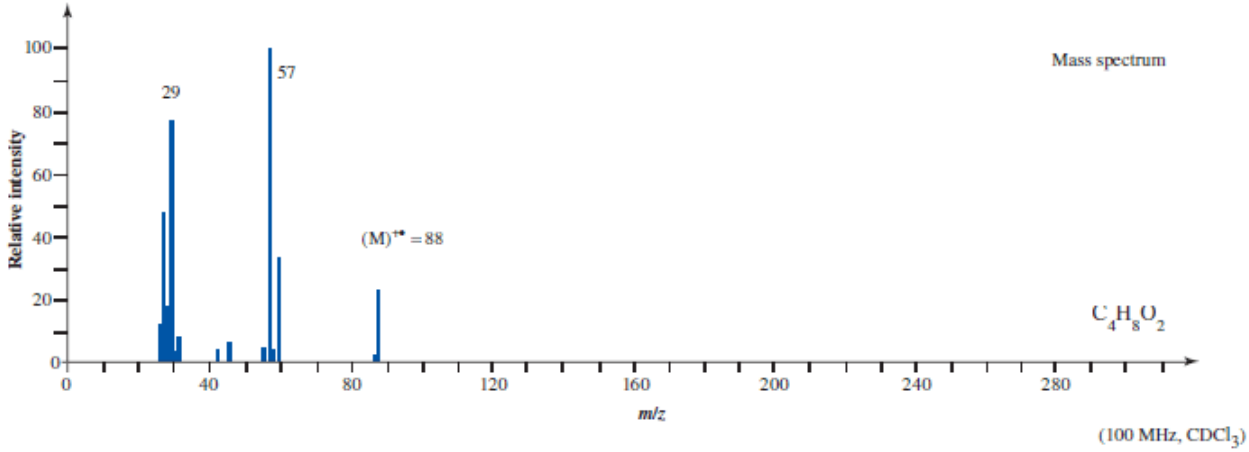
20.81 Propose a structural formula for compound *Z*, $C_6H_{14}O$, based on the following IR and ^{1}H-NMR spectra.

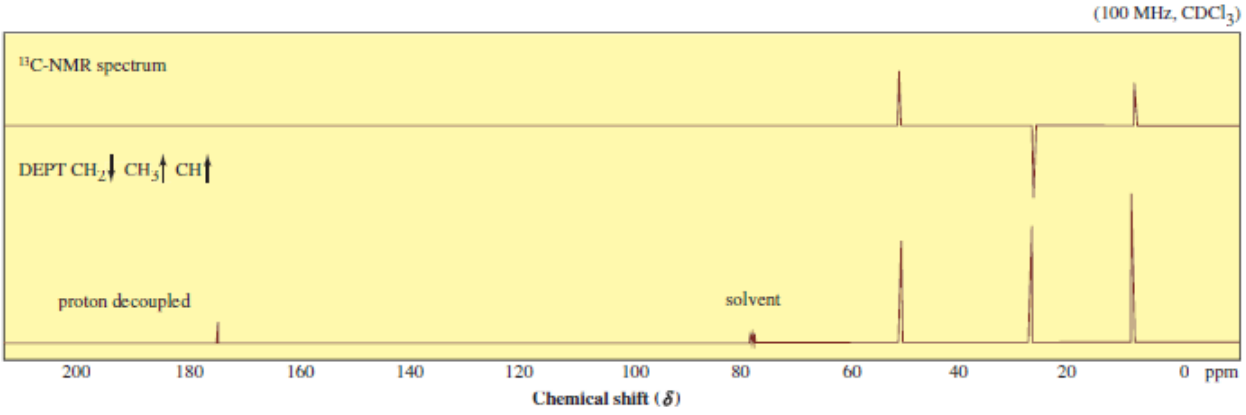


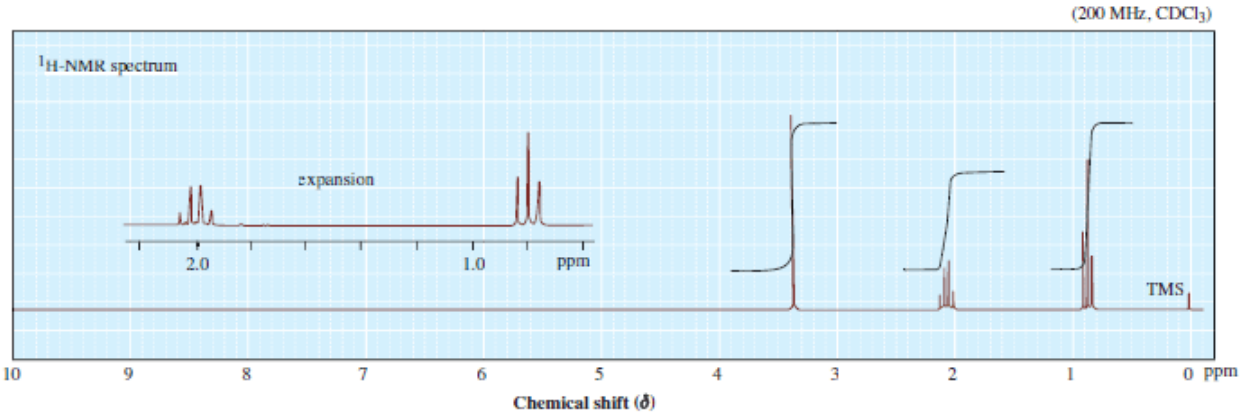


20.82 Determine the structure of the unknown compound with the spectroscopic data given on this and the next pages. *Note:* DEPT spectra are a special type of ^{13}C-NMR spectroscopy in which we can determine the number of hydrogen atoms on each carbon atom. In the DEPT component of the ^{13}C-NMR spectrum, the signals pointing upwards are due to either —CH or —CH_3 groups, while those pointing downwards are due to —CH_2 groups. Quaternary carbons (those without any hydrogen atoms) are not observed in DEPT spectra.

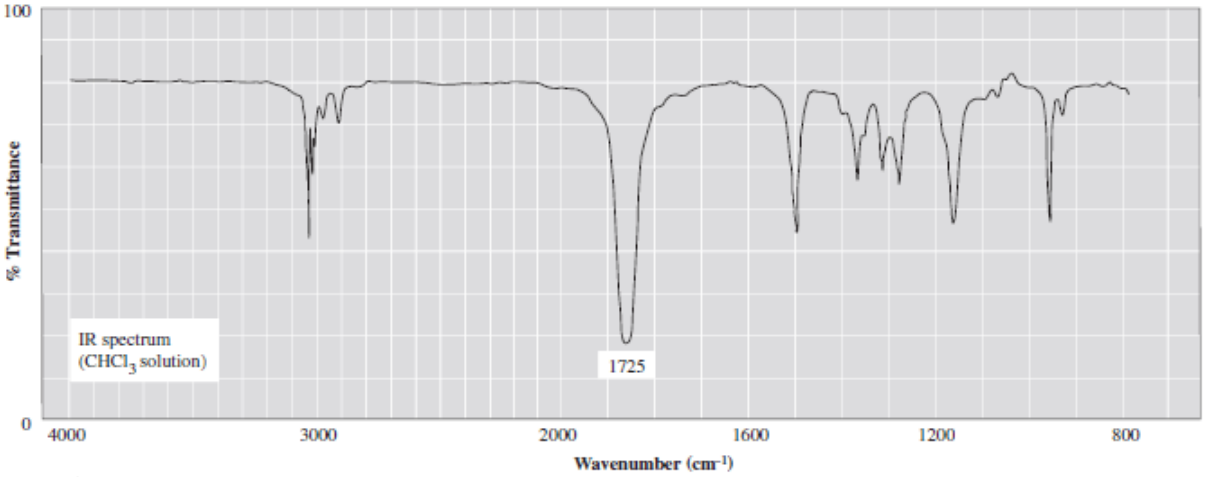

100
% Transmittance
0
IR spectrum
(CCl_4 solution)
1744
4000
3000
2000
1600
1200
800
Wavenumber (cm^{-1})

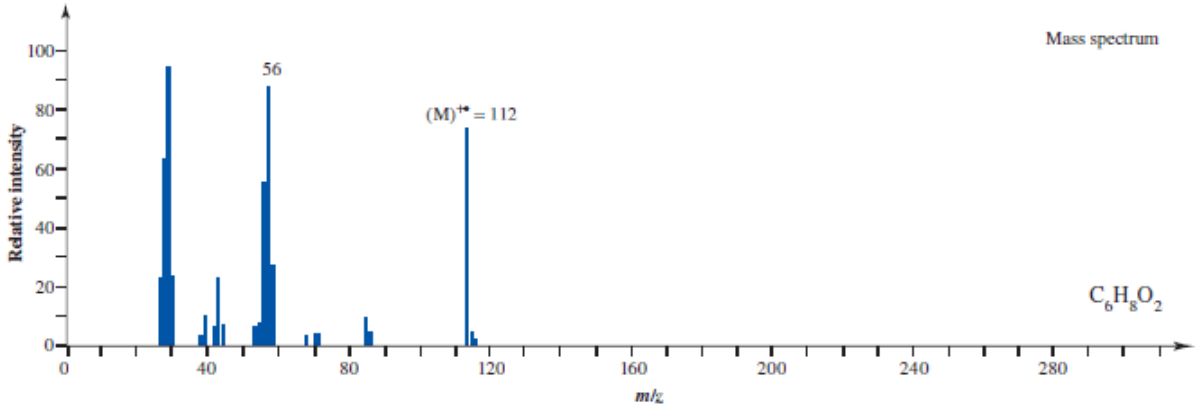

Mass spectrum
Relative intensity
100
80
60
40
20
0
29
57
$(M)^{+\bullet} = 88$
$C_4H_8O_2$
0
40
80
120
160
200
240
280
m/z

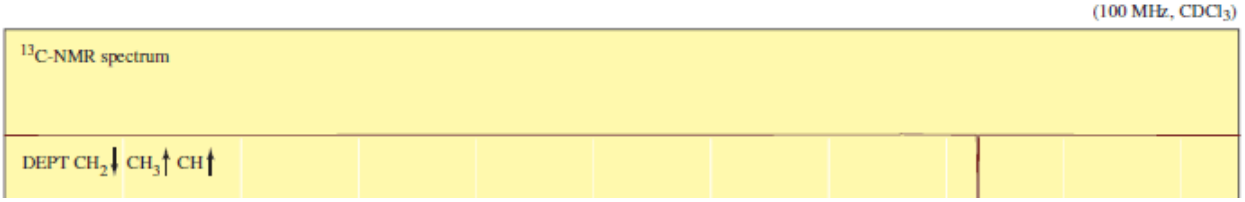

(100 MHz, $CDCl_3$)
^{13}C-NMR spectrum
DEPT CH_2 CH_3 CH
proton decoupled
solvent
200
180
160
140
120
100
80
60
40
20
0 ppm
Chemical shift (δ)

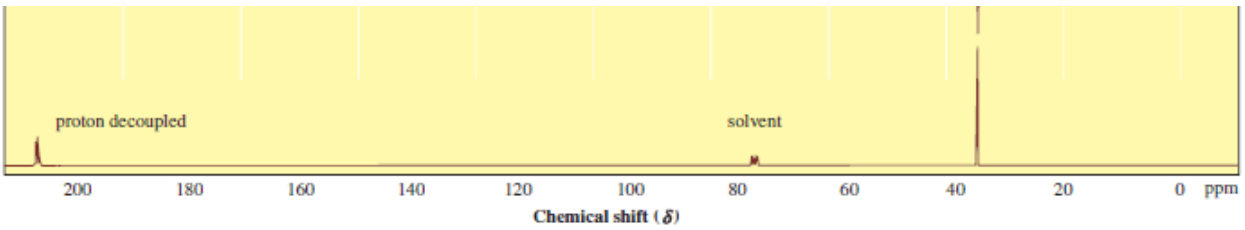


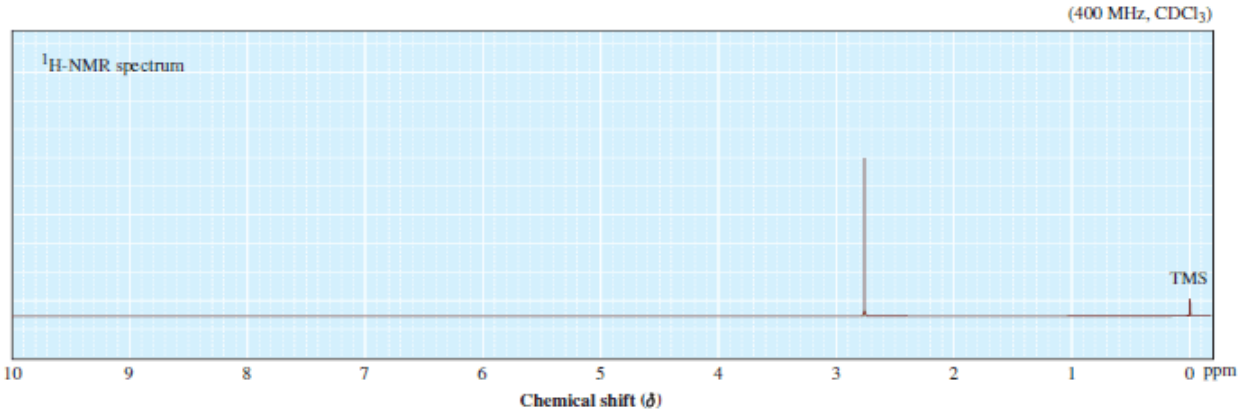
20.83 Determine the structure of the unknown compound with the spectroscopic data on this and the next pages.











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KEY TERMS

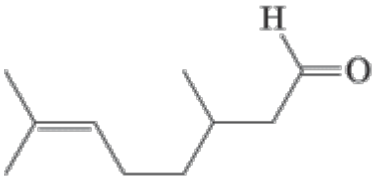
(n + 1) rule
^{13}C-NMR spectroscopy
^{1}H-NMR spectroscopy
Beer–Lambert law
bending
chemical shift (δ)
complex splitting patterns
correlation tables
deshielded
double bond equivalents
doublet
downfield
electromagnetic radiation
electron paramagnetic resonance (EPR)
Electron spin resonance (ESR)
equivalent hydrogen atoms
fingerprint region
frequency
Hertz (Hz)
high resolution mass spectrometry
index of hydrogen deficiency (IHD)
infrared active
infrared radiation
integration
line of integration
local magnetic fields
mass spectrometry
molecular ions
multiplets
multiplicity
nuclear magnetic resonance (NMR) spectroscopy
quartet
radical cations
radio-frequency radiation
reference compound
resonance
shielded
signal splitting
singlet
splitting pattern
stretching
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triplet
upfield
UV/visible spectroscopy
vibrational infrared
Wavelength
wavenumber ($\tilde{\nu}$)
X-ray crystallography

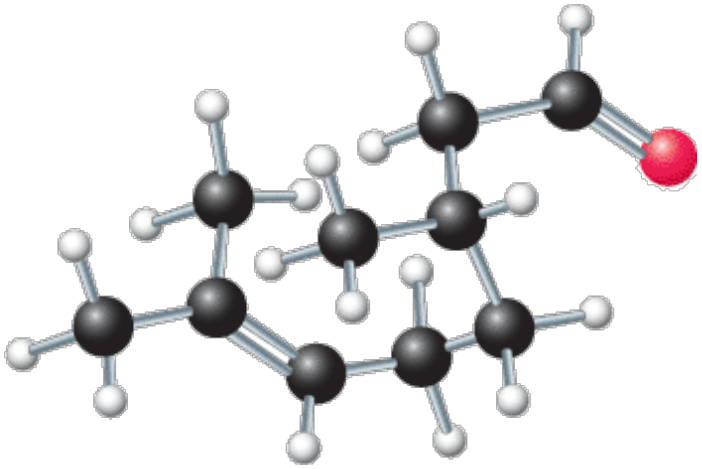
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CHAPTER

21 Aldehydes and Ketones

Evening barbecues and pool parties are common summer leisure activities in Australia and New Zealand. However, also common are the dreaded mosquitoes and sandflies. Citronella candles are an increasingly popular weapon in the battle to prevent mosquito bites. Citronella (structure shown below) is a principal component of citronella oil and belongs to the family of natural products known as terpenes. It has a pleasant lemony scent and is widely used as a fragrance in soaps. Of the two functional groups in citronellal, an alkene and an aldehyde, it is the aldehyde group that is of most interest here.





In this and several of the following chapters, we study the physical and chemical properties of compounds containing the carbonyl group, C═O. Since the carbonyl group is present in aldehydes, ketones, and carboxylic acids and their derivatives, it is one of the most important functional groups in organic chemistry. The chemical properties of the carbonyl group are straightforward, and an understanding of its characteristic reactions leads to an understanding of a wide variety of organic reactions.





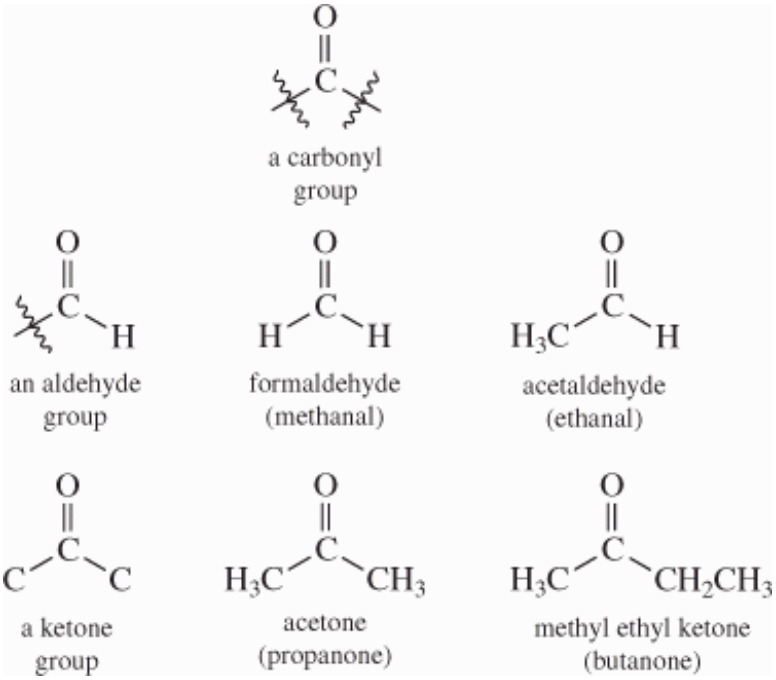
KEY TOPICS

21.1 Structure and bonding
21.2 Nomenclature
21.3 Physical properties
21.4 Preparation of aldehydes and ketones
21.5 Reactions
21.6 Keto–enol tautomerism

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21.1 Structure and Bonding

When a carbonyl group is bonded to a hydrogen atom and a hydrocarbon group (or a second hydrogen atom), the compound is an **aldehyde**. The simplest aldehyde, formaldehyde (methanal), has the carbonyl group bonded to two hydrogen atoms. In all other aldehydes, the carbonyl group is bonded to one hydrogen atom and one carbon atom. When the carbon atom of the C═O group is bonded to two hydrocarbon groups, the compound is a **ketone**. The following are Lewis structures for the aldehydes formaldehyde (methanal) and acetaldehyde (ethanal), and for the simplest ketones, acetone (propanone) and methyl ethyl ketone (butanone). The IUPAC name of each compound is in parentheses.



The aldehyde group is often written —CHO, the double bond of the carbonyl group being implied. The abbreviation COH is *not* appropriate because it suggests an alcohol functional group. The ketone group is sometimes condensed to CO.

The carbonyl group is a planar group comprising a carbon atom bonded to an oxygen atom and two other atoms. The bond angles around the carbonyl carbon atom are approximately 120°. According to the valence bond theory (see section 5.6), a carbon–oxygen double bond consists of one σ bond formed by the overlap of the sp^2 hybrid orbitals of carbon and oxygen, and one π bond formed by the overlap of two parallel 2*p* orbitals. The two nonbonding pairs of electrons on the oxygen atom lie in the two remaining sp^2 hybrid orbitals (figure 21.1).

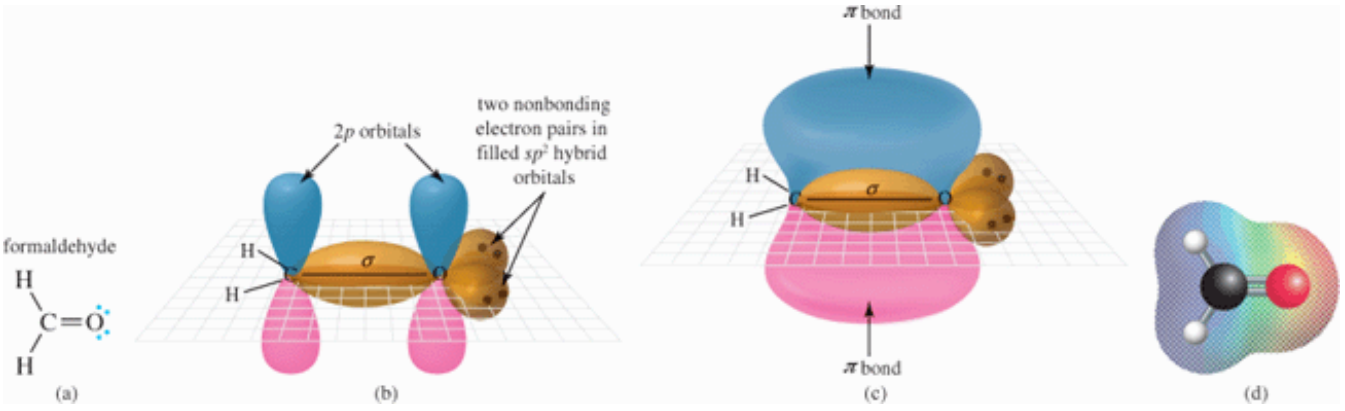


FIGURE 21.1 Representations of a carbon–oxygen double bond: (a) Lewis structure of formaldehyde, CH_2O

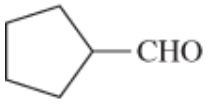
(a) Lewis structure of formaldehyde, CH_2O,
(b) the σ-bond framework and nonoverlapping parallel 2*p* atomic orbitals,
(c) overlap of parallel 2*p* atomic orbitals to form a π bond and
(d) an electron density model showing the uneven distribution of electrons in the carbonyl group.

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21.2 Nomenclature

The IUPAC system of nomenclature for aldehydes and ketones follows the pattern of first selecting the longest chain of carbon atoms that contains the functional group as the parent alkane. We show the presence of the aldehyde group by changing the suffix *-e* of the parent alkane to *-al*, as in methanal (section 2.3). As the carbonyl group of an aldehyde can appear only at the end of a parent chain, its position is unambiguous — there is no need to use a number to locate it.

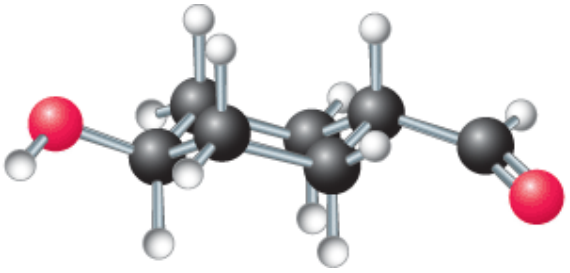
For cyclic molecules in which the —CHO group is bonded directly to the ring, we name the molecule by adding the suffix *-carbaldehyde* to the name of the ring. We number the atom of the ring bearing the aldehyde group as 1.



cyclopentane-carbaldehyde



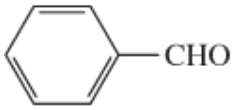
trans-4-hydroxycyclo-hexanecarbaldehyde



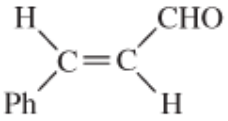
The common name for an aldehyde is derived from the common name of the corresponding carboxylic acid by dropping the word 'acid' and changing the suffix *-ic* or *-oic* to *-aldehyde*. We can illustrate this using two common names of carboxylic acids with which you are familiar. The name formaldehyde is derived from formic acid, and the name acetaldehyde from acetic acid.

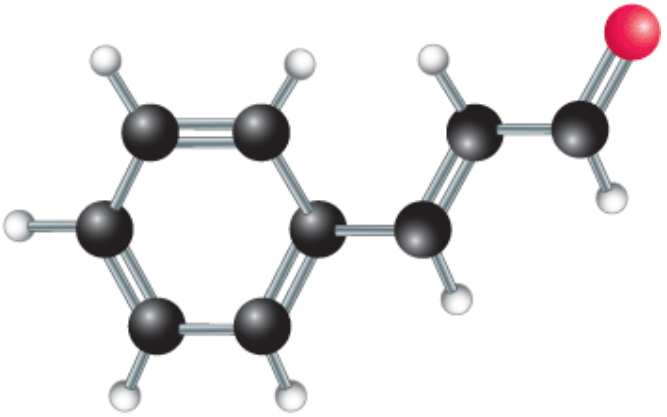


Among the aldehydes for which the IUPAC system retains common names are: formaldehyde, acetaldehyde, benzaldehyde and cinnamaldehyde.



benzaldehyde

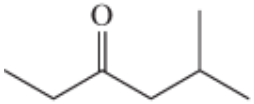




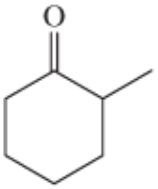
trans-3-phenylpropenal (cinnamaldehyde)

Note here the alternative ways of writing the phenyl group (C_6H_5—). In benzaldehyde, it is written as a line-structure, while in cinnamaldehyde it is abbreviated to Ph.

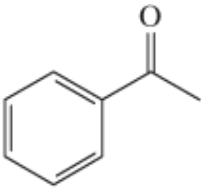
In the IUPAC system, we name ketones by selecting the longest chain that contains the carbonyl group and making it the parent alkane. The presence of the ketone is indicated by changing the suffix from *-e* to *-one* (section 2.3). We number the parent chain so that the carbonyl carbon atom has the smallest number. The IUPAC system retains the common names acetone, acetophe-none and benzophenone.



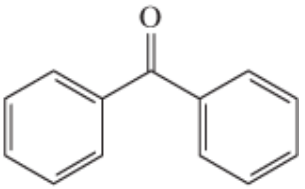
5-methylhexan-3-one



2-methyl-cyclohexanone

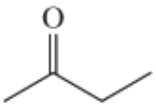


acetophenone

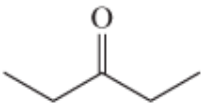


benzophenone

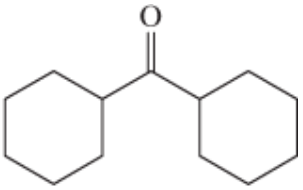
Common names for ketones are derived by naming each alkyl or aryl group bonded to the carbonyl group as a separate word, followed by the word 'ketone'. Groups are generally listed in order of increasing atomic weight. For example, methyl ethyl ketone, MEK, is a common solvent for varnishes and lacquers.



methyl ethyl ketone (MEK) (butanone)



diethyl ketone (pentan-3-one)

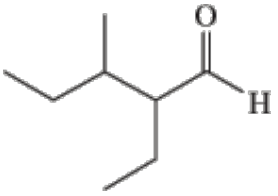


dicyclohexyl ketone

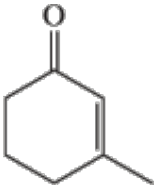
WORKED EXAMPLE 21.1

Naming Aldehydes and Ketones

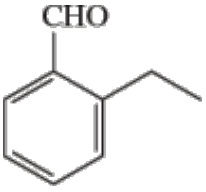
(a)



(b)



(c)



Analysis

(a) Identify the longest chain containing the aldehyde group. This will be the parent chain. Number the chain starting from the aldehyde group.

(b) Number the six-membered ring beginning with the carbonyl carbon atom.

(c) This molecule is derived from benzaldehyde, so it should be named as a substituted benzaldehyde.

Solution

(a) The IUPAC name of this compound is 2-ethyl-3-methylpentanal.

(b) The IUPAC name of this compound is 3-methylcyclohex-2-enone.

(c) The IUPAC name of this compound is 2-ethylbenzaldehyde.

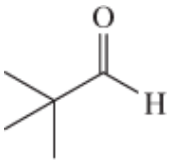
Is our answer reasonable?

Check that the answer leads unambiguously to the given structure. Check that the structure is numbered from the correct end and that the substituents are numbered appropriately.

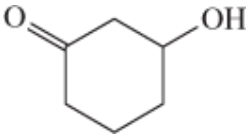
PRACTICE EXERCISE 21.1

Write the IUPAC name for each of the following compounds, and specify the configuration of (c).

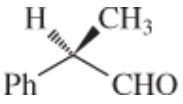
(a)



(b)



(c)



WORKED EXAMPLE 21.2

Drawing Structural Formulae for Ketones

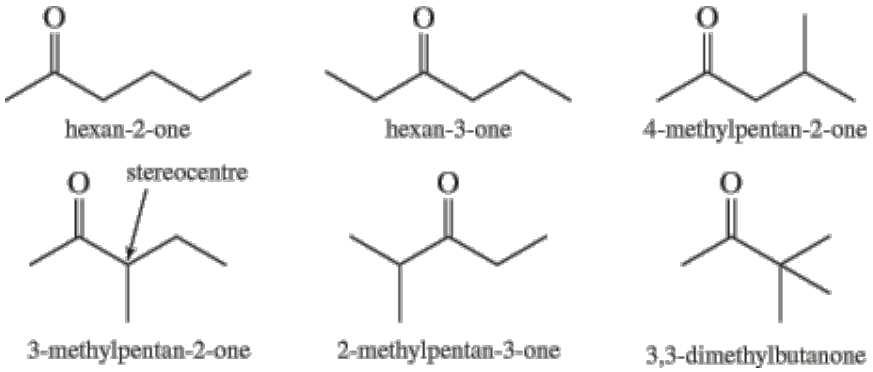
Write structural formulae for all ketones with the molecular formula $C_6H_{12}O$, and give each its IUPAC name. Which of these ketones are chiral?

Analysis

Firstly, identify the possible skeletal arrangements with six carbon atoms that could give a ketone. The possible ketones are derived from hexane, 2- and 3-methylpentane, and 2,2-dimethylbutane. A chiral ketone has at least one stereocentre (bonded to four different groups).

Solution

The following are line structures and IUPAC names for the six ketones with the molecular formula $C_6H_{12}O$.



Only 3-methylpentan-2-one has a stereocentre and is chiral.

Is our answer reasonable?

The most common error is to duplicate or miss some structures. Check that each structure is different (to avoid duplication). The best way to ensure that you have included all the possible structures is to check that the basic skeletal frameworks are covered (as given in the analysis) and then systematically move the carbonyl group to each possible position.

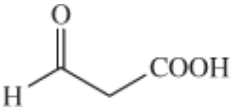
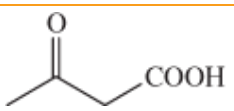
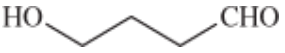
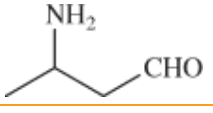
PRACTICE EXERCISE 21.2

Write structural formulae for all aldehydes with the molecular formula $C_6H_{12}O$, and give each its IUPAC name. Which of these aldehydes are chiral?

IUPAC Names for Compounds with More than One Functional Group

In naming compounds that contain more than one functional group, IUPAC has established an **order of precedence of functional groups**. That is, a system for prioritising functional groups for the purposes of IUPAC nomenclature. Table 21.1 gives the order of precedence for six functional groups.

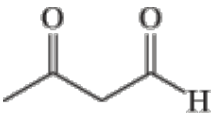
TABLE 21.1 Decreasing order of precedence of six functional groups.

Functional group	Suffx	Prefix	Example of when the functional group is not highest priority and is used as a prefix	
carboxyl group	-oic acid	—		
aldehyde group	-al	oxo-	3-oxopropanoic acid	
ketone group	-one	oxo-	3-oxobutanoic acid	
alcohol group	-ol	hydroxy-	4-hydroxybutanal	
amino group	-amine	amino-	3-aminobutanal	
sulfhydryl	-thiol	mercapto-	2-mercaptoethanol	

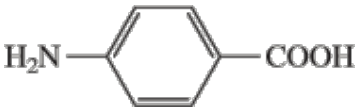
Naming Complex Aldehydes and Ketones

Write the IUPAC name for each of the following compounds.

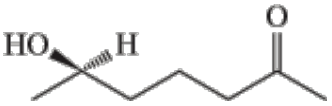
(a)



(b)



(c)



Analysis

(a) An aldehyde has higher precedence than a ketone, so we indicate the presence of the carbonyl group of the ketone by the prefix *oxo*-.

(b) The carboxyl group has higher precedence than the amino group, so we indicate the presence of the amino group by the prefix *amino*-.

(c) The carbonyl group has higher precedence than the hydroxyl group, so we indicate the hydroxyl group by the prefix *hydroxy*-. To determine the *R*,*S* configuration, follow the pro cedure in section 17.3.

Solution

(a) The IUPAC name of this compound is 3-oxobutanal.

(b) The IUPAC name is 4-aminobenzoic acid. Alternatively, the compound may be named *p*-aminobenzoic acid, abbreviated PABA. PABA, a growth factor of micro-organisms, is required for the synthesis of folic acid.

(c) The IUPAC name of this compound is (*R*)-6-hydroxyheptan-2-one.

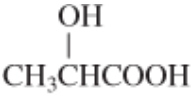
Is our answer reasonable?

To check each answer, draw a structure from the name that has been determined. It should be the same as the compound from the question.

PRACTICE EXERCISE 21.3

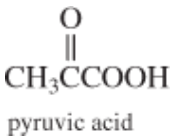
Write IUPAC names for the following compounds, each of which is important in metabolic processes.

(a)



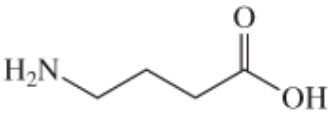
lactic acid

(b)



pyruvic acid

(c)



γ-aminobutyric acid

The name shown is the compound's common name as used in the biological sciences.

Chemistry Research

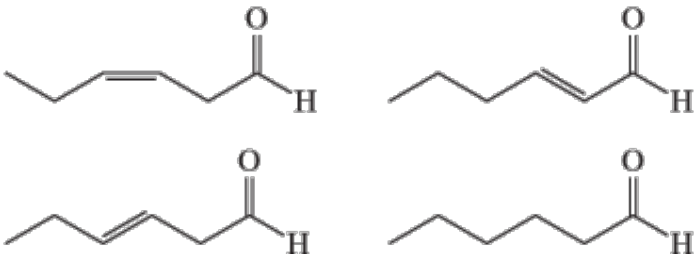
Plant Protection

Associate Professor Emilio Ghisalberti, University of Western Australia

Aldehydes and ketones occur very widely in nature. Many substances required by, and produced by, living organisms contain these functional groups. In the chemical industry, simple aldehydes and ketones are produced in large quantities as solvents and for use in the preparation of other compounds. Many have pleasant odours and flavours and are used in perfumes, soaps and in food technology.

In recent years, scientists have discovered that some aldehydes and ketones are used by living organisms to communicate with members of the same species and to defend themselves from predators. Plants have developed methods that use aldehydes and ketones to defend themselves from herbivores, particularly insects.

The production of defence compounds by plants when they are injured can be easily demonstrated. If a few blades of grass, or a plant leaf, are crushed between the fingers, a distinctive smell can be detected after a few seconds. This smell, often referred to as ‘the smell of freshly cut grass’ or ‘green odour’, is due to eight different compounds including the four aldehydes shown below.

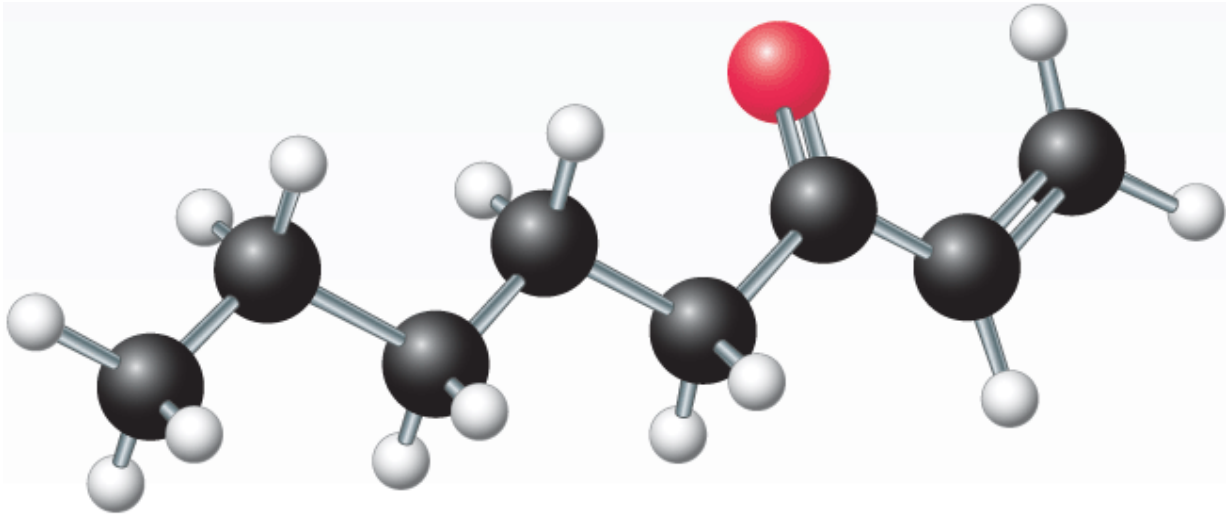


The redlegged earth mite is a significant pest of pastures, crops and vegetables in South Africa, Australia and New Zealand. In Australia, it is a pest of subterranean clover (figure 21.2) and is responsible for losses in pasture crops of an estimated $100 million.



FIGURE 21.2 *Trifolium subterraneum* — a type of subterranean clover that grows in Australia. SPL/Maria & Bruno Petriglia

Fortunately, some varieties of subterranean clover show resistance to the mite and deter the mite from feeding on them. It was suggested that when the mite probed the leaf surface with its mouth parts, the resistant varieties produced a compound unpalatable to the mite. After a considerable amount of work, the Ghisalberti research group, working in collaboration with the entomology section of CSIRO, showed this to be the case. In fact, the compound that deters the mites from feeding was shown to be the ketone oct-1-en-3-one (shown below). This non-toxic compound can be used instead of pesticides to protect the crop.

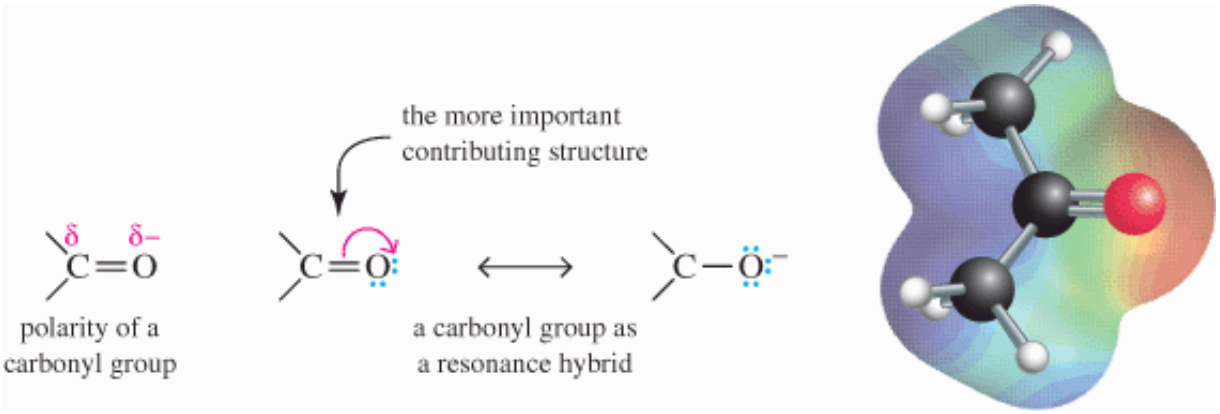


oct-1-en-3-one

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21.3 Physical Properties

Oxygen is more electronegative (see chapter 5, p. 168) than carbon (χ = 3.5 compared with 2.5); therefore, a carbon–oxygen double bond is polar, with the oxygen atom bearing a partial negative charge and the carbon atom bearing a partial positive charge. Resonance effects also contribute to the polarity of the carbonyl groups.



The electron density model (above) shows that the partial charge on an acetone molecule is distributed both on the carbonyl carbon atom and on the two attached groups. Because of the polarity of the carbonyl group, aldehydes and ketones are polar compounds and interact in the liquid state through dipole–dipole interactions. As a result, aldehydes and ketones have higher boiling points than nonpolar compounds with a comparable number of electrons. Table 21.2 lists the boiling points of six compounds with a similar number of electrons.

TABLE 21.2 Boiling points of six compounds of comparable molar mass and similar numbers of electrons.

Name	Structural formula	Number of electrons	Boiling point (°C)
diethyl ether	$CH_3CH_2OCH_2CH_3$	42	34
pentane	$CH_3CH_2CH_2CH_2CH_3$	42	36
butanal	$CH_3CH_2CH_2CHO$	40	76
butanone	$CH_3CH_2COCH_3$	40	80
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	42	117
propanoic acid	CH_3CH_2COOH	40	141

Pentane and diethyl ether have the lowest boiling points of these six compounds. Both butanal and butanone are polar compounds, and have higher boiling points because of the intermolecular attraction between carbonyl groups. Alcohols (section 19.1) and carboxylic acids (section 23.1) are also polar compounds, and because their molecules associate by hydrogen bonding their boiling points are higher than those of butanal and butanone—compounds that cannot form intermolecular hydrogen bonds between like molecules.

Low-molar-mass aldehydes and ketones are more soluble in water than nonpolar compounds of similar molar mass because carbonyl groups interact with water molecules by hydrogen bonding. The carbonyl group is a hydrogen bond acceptor (the oxygen atom provides the electrons to form the hydrogen bond with water), as shown on the right.

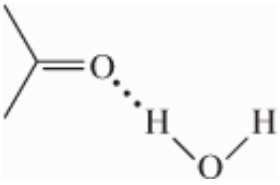


Table 21.3 lists the boiling points and solubilities in water of several low-molar-mass aldehydes and ketones.

TABLE 21.3 Physical properties of selected aldehydes and ketones.

IUPAC name	Common name	Structural formula	Boiling point (°C)	Solubility (g/100 g water)
methanal	formaldehyde	HCHO	-21	infinite
ethanal	acetaldehyde	CH_3CHO	20	infinite
propanal	propionaldehyde	CH_3CH_2CHO	49	16
butanal	butyraldehyde	$CH_3CH_2CH_2CHO$	76	7
hexanal	caproaldehyde	$CH_3(CH_2)_4CHO$	129	slight
propanone	acetone	CH_3COCH_3	56	infinite
butanone	methyl ethyl ketone	$CH_3COCH_2CH_3$	80	26
pentan-3-one	diethyl ketone	$CH_3CH_2COCH_2CH_3$	101	5

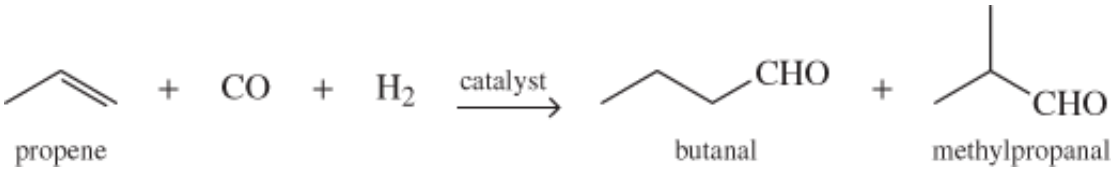
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21.4 Preparation of Aldehydes and Ketones

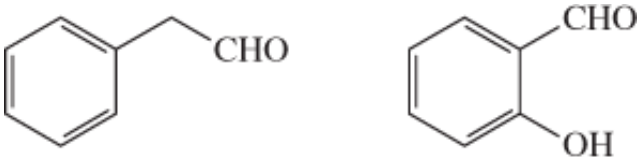
Aldehydes and ketones can be prepared from many functional groups using various reactions. Some of these will be discussed briefly here and in more detail elsewhere in this text. However, before describing specific examples of the synthesis of aldehydes and ketones, we will look briefly at some of the more industrially important compounds in this class.

Industrially Important Aldehydes and Ketones

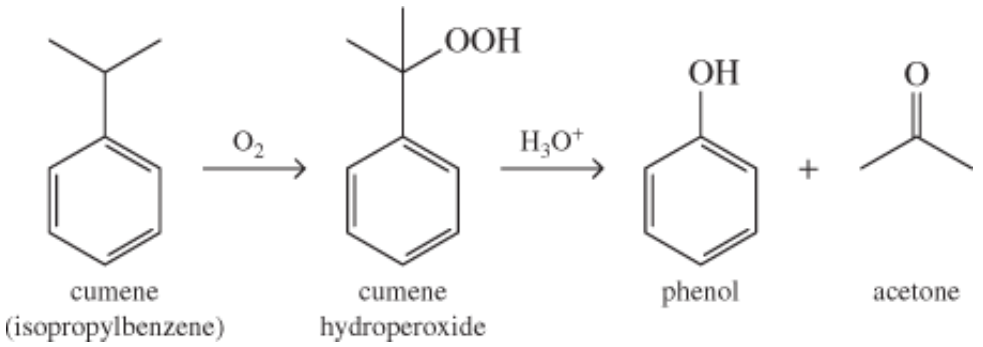
Formaldehyde is probably the most important aldehyde produced on an industrial scale, with over 17 million tonnes produced annually, principally by the oxidation of methanol. It is used mainly in the manufacture of resins for the construction industry, particularly in the production of wood-based products. The next most abundantly produced aldehydes are the butanals (butanal and methylpropanal). These are produced by the hydroformylation (addition of carbon monoxide and hydrogen) of propene by a process known as the oxo-process (see the equation below). Approximately 6 million tonnes of butanals are produced annually, mainly for the manufacture of plasticisers. The aliphatic aldehydes with 6 to 13 carbon atoms are used extensively in the fragrance industry.



Industrially important aromatic aldehydes include phenylacetaldehyde (used in the flavour and fragrance industry) and salicylaldehyde (2-hydroxybenzaldehyde), which is used in the synthesis of coumarin for the electroplating industry and also for the synthesis of agrochemicals, pharmaceuticals and fragrances.



Acetone is the simplest and most important ketone and finds ubiquitous use as a solvent. Higher members of the aliphatic methyl ketone series (such as methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone) are also industrially significant solvents. Acetone has been produced industrially for over a century by a variety of methods. However, today, most of the world's supply is obtained as a co-product in the preparation of phenol by the hydroperoxidation of cumene. Acetone is used as a solvent in the preparation of methyl methacrylate and bisphenol A (both used in the production of polymers). The other ‘methyl ketones’, including methyl ethyl ketone (MEK, butanone) and methyl isobutyl ketone (MIBK, 4-methylpentanone) are also important industrial solvents, particularly for coatings and inks.

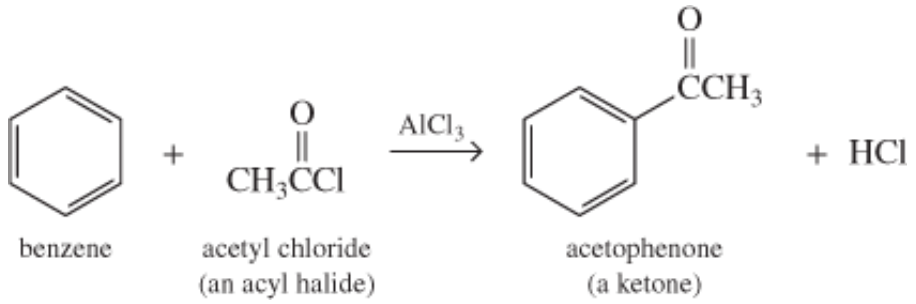


Important aromatic ketones include, acetophenone, propiophenone (ethyl phenyl ketone) (used in the manufacture of ephedrine and as a fragrance enhancer) and benzophenone (used as a photoinitiator in UV-curable inks and coatings).

Friedel–crafts Acylation

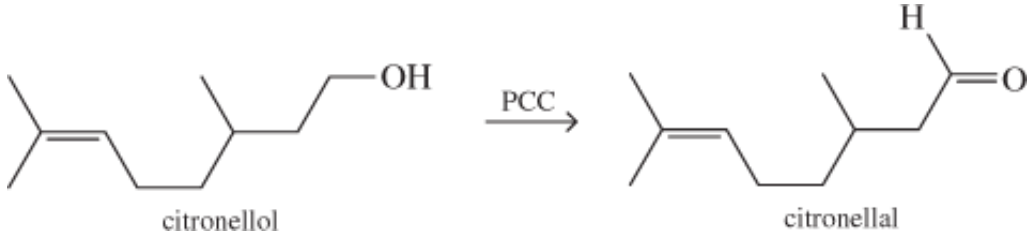
Ketones can be prepared by Friedel–Crafts acylation of aromatic compounds (see section 16.8) as illustrated by the reaction of benzene and acetyl chloride in the presence of aluminium chloride to give acetophenone.

Acetophenone is produced industrially by this process and is used in the preparation of paints and resins, and in pharmaceuticals, perfumes and pesticides.

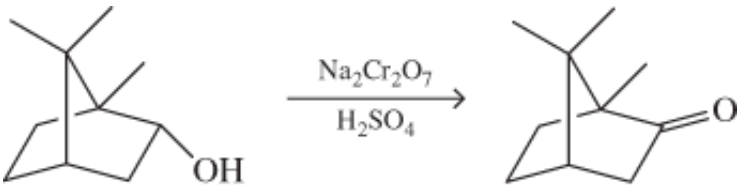


Oxidation of Alcohols

We have already seen in chapter 19 that primary alcohols can be oxidised under mild conditions to give aldehydes (for more examples of this reaction see section 19.2).



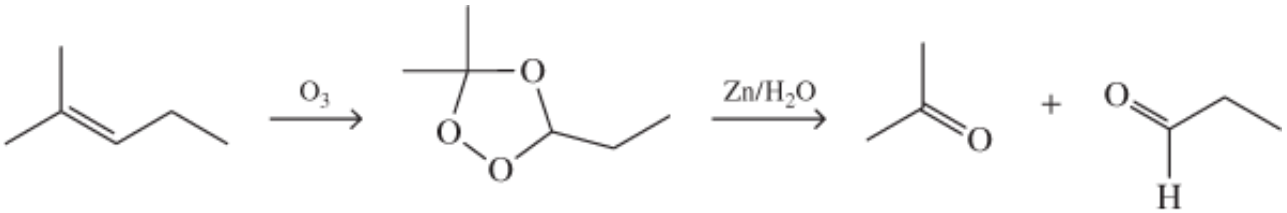
PCC (pyridinium chlorochromate) is a mild oxidising agent that will oxidise primary alcohols to aldehydes but will not further oxidise aldehydes to carboxylic acids. Ketones can be obtained by the oxidation of secondary alcohols (for more examples of this reaction see section 19.2).



borneol camphor

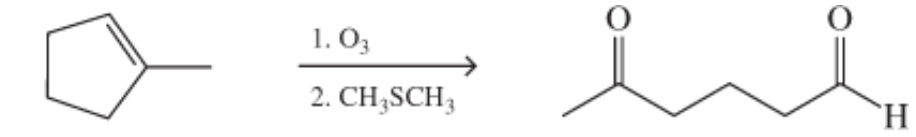
Ozonolysis of Alkenes

Alkenes are readily cleaved by reaction with ozone followed by reductive hydrolysis to give aldehydes and/or ketones. Ozone is bubbled through a solution of the alkene in an inert solvent to produce an unstable ozonide. This ozonide is not isolated but treated with a mild reducing agent (typically zinc/water/acid or dimethyl sulfide) to give carbonyl compounds as shown below (along with inorganic products, which are not shown).



2-methylpent-2-ene an ozonide acetone (a ketone) propanal (an aldehyde)

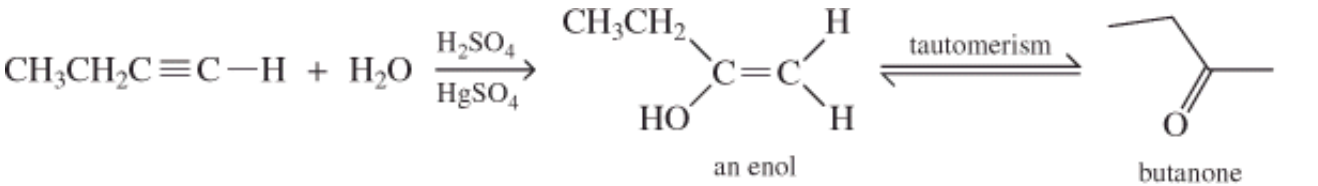
Although the reaction may look complex, the final outcome is simply the cleavage of a C═C bond and its replacement with two C═O groups. When the alkene is part of a ring, a single compound with two carbonyl groups is formed.



1-methylcyclopentene 5-oxohexanal

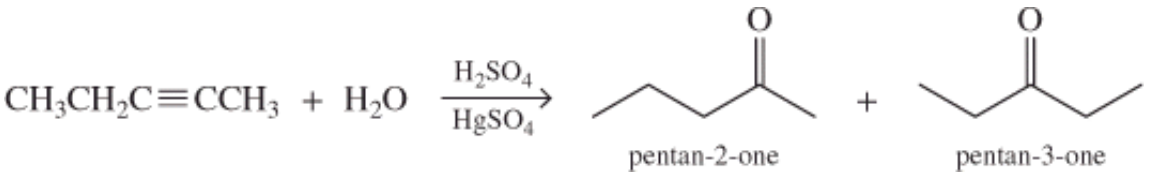
Hydration of Alkynes

In section 16.5, the electrophilic addition of water to alkenes (hydration) to give alcohols was discussed. Water can also be added to alkynes under acidic conditions in the presence of a mercuric sulfate catalyst. The initial product of this reaction is an enol (an alkene with an ═OH group) which undergoes tautomerism (see section 21.6) to give a ketone. The addition obeys Markov-nikov's rule (section 16.5), and terminal alkynes (those with the alkyne group at the end of the chain) give methyl ketones.



an enol butanone (ethyl methyl ketone)

Internal alkynes give a mixture of two ketones (the intermediate enol is not shown).



pentan-2-one pentan-3-one

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21.5 Reactions

Aldehydes and ketones are very reactive due to the polarity and structure of the carbonyl group (figure 21.3). They are electron-rich groups due to the π bond and the two nonbonding pairs of electrons on the oxygen atom. The polarity of the C═ bond enhances the attraction of nucleophiles (to the δ + carbon atom) and electrophiles (to the δ - oxygen atom), while the flat structure allows easy access to these reactive centres. Aldehydes are usually more reactive than ketones because access to the carbonyl carbon atom is easier as they have only one alkyl group (which is bulkier than a hydrogen atom) attached.

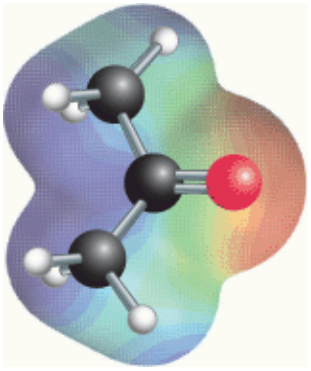
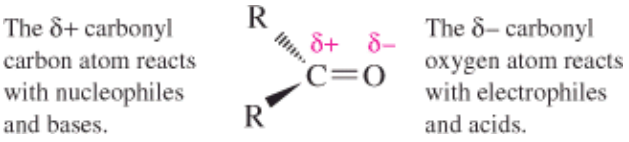
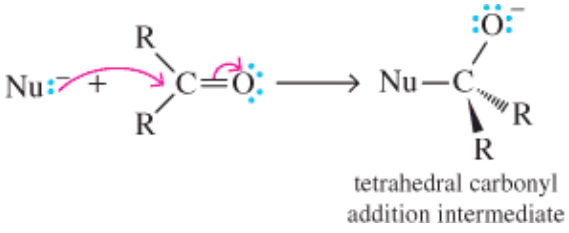


FIGURE 21.3 An electron density model highlighting the polarity of the carbonyl group.



The most common reaction theme of the carbonyl group is the addition of nucleophiles to form **tetrahedral carbonyl addition intermediates**. In the following general reaction, the nucleophilic reagent is written as Nu:⁻ to emphasise the presence of an unshared pair of electrons.



Addition of Grignard Reagents

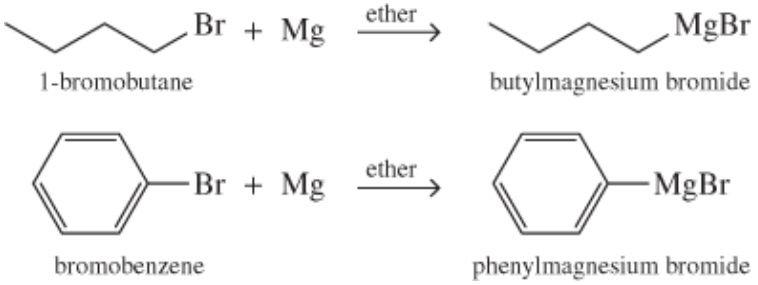
The addition of carbon nucleophiles is among the most important types of nucleophilic addition to carbonyl groups, because these reactions form new carbon–carbon bonds. In this section, we describe the preparation and reactions of Grignard reagents, and their reaction with aldehydes and ketones.

Formation and Structure of Organomagnesium Compounds

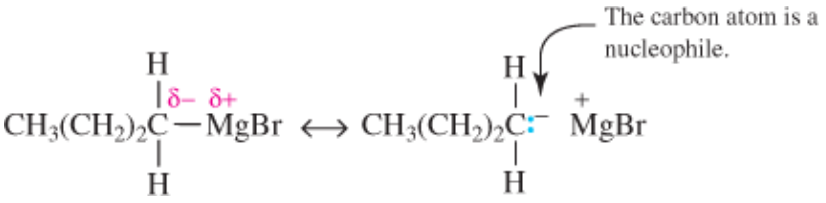
Alkyl, aryl and vinylic halides react with group 1, group 2 and certain other metals to form **organometallic compounds**. An organometallic compound is a compound containing a carbon–metal bond. Organomagnesium compounds are among the most readily available, easily prepared and easily handled organometallic compounds. Organomagnesium compounds of the type RMgX or ArMgX are commonly named **Grignard reagents**, after Victor Grignard, who was awarded the 1912 Nobel Prize in chemistry for their discovery and their application to organic synthesis.

Grignard reagents are typically prepared by the slow addition of alkyl, aryl or vinyl halides to a stirred suspension of

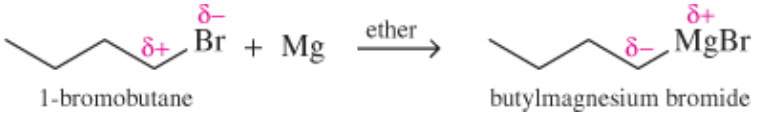
magnesium metal in an ether solvent, most commonly diethyl ether or tetrahydrofuran (THF). Organoiodides and bromides generally react rapidly under these conditions, whereas chlorides react more slowly. Butylmagnesium bromide, for example, is prepared by adding 1-bromobutane to an ether suspension of magnesium metal. Aryl Grignards, such as phenylmagnesium bromide, are prepared in a similar manner.



Given that the difference in electronegativity between carbon and magnesium is 1.3 (2.5 - 1.2), the carbon–magnesium bond is best described as polar covalent, with the carbon atom bearing a partial negative charge and the magnesium atom bearing a partial positive charge. In the structural formula below right, the carbon–magnesium bond is shown as ionic to emphasise its nucleophilic character. Note that, although we can write a Grignard reagent as a **carbanion** (an anion in which the carbon atom has an unshared pair of electrons and bears a negative charge), a more accurate representation shows it as a polar covalent compound (below left) and, in fact, each of these represents a resonance form of the actual C—Mg bond.

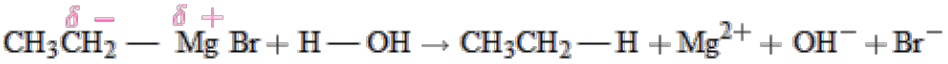


In chapter 18, you learned that the carbon atoms bonded to halogens are electrophilic (they are δ+ and undergo reactions with nucleophiles). The feature that makes Grignard reagents so valuable in organic synthesis is that the carbon atom bearing the halogen is transformed from an electrophile (δ+) into a nucleophile (δ-), as shown in the equation below.



Reaction With Protic Acids

Grignard reagents are very strong bases and react readily with a wide variety of acids (proton donors) to form alkanes. Ethylmagnesium bromide, for example, reacts instantly with water to give ethane and magnesium salts. This reaction is an example of a very strong base completely deprotonating water.



Any compound containing an O—H, N—H or S—H bond will react with a Grignard reagent by proton transfer. The following are examples of compounds containing those functional groups.

HOH	ROH	ArOH	RCOOH	RNH_2	RSH
water	alcohols	phenols	carboxylic acids	amines	thiols

Because Grignard reagents react so rapidly with these protic acids, they cannot be made from any halogen-containing compounds that also contain protic acids.

WORKED EXAMPLE 21.4

Reactions of Grignard Reagents

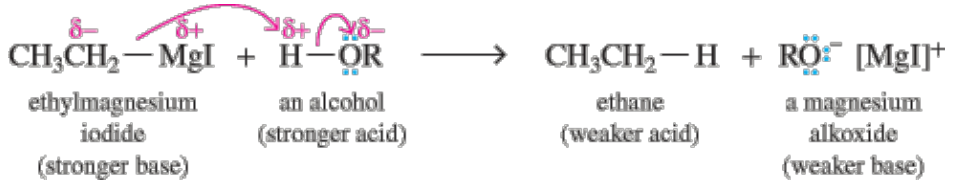
Write an equation for the acid–base reaction between ethylmagnesium iodide and an alcohol. Use curved arrows to show the bond-breaking and bond-forming processes in this reaction. In addition, show that the reaction is an example of a Brønsted–Lowry acid–base reaction.

Analysis

First, identify the polarity of the species (δ+/δ-). The electrons will come from the δ- portion to form a bond with the δ+ portion. In this acid–base reaction the alcohol group provides the proton.

Solution

The alcohol is a weak acid and the ethyl carbanion is a very strong base.

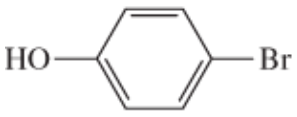


Is our answer reasonable?

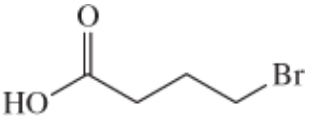
Check that the curved arrows start at an electron-rich region (atom or bond) and end at an electron-poor atom. Check that the δ+ atoms are paired with the δ- atoms.

PRACTICE EXERCISE 21.4

Explain why Grignard reagents cannot be formed from the following organohalides. What would be produced when magnesium metal is treated with (a) 4-bromophenol and (b) 4-bromobutanoic acid?



4-bromophenol

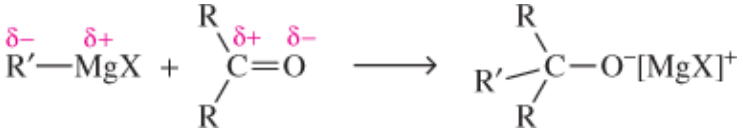


4-bromobutanoic acid

Addition of Grignard Reagents to Aldehydes and Ketones

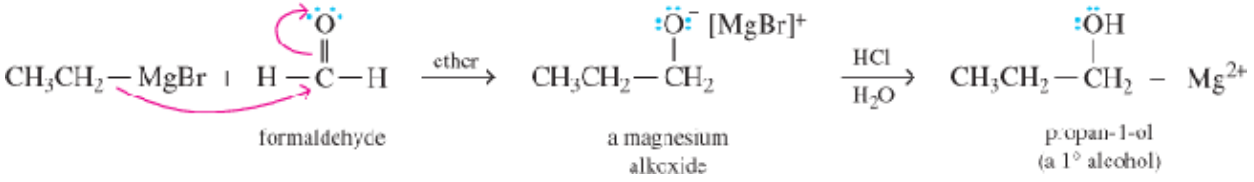
The special value of Grignard reagents is that they provide excellent ways to form new carbon–carbon bonds. In their reactions, Grignard reagents behave as though they were carbanions. A carbanion is a good nucleophile and adds to the carbonyl group of an aldehyde or ketone to form a tetrahedral carbonyl addition compound (see equation below). The reason for these reactions occurring so readily is the attraction between the partial negative charge on the carbon atom of the organometallic compound and the partial positive charge of the carbonyl carbon atom. In the examples that follow, the magnesium–oxygen bond is written as $—O^-[MgBr]^+$ to emphasise its ionic character. The alkoxide ions formed in Grignard reactions are strong bases and form alcohols when treated with an aqueous acid such as HCl or aqueous NH_4Cl during separation of the reaction products, by-products and unreacted starting material. A general scheme for the reaction of Grignard reagents with carbonyl compounds showing the polarity of the reacting species is given below. An easy way to determine the product is to identify the polarity of the species (δ

+/δ-). The product is the result of the δ- part of the Grignard reagent forming a bond with the δ+ carbon atom of the carbonyl group (and between the δ+ part of the Grignard reagent and the δ- oxygen atom of the carbonyl group).



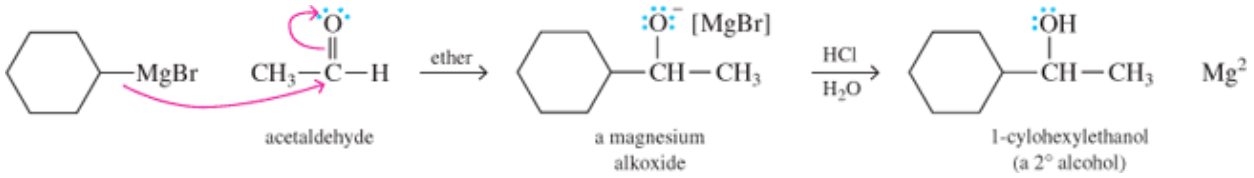
Addition to Formaldehyde (Methanal) Gives a 1° Alcohol

Treatment of a Grignard reagent with formaldehyde (methanal), followed by hydrolysis in aqueous acid, gives a primary alcohol.



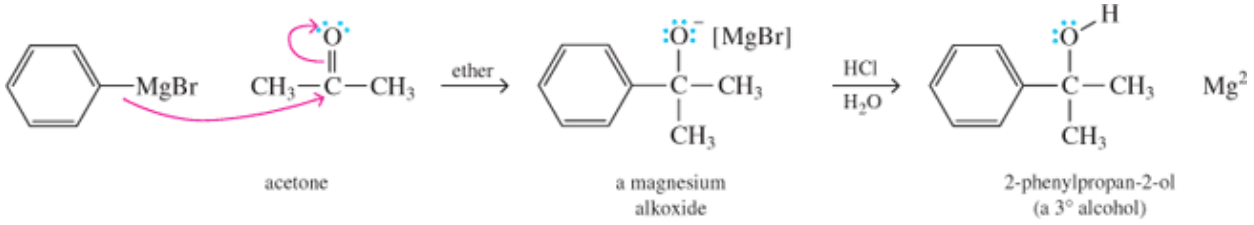
Addition to an Aldehyde (Except Formaldehyde) Gives a 2° Alcohol

The treatment of a Grignard reagent with any aldehyde other than formaldehyde, followed by hydrolysis in aqueous acid, gives a secondary alcohol. The steps required for this reaction are shown below.



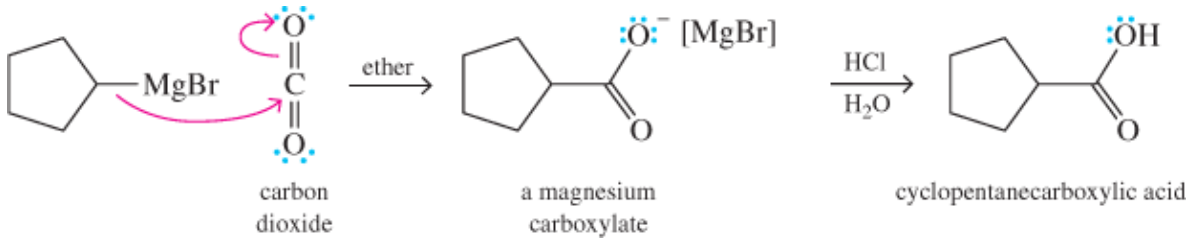
Addition to a Ketone Gives a 3° Alcohol

Treatment of a Grignard reagent with a ketone, followed by hydrolysis in aqueous acid, gives a tertiary alcohol.



Addition to Carbon Dioxide Gives a Carboxylic Acid

Grignard reagents react with carbon dioxide to give a magnesium carboxylate, which is converted into a carboxylic acid by acidification. This reaction is applicable to alkyl and aryl halides, and produces carboxylic acids with one carbon atom more than the original organohalide, as shown in the scheme below.



WORKED EXAMPLE 21.5

Synthesis of 3° Alcohols Using Grignard Reagents

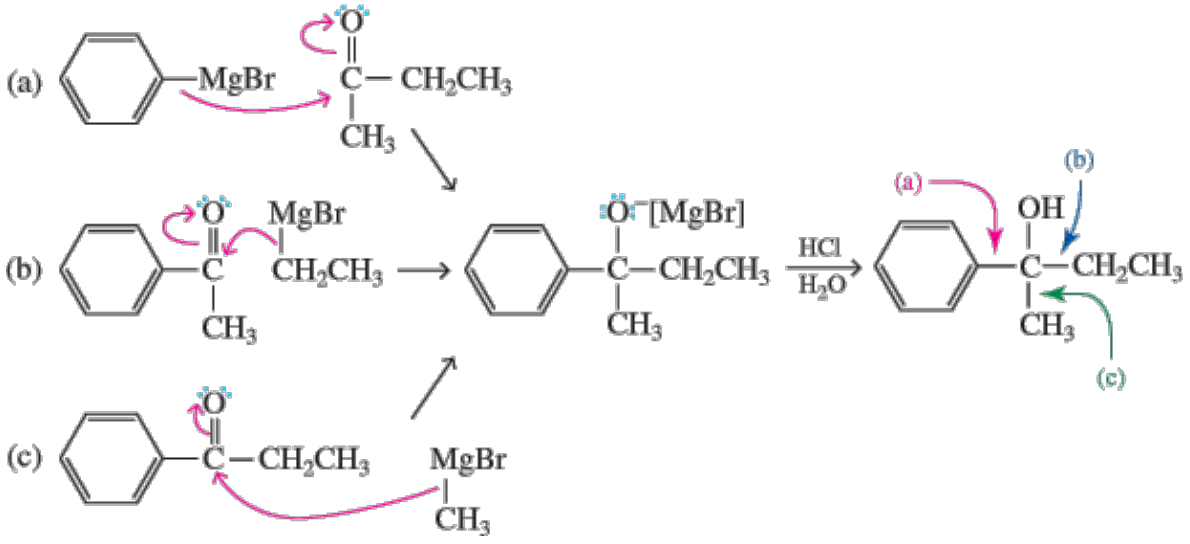
The tertiary alcohol 2-phenylbutan-2-ol can be synthesised by three different combinations of a Grignard reagent and a carbonyl compound. Show each combination.

Analysis

First, draw the structure of 2-phenylbutan-2-ol. As a tertiary alcohol, it can be produced by the reaction of a ketone with a Grignard reagent. To determine which ketones are suitable, identify the carbon atom bonded to the —OH group; this was the carbonyl carbon atom. Two of the groups bonded to this carbon atom form the ketone and the third forms the Grignard reagent. As there are three different groups we can have three different Grignard reagents and, by a process of elimination, three different ketones.

Solution

Curved arrows in each solution show the formation of the new carbon–carbon bond and the alkoxide ion, and labels on the final product show which set of reagents forms each bond.



Is our answer reasonable?

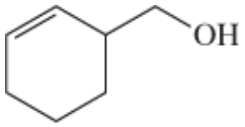
A simple way to check if your answers make sense is to count the carbon atoms in the starting materials and compare this number with the product (10 carbon atoms). If these agree, then check that each case has a methyl, an ethyl and a phenyl group.

PRACTICE EXERCISE 21.5

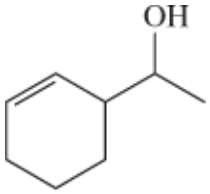
Show how the following three compounds can be

synthesised from the same Grignard reagent.

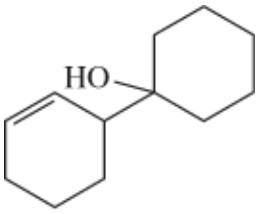
(a)



(b)

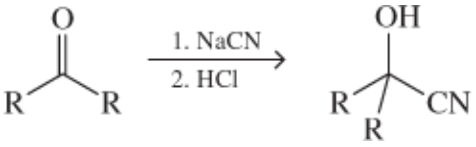


(c)

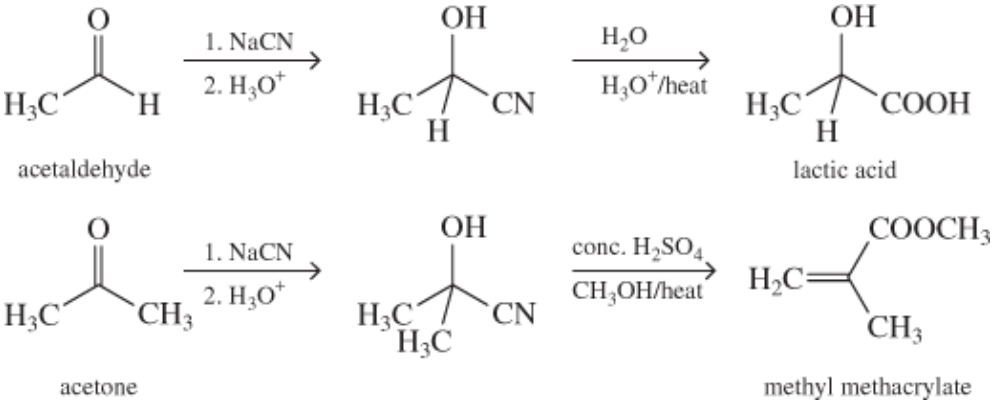


Addition of Other Carbon Nucleophiles

Treatment of aldehydes and some ketones with sodium cyanide and dilute acid produces **cyanohydrins**, compounds with an —OH and a —CN group bonded to the same carbon atom. Ketones with bulky groups do not undergo this reaction. In this reaction, the negatively charged carbon atom of the cyanide ion adds to the δ+ carbonyl carbon atom, and then the proton from the acid adds to the resulting negative oxygen atom.



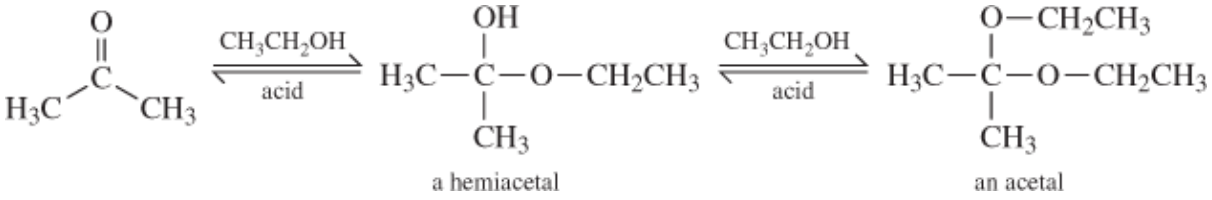
Cyanohydrins are useful compounds in organic chemistry because they can be converted to α-hydroxycarboxylic acids or α,β-unsaturated acids (depending on conditions used), or β-amino alcohols (see section 23.5).



Note that we have now seen three convenient methods of adding one carbon atom to a carbon chain: the addition of cyanide ions to carbonyl compounds, and reactions of Grignard reagents with formaldehyde and with carbon dioxide.

Addition of Alcohols

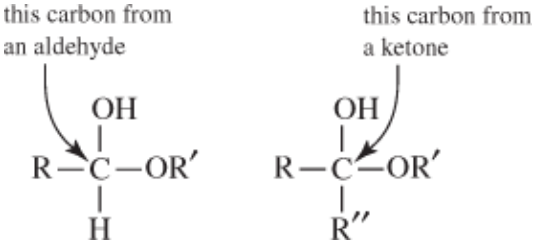
Treatment of aldehydes and ketones with alcohols in the presence of an acid catalyst produces **acetals**. The intermediate **hemiacetals** (half-acetals) are generally unstable and are only minor components of an equilibrium mixture, except in one important type of molecule (as discussed below).



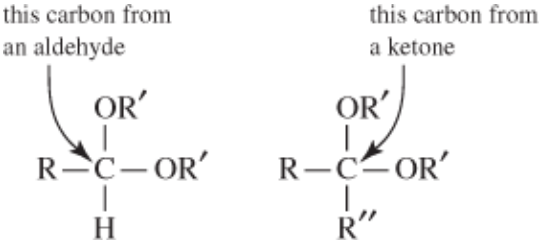
a hemiacetal

an acetal

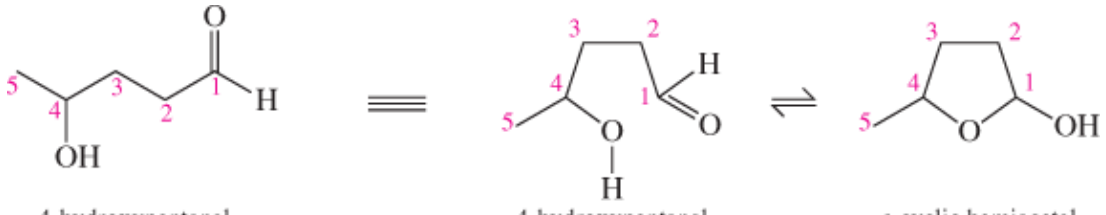
The hemiacetal group is a carbon atom bonded to an —OH group and an —OR or —OAr group. A hemiacetal derived from a ketone is sometimes referred to as a hemiketal.



The acetal functional group is a carbon atom bonded to two—OR or—OAr groups. Acetals derived from ketones are sometimes referred to as **ketals**.



Hemiacetals are stable when a hydroxyl group is part of the same molecule that contains the carbonyl group, and five- or six-membered rings can form. In these cases, the compound exists almost entirely in a cyclic hemiacetal form.



4-hydroxypentanal

4-hydroxypentanal

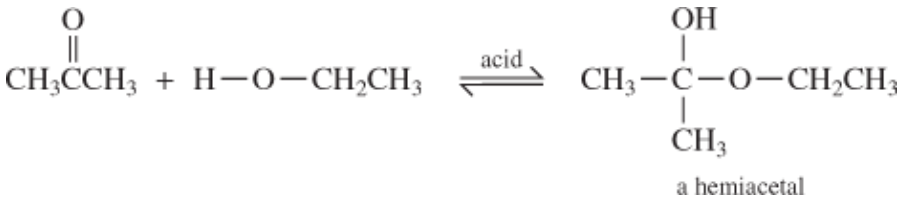
a cyclic hemiacetal (major form present at equilibrium)

We examine cyclic hemiacetals in more detail when we consider the chemistry of carbohydrates in chapter 22.

For clarity, we will study the reaction of alcohols with aldehydes and ketones in two stages: (i) the formation of hemiacetals and (ii) the subsequent transformation of hemiacetals into acetals.

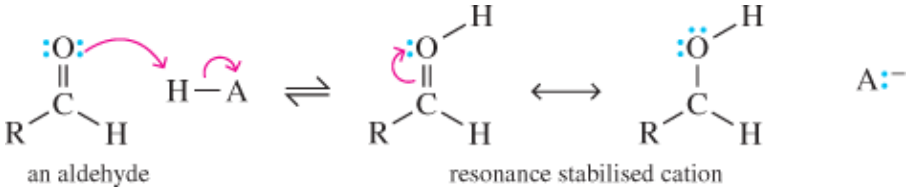
The reaction of alcohols with aldehydes and ketones is an acid-catalysed example of addition to a carbonyl

compound to produce a tetrahedral carbonyl addition intermediate (in this case, the hemiacetal). In this process, H^+ adds to the δ^- carbonyl oxygen atom, and the δ- oxygen atom of the alcohol adds to the δ+ carbonyl carbon atom. This is another example of 'δ- goes with δ+'.

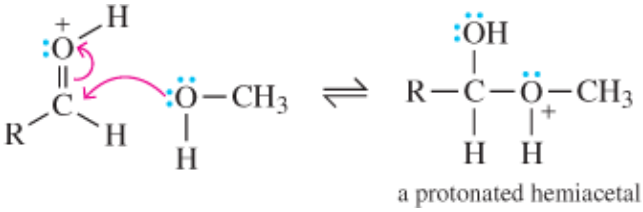


A mechanism for the formation of hemiacetals can be divided into three steps. Note that the acid H—A is a true catalyst in this reaction; it is used in step 1 and is regenerated in step 3.

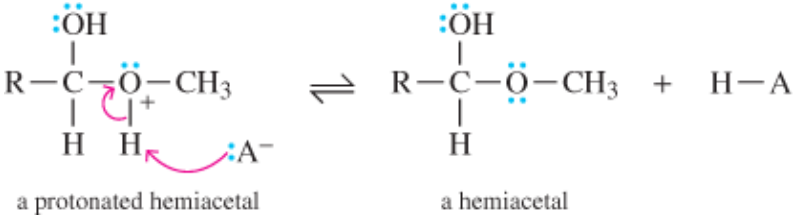
Step 1: Proton transfer from the acid, H—A, to the carbonyl oxygen atom gives a resonance stabilised cation.



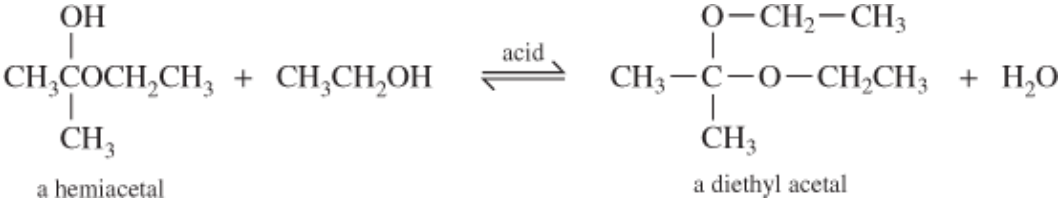
Step 2: Reaction of the resonance-stabilised cation (an electrophile) with methanol (a nucleophile) gives the conjugate acid of a hemiacetal.



Step 3: Proton transfer from the protonated hemiacetal to A- gives the hemiacetal and regenerates the acid catalyst, H—A.

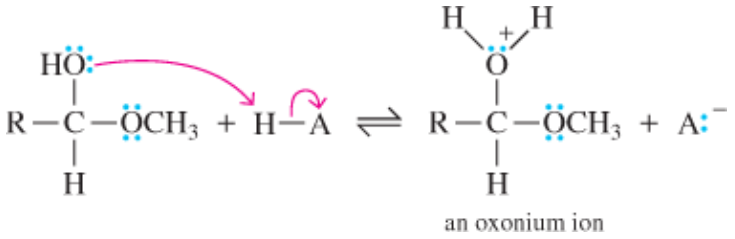


Hemiacetals can react further with alcohols to form acetals plus a mole equivalent of water.

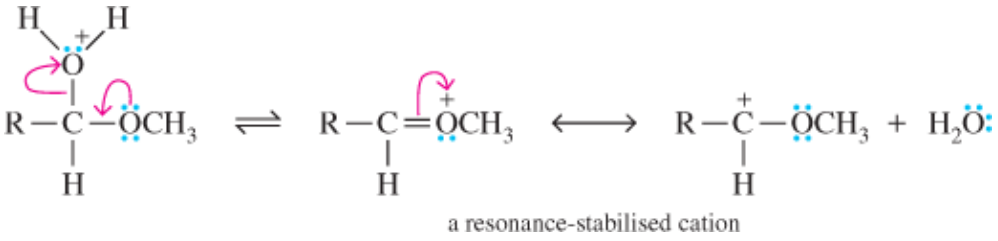


A mechanism for the acid-catalysed conversion of hemiacetals to acetals can be divided into four steps. Note that the acid, H—A, is also a catalyst in this reaction; it is used in step 1 and is regenerated in step 4.

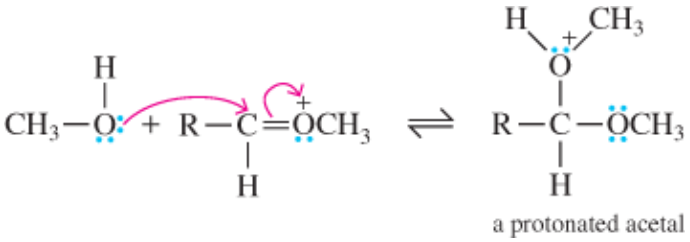
Step 1: Proton transfer from the acid, H—A, to the hemiacetal —OH group gives an oxonium ion.



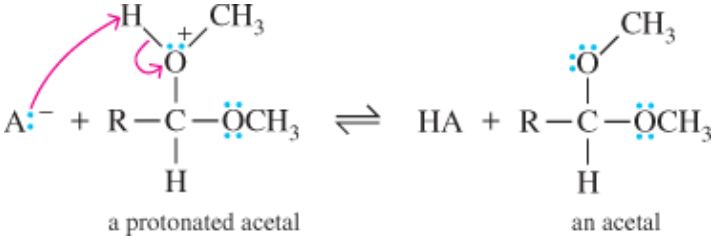
Step 2: Loss of water from the oxonium ion gives a resonance-stabilised cation.



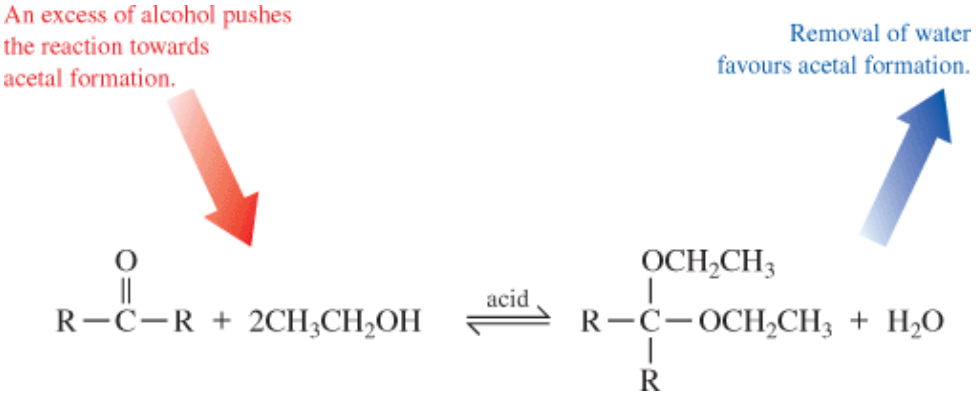
Step 3: Reaction of the resonance-stabilised cation (an electrophile) with methanol (a nucleophile) gives the conjugate acid of the acetal.



Step 4: Proton transfer from the protonated acetal to A- gives the acetal and generates a new molecule of H—A.



Formation of acetals is often carried out using the alcohol as a solvent and dissolving dry HCl (hydrogen chloride), concentrated H_2SO_4 or arenesulfonic acid ($ArSO_3H$) in the alcohol. Because the alcohol is both a reactant and the solvent, it is present in a large molar excess, which drives the reaction to the right and favours acetal formation. Alternatively, the reaction may be driven to the right by the removal of water as it is formed.



Note that, as water is a product in this reaction, the reagents (the carbonyl compound and the alcohol) must be anhydrous. Any excess water in the reaction mixture limits the amount of product formed.

WORKED EXAMPLE 21.6

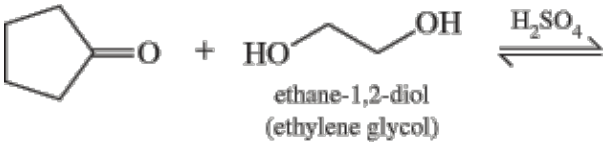
Formation of Acetals

Show the reaction of the carbonyl group of each of the following ketones with one mole equivalent of alcohol to form a hemiacetal. Then show the reaction with a second mole equivalent of alcohol to form an acetal (note that, in part (b), ethane-1,2-diol (ethylene glycol) is a diol and provides both —OH groups).

(a)



(b)



ethane-1,2-diol
(ethylene glycol)

Analysis

The carbonyl carbon atom will become the hemiacetal, and then the acetal, so highlight this atom. The hemiacetal is formed by first forming an O—H bond between the carbonyl oxygen atom and the acid catalyst, and then a C—OR bond between the carbonyl carbon atom and the alcohol oxygen atom. The acetal is formed by replacing the —OH group with an —OR group.

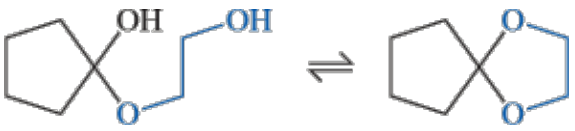
Solution

Here are structural formulae of the hemiacetal and then the acetal.

(a)



(b)



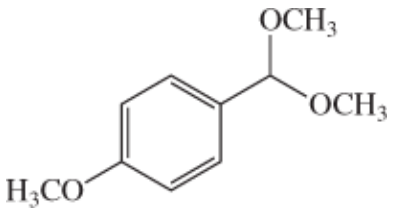
Is our answer reasonable?

A simple way to check if your structures make sense is to check that the number of carbon atoms on the left-hand side of the reaction is the same as the right-hand side. If these agree, then check that each hemiacetal has a carbon atom with an —OH and an —OR group and, for the acetal, this carbon atom now has two —OR groups.

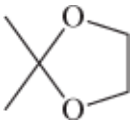
PRACTICE EXERCISE 21.6

The hydrolysis of an acetal forms an aldehyde or a ketone and two equivalents of alcohol. The following are structural formulae for three acetals.

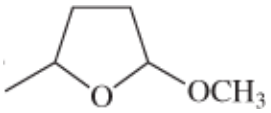
(a)



(b)



(c)

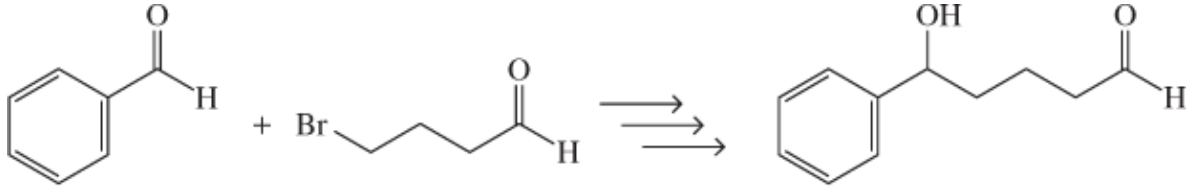


Draw the structural formulae for the products of the hydrolysis of each acetal in aqueous acid.

Like ethers, acetals are unreactive to bases, reducing agents, Grignard reagents and oxidising agents (except, of course, those which involve aqueous acid). Because of their lack of reactivity with these reagents, acetals are often used to protect the carbonyl groups of aldehydes and ketones while reactions are carried out on functional groups in other parts of the molecule. The acetal group can then be readily removed in high yield by mild acid hydrolysis.

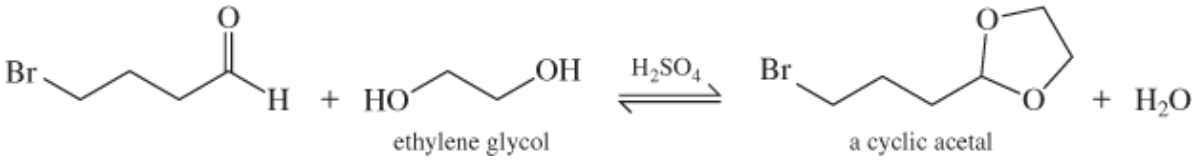
Acetals as Carbonyl-protecting Groups

The use of acetals as carbonyl-protecting groups is illustrated by the synthesis of 5-hydroxy-5-phenylpentanal from benzaldehyde and 4-bromobutanal.



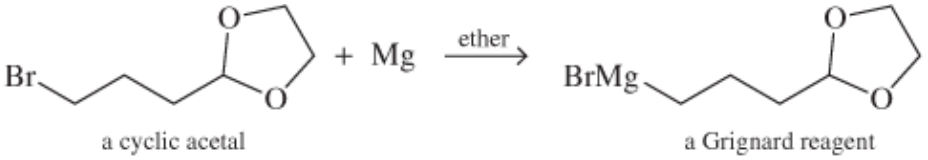
benzaldehyde 4-bromobutanal 5-hydroxy-5-phenylpentanal

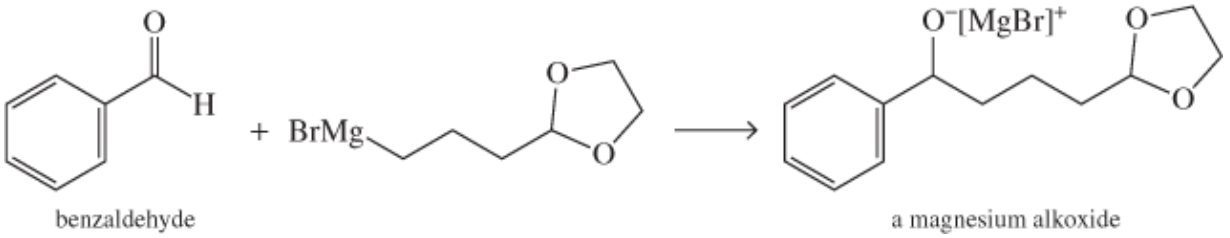
One obvious way to form a new carbon–carbon bond between these two molecules is to treat benzaldehyde with the Grignard reagent formed from 4-bromobutanal. This Grignard reagent, however, would react immediately with the carbonyl group within the same molecule or in another molecule of 4-bromobutanal, causing it to self-destruct during preparation. A way to avoid this problem is to protect the carbonyl group of 4-bromobutanal by converting it to an acetal. Cyclic acetals are often used because they are particularly easy to prepare and are more stable to hydrolysis. This is similar to the chelate effect observed in the coordination of bidentate ligands to metal ions (see section 13.4).



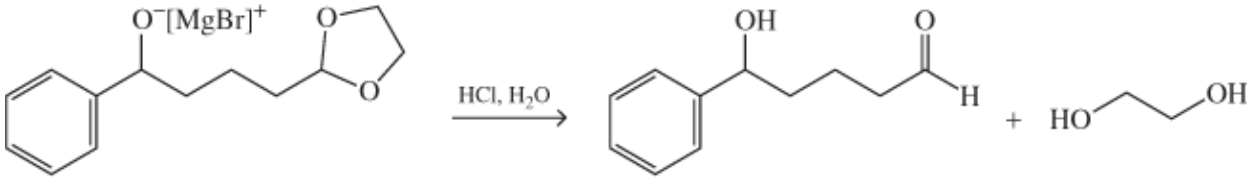
ethylene glycol a cyclic acetal

Treatment of the protected bromoaldehyde with magnesium in diethyl ether, followed by the addition of benzaldehyde, gives a magnesium alkoxide.



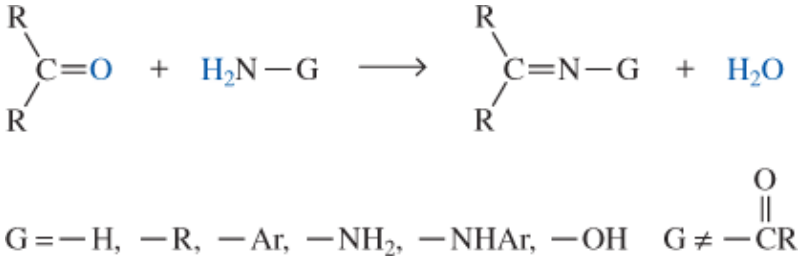


Treatment of the magnesium alkoxide with aqueous acid accomplishes two things. First, protonation of the alkoxide anion gives the desired hydroxyl group, and then, hydrolysis of the cyclic acetal regenerates the aldehyde group.



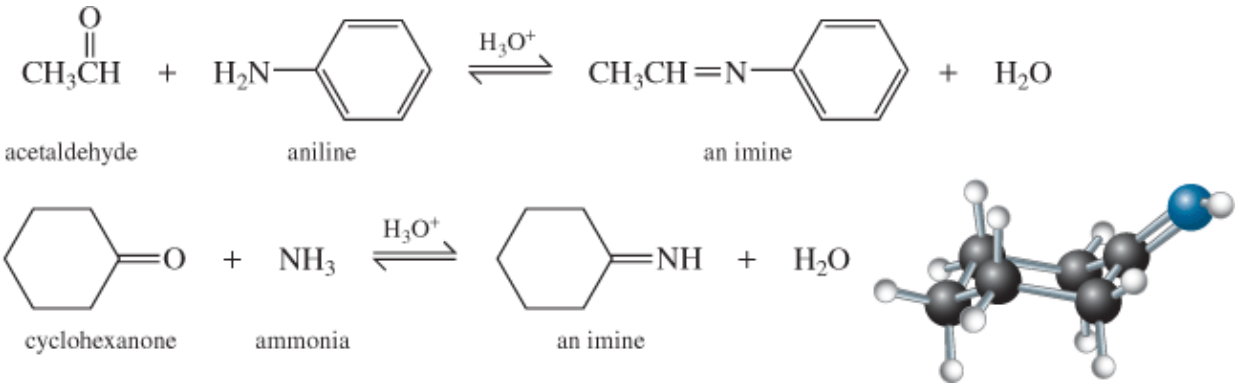
Addition of Ammonia, Amines and Related Compounds

The chemistry in this section can be summarised by the general reaction shown at the top of the next page where G can be a range of groups including —H, —R, —Ar, —NH_2, —NHAr and —OH but *not* an acyl group, —C(═O)R. Ultimately the carbonyl oxygen atom is replaced by a substituted nitrogen atom (N—G) with the formation of water as a by-product.



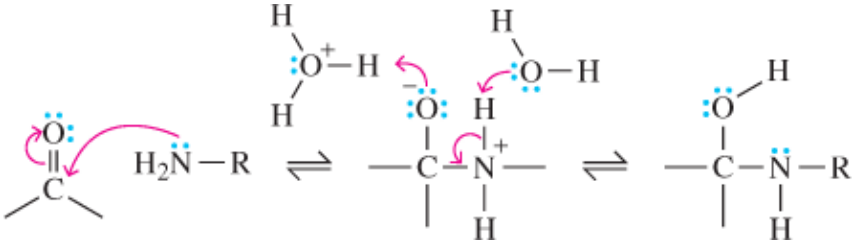
Formation of Imines

Ammonia, primary aliphatic amines, RNH_2, and primary aromatic amine, $ArNH_2$, react with the carbonyl group of aldehydes and ketones in the presence of an acid catalyst to give imines (compounds that contain a carbon–nitrogen double bond).



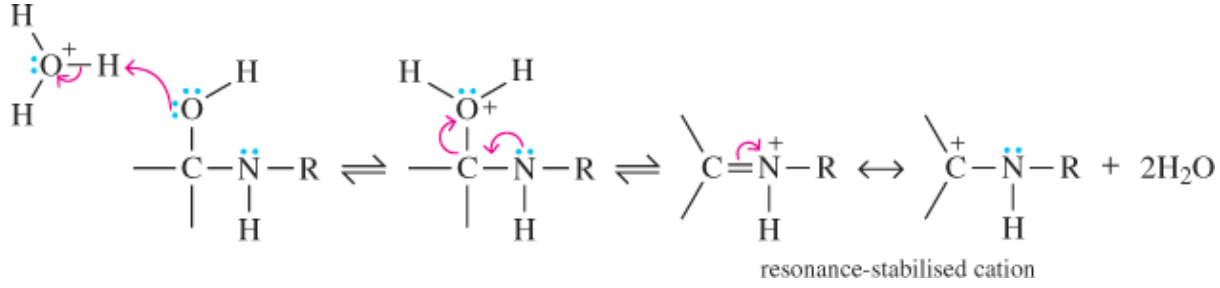
A mechanism is described in the following steps:

Step 1: Addition of the nitrogen atom of ammonia or a primary amine to the carbonyl carbon atom, followed by protonation of the oxygen atom and deprotonation of the nitrogen atom, gives a tetrahedral carbonyl addition intermediate.

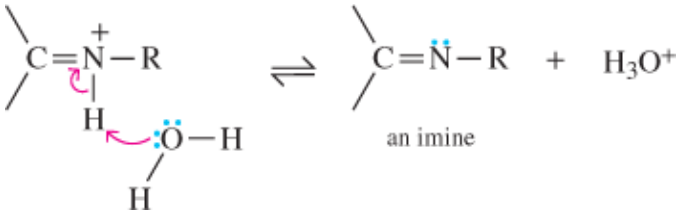


This step is analogous to the formation of hemiacetals, as both are examples of carbonyl addition reactions. The intermediate formed in step 1 is unstable, and step 2 occurs spontaneously.

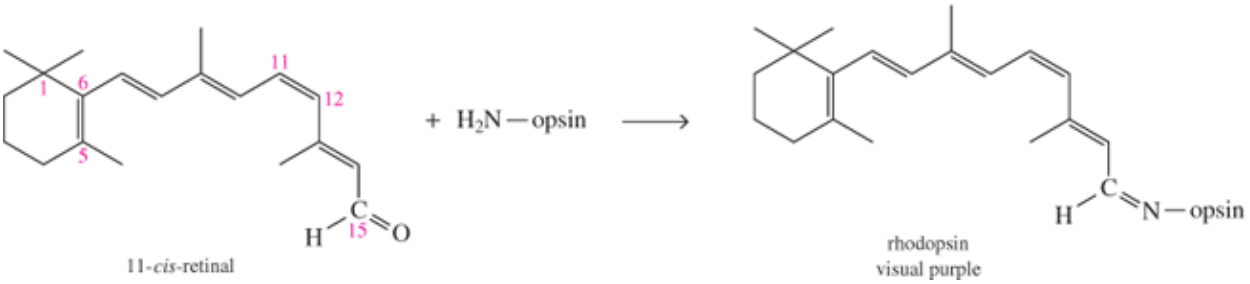
Step 2: Protonation of the —OH group, followed by loss of water and proton transfer to the solvent gives the imine. Notice that the loss of water and the proton transfer have the characteristics of an E2 reaction (see section 18.3). Two things happen simultaneously in this dehydration: the carbon–nitrogen double bond forms, and the leaving group (in this case, a water molecule) departs.



Step 3: Deprotonation of the nitrogen atom in the resonance-stabilised cation gives the imine.



One example of the importance of imines in biological systems is the active form of vitamin A aldehyde (retinal), which is bound to the protein opsin in the human retina in the form of an imine called rhodopsin or visual purple (see chapter 16, pp. 702–3). The amino acid lysine (table 21.1, p. 1057) provides the primary amino group for this reaction.



11-*cis*-retinal

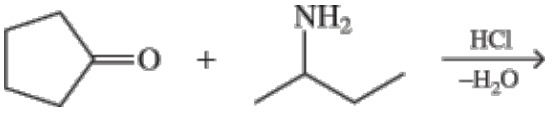
rhodopsin
visual purple

WORKED EXAMPLE 21.7

Structural Formulae for Imines

Write a structural formula for the imine formed in each of the following reactions.

(a)



(b)



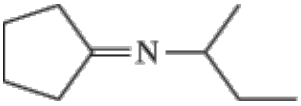
Analysis

The carbonyl carbon atom will be bonded to the nitrogen atom by a C═N double bond. The oxygen atom of the carbonyl group and the two hydrogen atoms of the —NH_2 group combine to form water.

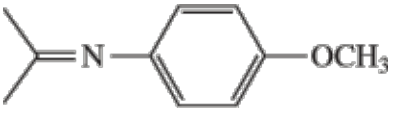
Solution

Below is a structural formula for each imine.

(a)



(b)



Is our answer reasonable?

Check that you get the starting materials if you cleave the C═N double bond and add an oxygen atom to the carbon atom and two hydrogen atoms to the nitrogen atom.

PRACTICE EXERCISE 21.7

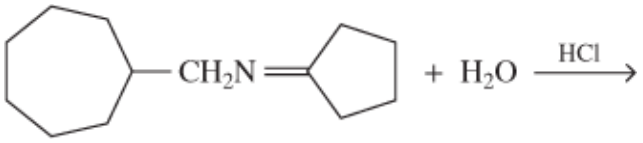
Acid-catalysed hydrolysis of an imine gives an amine and an aldehyde or a ketone. When one equivalent of acid is used, the amine is converted to its ammonium salt. For each of the following imines, write a structural formula for the products of

hydrolysis, using one equivalent of HCl.

(a)



(b)



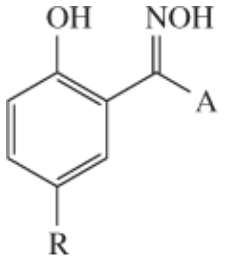
Formation of Oximes and Hydrazones

When aldehydes and ketones react with hydroxylamine, H_2NOH, they form **oximes** (compounds containing a C═NOH group).



an oxime

The LIX® reagents are examples of oximes and are produced industrially for the solvent extraction of copper and nickel from leach solutions. These reagents can be made to coordinate selectively to Cu^{2+} and Ni^{2+} ions by careful manipulation of the pH. The large alkyl group *para* to the phenol ensures the reagents have low solubility in aqueous solutions and remain in the organic solvent (usually kerosene).

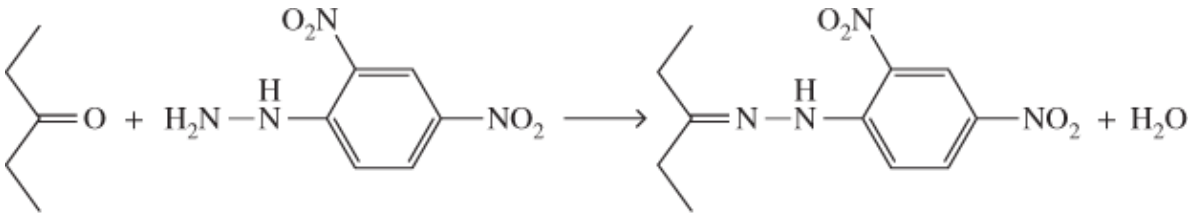


an LIX® reagent

A = H or CH_3

R = C_9H_{19} or $C_{12}H_{25}$

A convenient spot test for aldehydes and ketones involves the addition of a solution of 2,4-dinitrophenylhydrazine (Brady's reagent), also known as the 2,4-DNP test. In the presence of aldehydes or ketones this reagent forms bright orange/red hydrazones.



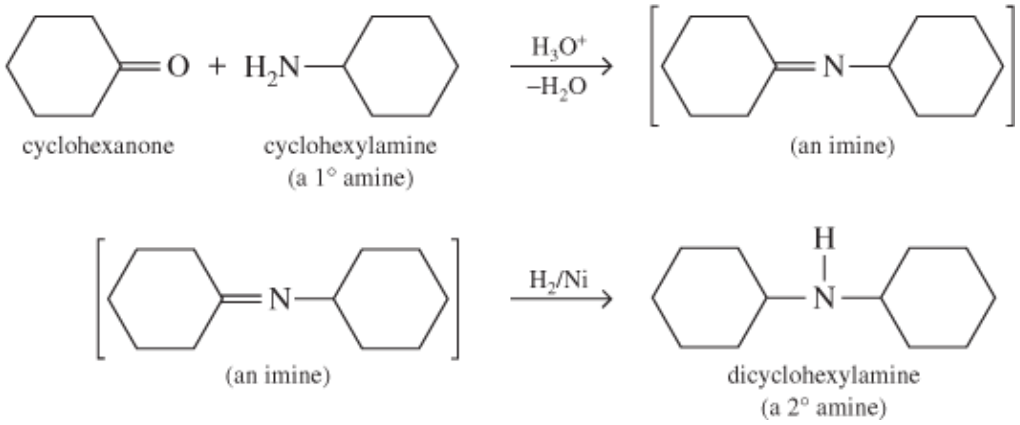
2,4-dinitrophenylhydrazine

a hydrazone
(a bright orange/red precipitate)

Reductive Amination of Aldehydes and Ketones

One of the chief values of imines is that the carbon–nitrogen double bond can be reduced to a carbon–nitrogen single bond by hydrogen in the presence of a catalyst (typically nickel, palladium or platinum). By this two-step

reaction, called **reductive amination**, a primary amine is converted into a secondary amine through an imine intermediate, as illustrated below by the conversion of cyclohexylamine to dicyclohexylamine.



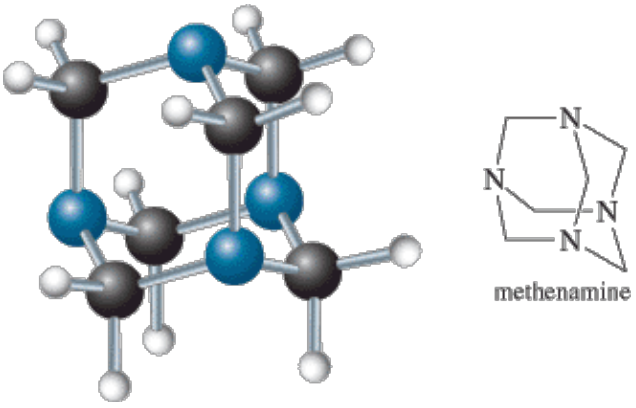
Conversion of an aldehyde or a ketone to an amine is generally carried out in one laboratory operation by mixing together the carbonyl-containing compound, the amine or ammonia, hydrogen, and the transition metal catalyst. The imine intermediate is not isolated.

Chemical Connections

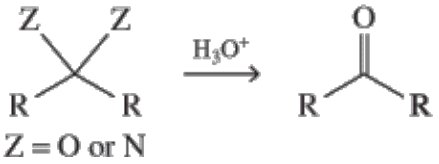
Drug Delivery by Hydrolysis

Methenamine as a prodrug of formaldehyde

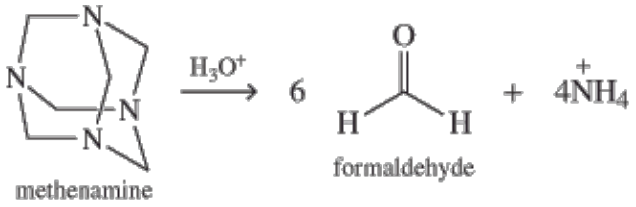
Formaldehyde has antiseptic properties and can be used to treat urinary tract infections due to its ability to react with nucleophiles present in urine. However, formaldehyde can be toxic when exposed to other regions of the body. Therefore, the use of formaldehyde as an antiseptic agent requires a method for selective delivery to the urinary tract. This can be accomplished by using a prodrug called methenamine.



This compound is a nitrogen analogue of an acetal. That is, each carbon atom is connected to two nitrogen atoms, very much like an acetal in which a carbon atom is connected to two oxygen atoms. A carbon atom that is connected to two heteroatoms (O or N) can undergo acid-catalysed hydrolysis.



Each of the carbon atoms in methenamine can be hydrolysed, releasing formaldehyde.



Methenamine is placed in special tablets that do not dissolve as they travel through the acidic environment of the stomach, but do dissolve once they reach the basic environment of the intestinal tract. Methenamine is thereby released into the intestinal tract, where it is stable under basic conditions. Once it reaches the acidic environment of the urinary tract, methenamine is hydrolysed, releasing formaldehyde, as shown above. In this way, methenamine is used as a prodrug that enables delivery of formaldehyde specifically to the urinary tract. This method prevents the systemic release of formaldehyde to other organs of the body where it would be toxic.

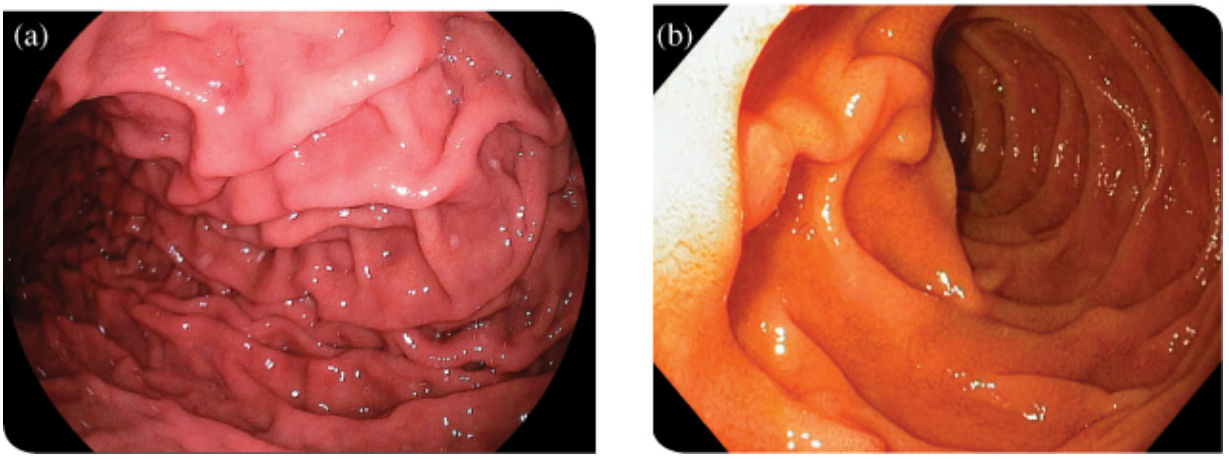


FIGURE 21.4 Methenamine is stable under basic but not acidic conditions. Therefore, it is administered in tablets that do not dissolve in

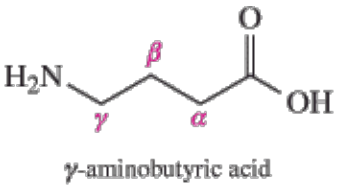
(a) the acidic environment of the stomach;

(b) the tablets dissolve when they reach the basic environment of the intestinal tract.

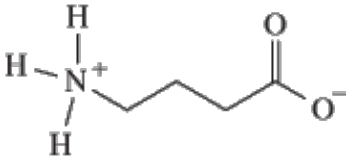
SPL/Gastrolab

Imines as prodrugs

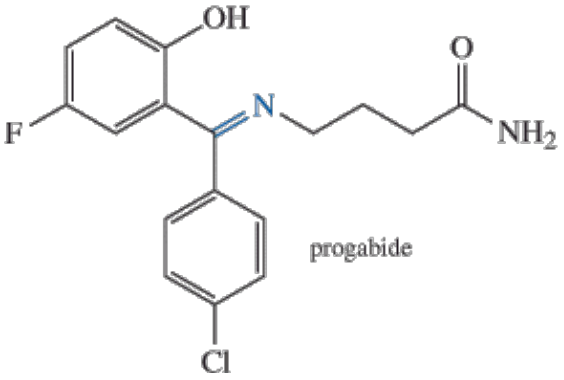
The imine moiety is used in the development of many prodrugs. Here we will explore one example. The compound below, γ-aminobutyric acid, is an important neurotransmitter.



A deficiency of this compound is that it can cause convulsions. Administering γ-aminobutyric acid directly to a patient is not an effective treatment because the compound does not readily cross the blood–brain barrier. This is because, at physiological pH, the amino group is protonated and the carboxylic acid moiety is deprotonated.

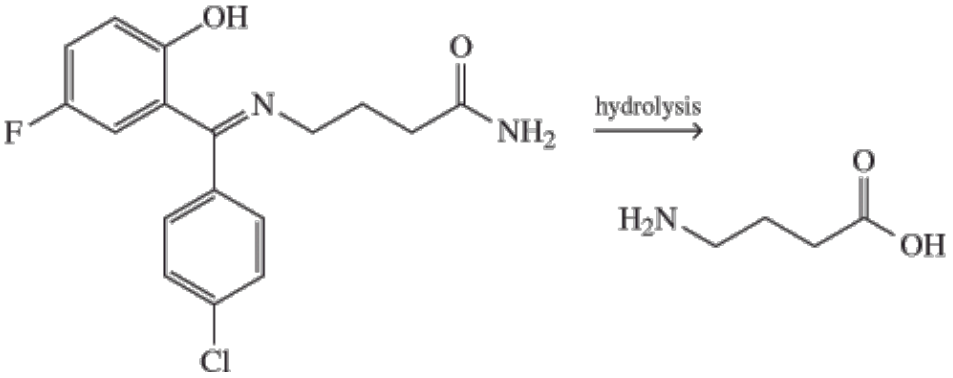


The compound exists primarily in this ionic form, which cannot cross the nonpolar environment of the blood–brain barrier. Progabide is a prodrug derivative used to treat patients who exhibit the symptoms of a deficiency of γ-aminobutyric acid.



The carboxylic acid has been converted to an amide, and the amino group has been converted into an imine (highlighted in blue above). At physiological pH, this compound exists primarily as a neutral compound (uncharged), and it can therefore cross the blood–brain barrier. Once in the brain, it is converted to γ-aminobutyric acid via hydrolysis of the imine and amide moieties.

Progabide is just one example in which the imine moiety has been used in the development of a prodrug.

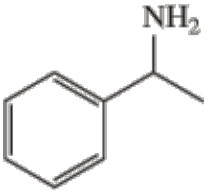


WORKED EXAMPLE 21.8

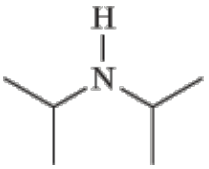
Synthesis of Amines

Show how to synthesise each of the following amines by reductive amination.

(a)



(b)



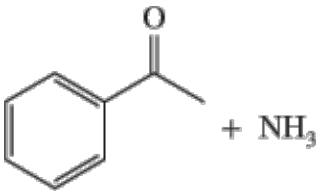
Analysis

In reductive amination, an imine is reduced to an amine by addition of hydrogen across the C═N double bond. Working backwards to determine the structure of the imine, simply 'draw in' a double bond between the C and N atoms (and remove a hydrogen atom from the nitrogen atom). In (a) there is only one C—N bond, so the choice is easy; in (b) there are two, but the groups are the same, so again the choice is easy. To determine the structure of the carbonyl compound, replace the C═NR group with a C ═O group. The identity of the amine is determined by adding two hydrogen atoms to the nitrogen atom of the ═NR group.

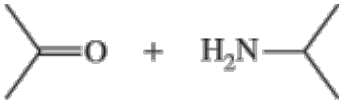
Solution

The carbonyl compound is treated with ammonia or an amine in the presence of H_2/Ni.

(a)



(b)



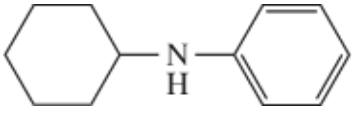
Is our answer reasonable?

Check that the skeletal structures of the carbonyl compounds and the amines are consistent with those of the imine intermediate and the target amines.

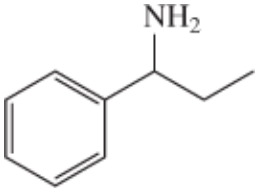
PRACTICE EXERCISE 21.8

Show how to prepare each of the following amines by the reductive amination of an appropriate aldehyde or ketone.

(a)



(b)



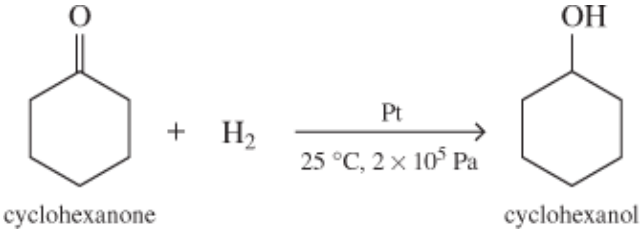
Reduction

Aldehydes are reduced to primary alcohols, and ketones are reduced to secondary alcohols.

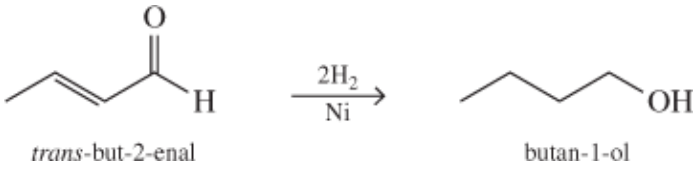


Catalytic Reduction

The carbonyl group of an aldehyde or a ketone is reduced to a hydroxyl group by hydrogen in the presence of a transition metal catalyst, most commonly finely divided palladium, platinum, nickel or rhodium. Reductions are generally carried out at temperatures from 25 °C to 100 °C and at pressures of hydrogen from 100 to 500 kPa (1–5 times atmospheric pressure). Under such conditions, cyclohexanone is reduced to cyclohexanol as shown below.

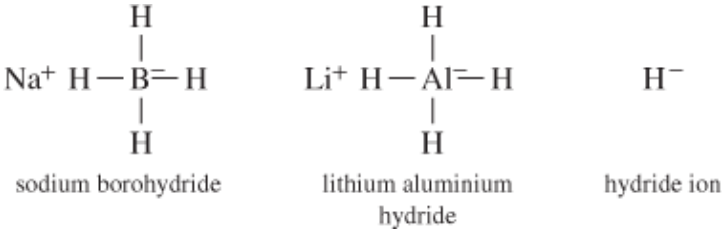


The catalytic reduction of aldehydes and ketones proceeds with generally very high yields, and isolation of the final product is very easy. However, a disadvantage is that some other functional groups are more reactive than aldehydes and ketones towards catalytic reduction (for example, carbon–carbon double bonds) and therefore are also reduced under these conditions.



Metal Hydride Reductions

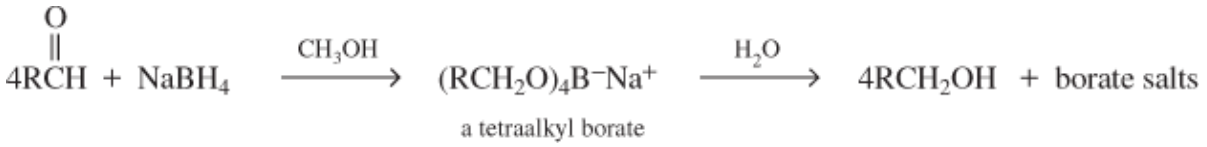
By far the most common laboratory reagents used to reduce the carbonyl group of an aldehyde or ketone to a hydroxyl group are sodium borohydride and lithium aluminium hydride. Each of these compounds behaves as a source of the **hydride ion**, H^-, which is a very strong nucleophile. A hydride ion is a hydrogen atom with two electrons in its valence shell, $H:^-$. The structural formulae drawn below show formal negative charges on boron and aluminium.



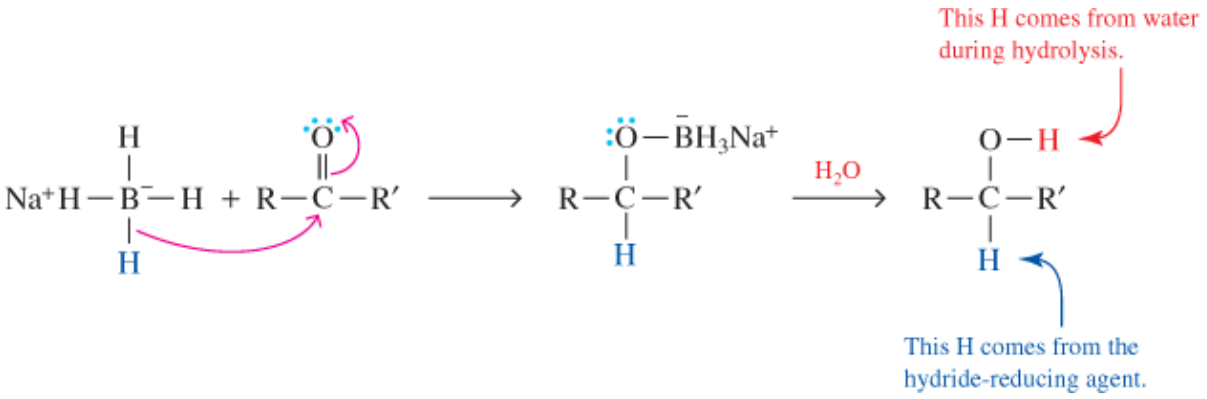
In fact, hydrogen is more electronegative than either boron or aluminium (H = 2.2, Al = 1.6 and B = 2.0) and the formal negative charge in the two reagents resides more on hydrogen atoms than on the metal.

Lithium aluminium hydride is a very powerful reducing agent; it rapidly reduces not only the carbonyl groups of aldehydes and ketones, but also those of carboxylic acids and their functional derivatives (section 23.5). Sodium borohydride is a much more selective reagent, reducing only aldehydes and ketones rapidly.

Reductions using sodium borohydride are most commonly carried out in aqueous methanol, pure methanol or ethanol. The initial product of reduction is a tetraalkyl borate, which is converted to an alcohol and sodium borate salts upon treatment with water. One mole of sodium borohydride reduces 4 moles of aldehyde or ketone.

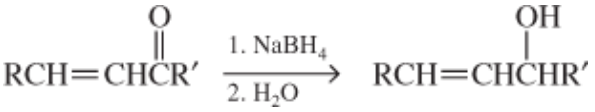


The key step in the metal hydride reduction of an aldehyde or ketone is the transfer of a hydride ion from the reducing agent to the carbonyl carbon atom to form a tetrahedral carbonyl addition compound. In this reaction, only the hydrogen atom attached to the carbon atom comes from the hydride-reducing agent; the hydrogen atom bonded to the oxygen atom comes from the water added to hydrolyse the metal alkoxide salt.

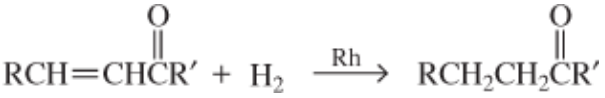


The next two equations illustrate the selective reduction of a carbonyl group in the presence of a carbon–carbon double bond and, alternatively, the selective reduction of a carbon–carbon double bond in the presence of a carbonyl group.

Selective reduction of a carbonyl group can be carried out using sodium borohydride.



Selective reduction of a carbon–carbon double bond can be achieved using hydrogen in the presence of a transition metal catalyst. Note that this reaction is possible because alkenes are easier to reduce by catalytic reduction than ketones. By carefully monitoring the reaction and stopping it after one mole equivalent of hydrogen has been consumed, we can readily obtain the carbonyl compound.

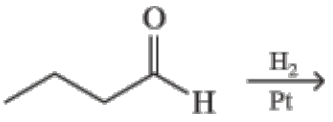


WORKED EXAMPLE 21.9

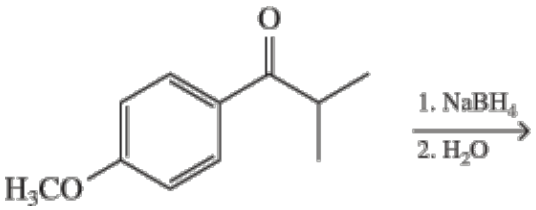
Reduction of Aldehydes and Ketones

Complete the following reductions.

(a)



(b)



Analysis

The key here is to recognise that the carbon atom of the carbonyl group will become the alcohol carbon atom. To determine the structure of the reduction product, simply add a hydrogen atom to both the carbon and the oxygen atoms.

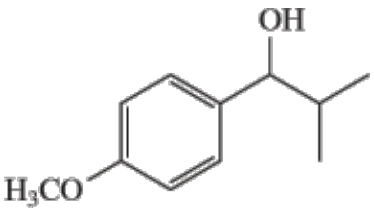
Solution

The carbonyl group of the aldehyde in (a) is reduced to a primary alcohol, and that of the ketone in (b) is reduced to a secondary alcohol.

(a)



(b)



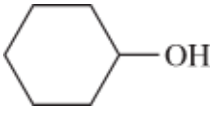
Is our answer reasonable?

The reduction of aldehydes gives primary alcohols, and reduction of ketones gives secondary alcohols. Check that your proposed structures agree with this rule.

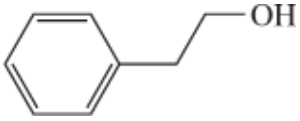
PRACTICE EXERCISE 21.9

What aldehyde or ketone gives each of the following alcohols upon reduction by $NaBH_4$?

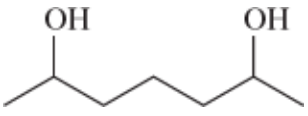
(a)



(b)

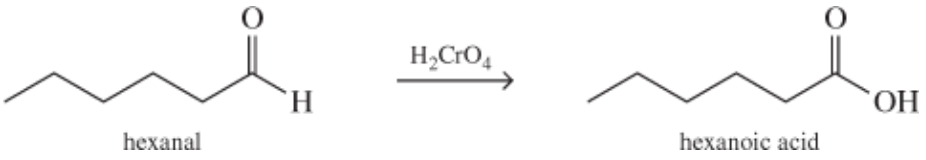


(c)



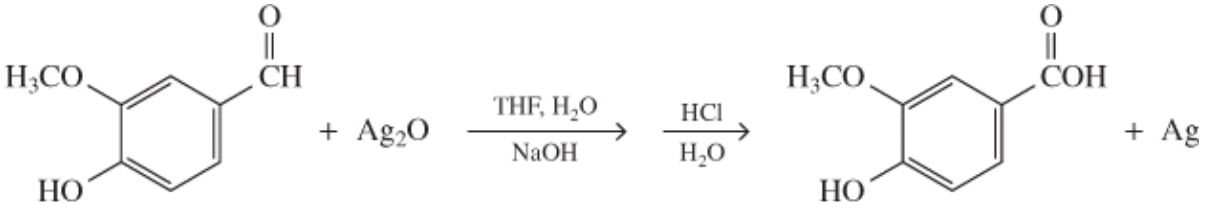
Oxidation of Aldehydes to Carboxylic Acids

Aldehydes are oxidised to carboxylic acids by a variety of common oxidising agents, including chromic acid and molecular oxygen. In fact, aldehydes are one of the most easily oxidised functional groups. Oxidation by chromic acid is illustrated below by the conversion of hexanal to hexanoic acid.



hexanal — hexanoic acid

Aldehydes are also oxidised to carboxylic acids by silver(I) ions. One laboratory procedure is to shake a solution of the aldehyde dissolved in aqueous ethanol or tetrahydrofuran (THF) with a slurry of Ag_2O.



vanillin (from vanilla) — vanillic acid

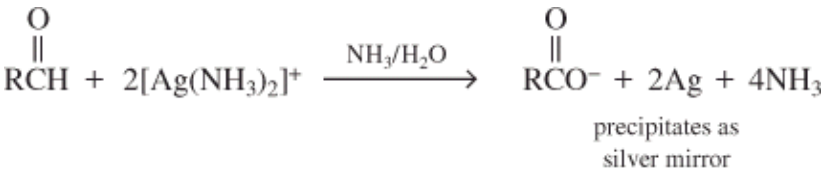
Tollens' reagent, another form of silver(I) ion, is prepared by dissolving $AgNO_3$ in aqueous ammonia to give the silver–ammonia complex ion diamminesilver(I) nitrate.

$$Ag^+NO_3^- + 2NH_3 \xrightarrow{NH_3/H_2O} [Ag(NH_3)_2]^+NO_3^-$$

When Tollens' reagent is added to an aldehyde, the aldehyde is oxidised to a carboxylate anion, and silver ions are reduced to metallic silver. If this reaction is carried out properly, silver precipitates as a smooth, mirror-like deposit, hence the name **silver-mirror test** (figure 21.5).

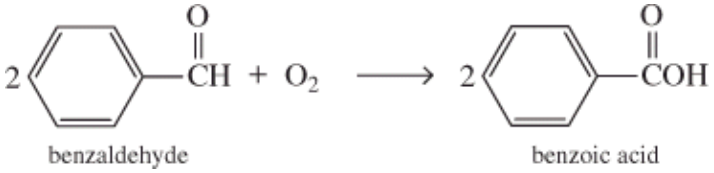


FIGURE 21.5 A silver mirror has been deposited on the inside of this flask by the reaction of an aldehyde with Tollens' reagent.
Charles D Winters



Nowadays, silver ions are rarely used for the oxidation of aldehydes because of the high cost of silver and because other, more convenient oxidation methods exist. The reaction, however, is still commonly used for silvering mirrors. In this process, formaldehyde or glucose is used as the aldehyde to reduce the silver(I) ions.

Aldehydes are also oxidised to carboxylic acids by molecular oxygen and by hydrogen peroxide.



Molecular oxygen is the least expensive and most readily available of all oxidising agents, and, on an industrial scale, air oxidation of organic molecules, including aldehydes, is common. Air oxidation of aldehydes can also be a problem; aldehydes that are liquid at room temperature are so sensitive to oxidation by molecular oxygen that they must be protected from contact with air during storage. Often, this is done by sealing the aldehyde in a container under an atmosphere of nitrogen.

WORKED EXAMPLE 21.10

Oxidation of Aldehydes

Draw a structural formula of the product formed by treating each of the following compounds with Tollens' reagent, followed by acidification with aqueous HCl.

(a) pentanal

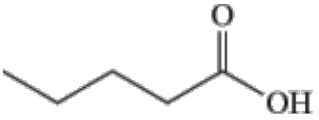
(b) cyclopentanecarbaldehyde

Analysis

Only the aldehyde group in each case is oxidised. This oxidation gives a carboxylic acid group.

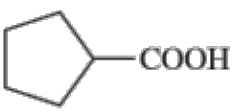
Solution

(a)



pentanoic acid

(b)



cyclopentanecarboxylic acid

Is our answer reasonable?

Check that the products are carboxylic acids and that the number of carbon atoms in the starting material is the same as the product.

PRACTICE EXERCISE 21.10

Complete the following oxidations.

(a) 3-oxobutanal + O_2 →

(b) 3-phenylpropanal + Tollens' reagent →

Chemistry Research

Making Molecules for Medicines

Professor Margaret Brimble, The University of Auckland

Matural products have long been regarded as 'nature's medicine chest' because they offer a rich source of compounds with complex and novel structures that inspire the development of new drugs. The synthesis of these challenging, naturally occurring compounds in the laboratory is a scientific endeavour that forms the backbone of the pharmaceutical industry. By synthesising natural compounds and closely related synthetic analogues, scientists glean valuable information about how the natural compounds work, ultimately producing even better compounds as drug candidates.

Professor Margaret Brimble's research group focuses on making and modifying complex, rare, bioactive compounds derived from plants, animal tissues, microbes, or marine and soil organisms that exhibit antimicrobial, anticancer or antiviral activity. The syntheses of the bioactive targets she and her team prepare often involve 30 or more steps and, as each step poses a unique challenge, the project can take years to complete.

One area of extensive research is the synthesis of shellfish toxins, which are associated with the algal blooms (figure 21.7) that occur in coastal waters ('red tide' phenomena). Such blooms may have a devastating effect on fish and marine species, often resulting in the closure of shellfish farms. In humans, the toxins cause symptoms ranging from diarrhoea to extreme cardiovascular and neurotoxic effects. Since shellfish toxins target ion channels to cause these biological effects, molecules that can modulate the function of ion channels are useful starting points for the rational design and development of drugs. These molecules may impact on clinical conditions ranging from pain, epilepsy and hypertension through to major diseases such as stroke and cancer. Shellfish toxins also represent some of the most complex molecular structures known, thus providing synthetic chemists significant challenges to achieve their synthesis.

One family of shellfish toxins under investigation is a family called the spirolides (see figure 21.6), which were isolated from the digestive glands of certain mussels and scallops during algal blooms in Canada. The prefix *spiro*– refers to structures that involve two rings joined at one common atom. The spirolides contain an unusual spiroacetal ring, where the two oxygen atoms of the acetal form the spiro structure, as well as a rare spiroimine ring. Imines involve a C ═N double bond and usually are readily hydrolysed. A similar spiroimine ring system is found in gymnodimine, which has been isolated from shell-fish collected after outbreaks of algal blooms in New Zealand.

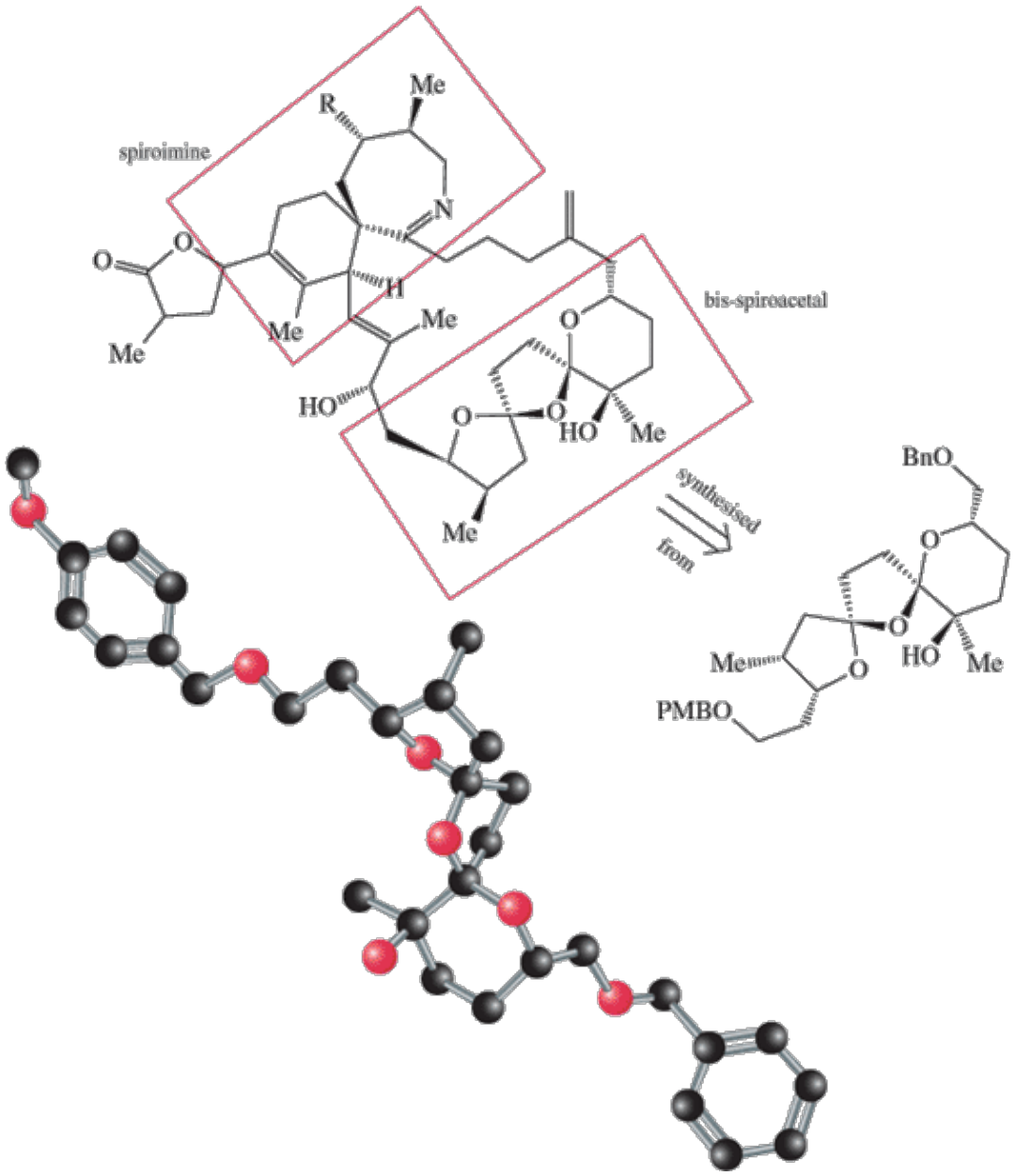


FIGURE 21.6 Structure of the spirolides.



FIGURE 21.7 An algal bloom near Cape Rodney, New Zealand.

The synthesis of the spirolides provides compounds for the development of pharmacological probes for the activation of L-type calcium channels, which are responsible for the contraction of myocardial and vascular smooth muscles. Compounds that block L-type calcium channels provide a therapeutic approach to treat cardiovascular conditions such as hypertension. The synthesis of spirolides requires an understanding that these molecules are chiral (see chapter 17) and knowledge of how the functional groups contained in these molecules react. To check whether the reactions used to construct the spirolides have in fact worked, NMR spectra are recorded for all of the synthetic intermediates (see chapter 20).

In other work, the Brimble group recently accomplished more efficient synthesis of *gamma*-rubromycin (figure 21.8), a potent inhibitor of human telomerase. Telomeres are the protective ends of chromosomes consisting of a repetitive sequence that shortens with each cell division. They serve as a mitotic clock that controls the number of divisions that a cell can undergo before entering senescence. The length of a telomere is maintained by telomerase, a unique enzyme that adds the telomeric repeats onto the ends of the chromosome. Telomerase helps prevent the fraying of chromosomes that underlies many ageing and cancer processes. The 2009 Nobel Prize in medicine was awarded for the discovery of telomeres and the telomerase enzyme.

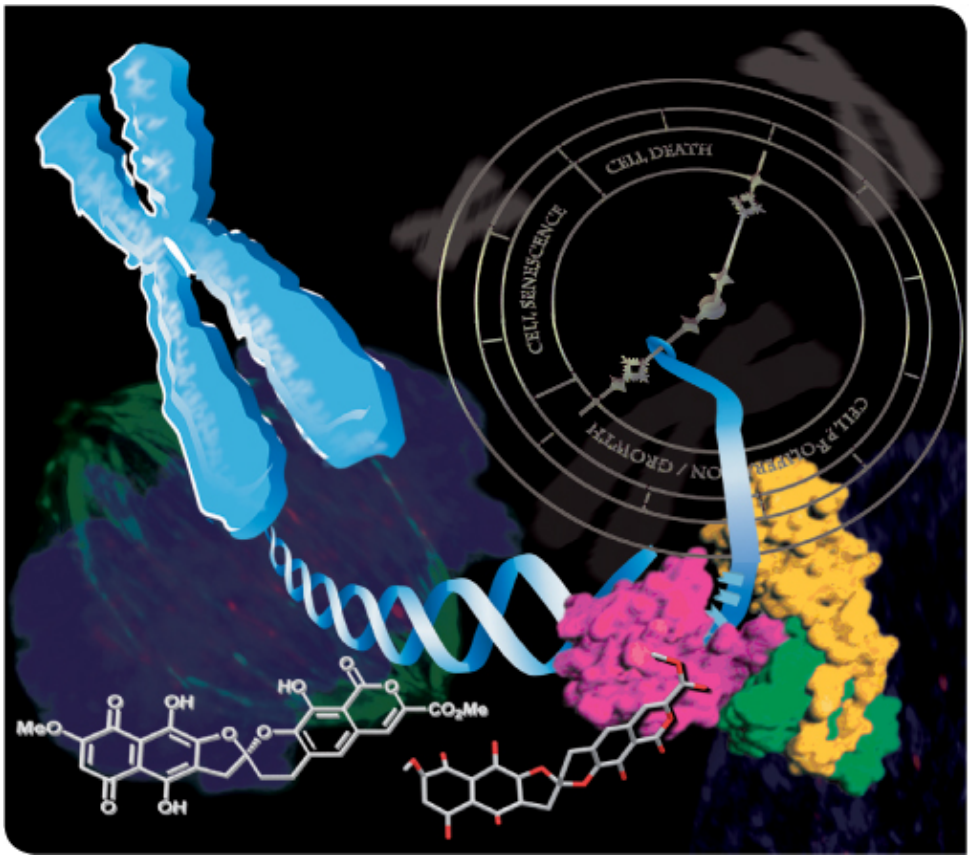


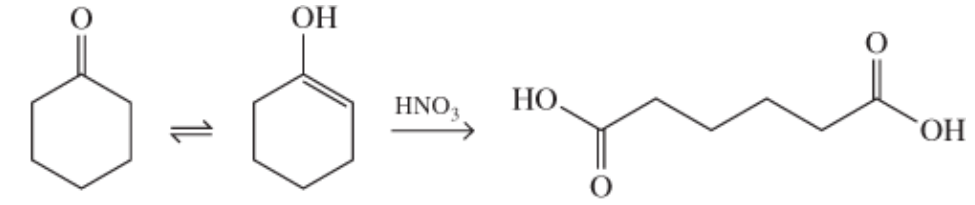
FIGURE 21.8 A conceptual depiction of *gamma*-rubromycin and its interaction with telomerase.

The new synthesis of *gamma*-rubromycin is more efficient than the previously reported approach and produces this important telomerase inhibitor in much better overall yield. However, more than 16 steps are still required to prepare *gamma*-rubromycin, and the tactics and synthetic manoeuvering required in a synthesis like this have been compared to the logic and rationale behind a game of chess. But, in this game, you first have to learn how the pieces move by understanding the reactions of functional groups.

Oxidation of Ketones to Carboxylic Acids

Ketones are much more resistant to oxidation than aldehydes. For example, ketones are not normally oxidised by chromic acid or potassium permanganate at room temperature. In fact, these reagents are used routinely to oxidise secondary alcohols to ketones in good yield (section 19.2).

Ketones undergo oxidative cleavage, via their enol form (see below), using potassium dichromate and potassium permanganate at higher temperatures, as well as by higher concentrations of nitric acid, HNO_3. The carbon–carbon double bond of the enol is cleaved to form two carboxyl or ketone groups, depending on the substitution pattern of the original ketone. An important industrial application of this reaction is the oxidation of cyclohexanone to hexanedioic acid (adipic acid), one of the two monomers required for the synthesis of the polymer nylon 6,6 (section 26.3).

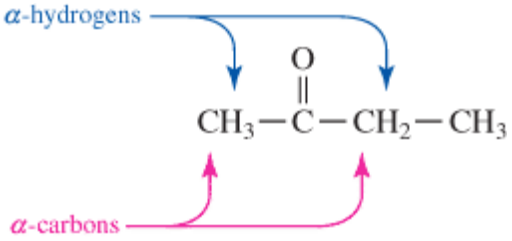


cyclohexanone (keto form) | cyclohexanone (enol form) | hexanedioic acid (adipic acid)

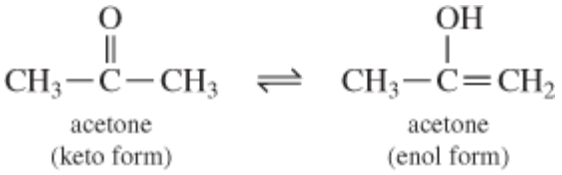
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21.6 Keto–enol Tautomerism

A carbon atom adjacent to a carbonyl group is called an **α-carbon**, and any hydrogen atoms bonded to it are called **α-hydrogens**.



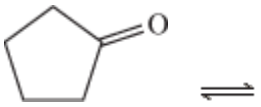
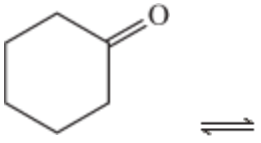
An aldehyde or ketone that has at least one α-hydrogen atom is in equilibrium with a constitutional isomer called an **enol**. The name 'enol' is derived from the IUPAC designation of it as both an alkene (*-en-*) and an alcohol (*-ol*).



Keto and enol forms are examples of **tautomers**, which are constitutional isomers in equilibrium with each other. Tautomers differ in the location of a hydrogen atom and a double bond relative to a heteroatom, most commonly O, S or N. This type of isomerism is called **tautomerism**.

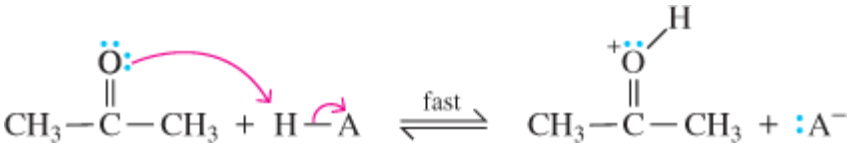
For most simple aldehydes and ketones, the position of the equilibrium in keto–enol tautomerism lies far on the side of the keto form (table 21.4), because a carbon–oxygen double bond is stronger than a carbon–carbon double bond.

TABLE 21.4 The position of keto–enol equilibrium for four aldehydes and ketones.

Keto form	Enol form	% Enol at equilibrium
		6×10^{-5}
		6×10^{-7}
		1×10^{-6}
		1×10^{-5}

The equilibration of keto and enol forms is catalysed by acid, as shown in the following two-step mechanism (note that a molecule of H—A is consumed in step 1, but another is generated in step 2):

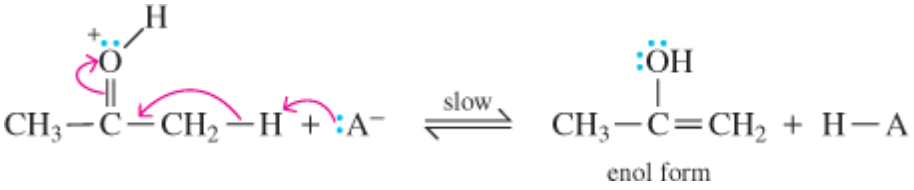
Step 1: Proton transfer from the acid catalyst, H—A, to the carbonyl oxygen atom forms the conjugate acid of the aldehyde or ketone.



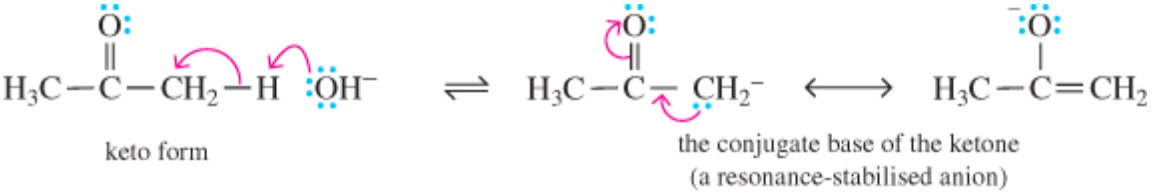
keto form

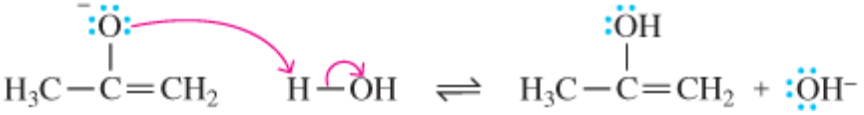
the conjugate acid of the ketone

Step 2: Proton transfer from the α-carbon atom to the base, A^-, gives the enol and generates a new molecule of the acid catalyst, H—A.



This tautomerism can also be base catalysed. The process is the reverse of the acid-catalysed process in that the base removes a proton from the α-carbon atom first. The resulting alkoxide then removes a proton from the conjugate acid (formed when the base removes the α-hydrogen atom).



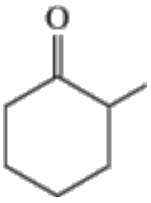


WORKED EXAMPLE 21.11

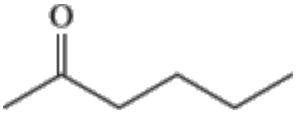
Enol Forms

Write two enol forms for each of the following compounds, and state which enol predominates at equilibrium.

(a)



(b)

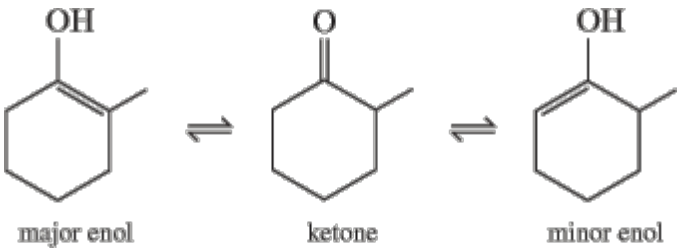


Analysis

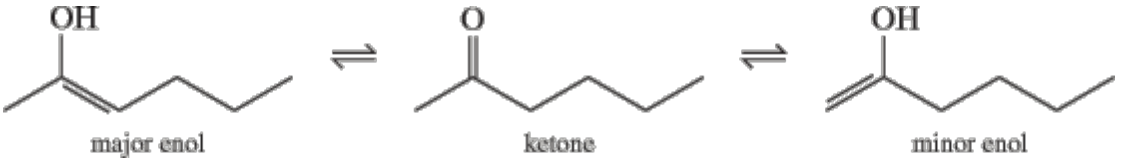
The carbon atom of the carbonyl group will remain sp^2 hybridised (it will be part of the alkene in the enol). The two possible enols are obtained by removal of an α-hydrogen atom from the two α-carbon atoms. Zaitsev's rule (section 18.3) will help predict the major enol form.

Solution In each case, the major enol form has the more substituted (the more stable) carbon–carbon double bond.

(a)



(b)



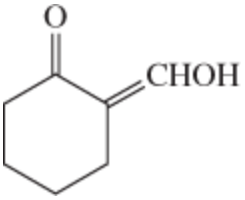
Is our answer reasonable?

Check that one of the atoms in the alkene group was the carbonyl carbon atom.

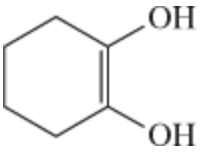
PRACTICE EXERCISE 21.11

Draw the structural formula for the keto form of each of the following enols.

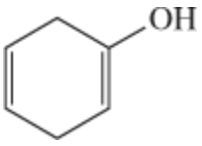
(a)



(b)

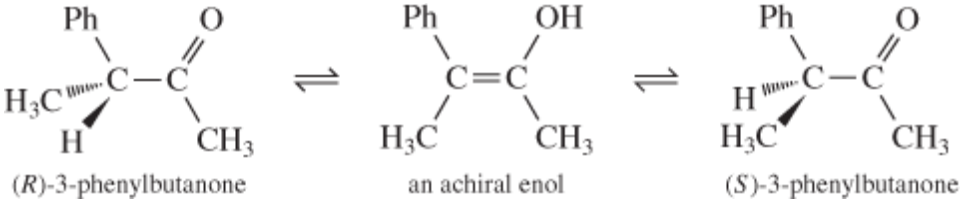


(c)



Racemisation at an α-carbon Atom

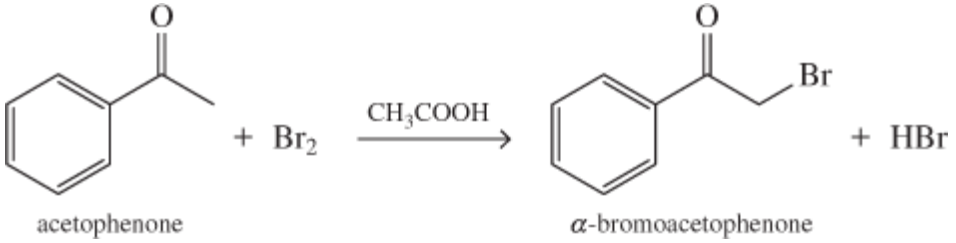
When enantiomerically pure (either *R* or *S*) 3-phenylbutanone is dissolved in ethanol, no change occurs in the optical activity of the solution over time. If, however, a trace of acid is added, the optical activity of the solution begins to decrease and gradually drops to zero. When 3-phenylbutanone is isolated from this solution, it is found to be a racemic mixture (section 17.5). This observation can be explained by the acid-catalysed formation of an achiral enol intermediate. In the tautomerism of the achiral enol to the chiral keto form, the hydrogen ion can add to carbon-3 of the enol ether from above or below to generate the *R* and *S* enantiomers with equal probability.



Racemisation by this mechanism occurs only at α-carbon stereocentres with at least one α-hydrogen atom.

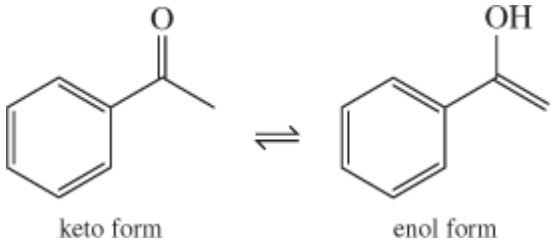
α-Halogenation

Aldehydes and ketones with at least one α-hydrogen atom react with bromine and chlorine at the α-carbon atom to give an α-haloaldehyde or α-haloketone. Acetophenone, for example, reacts with bromine in acetic acid to give α-bromoacetophenone, an α-bromoketone.

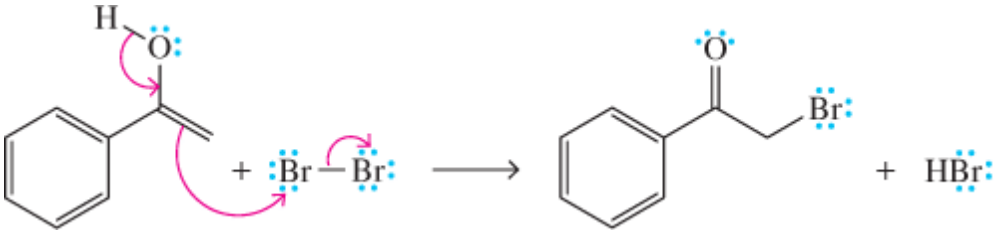


Acidic and basic conditions both catalyse α-halogenation. For acid-catalysed halogenation, the HBr or HCl generated catalyses further reaction.

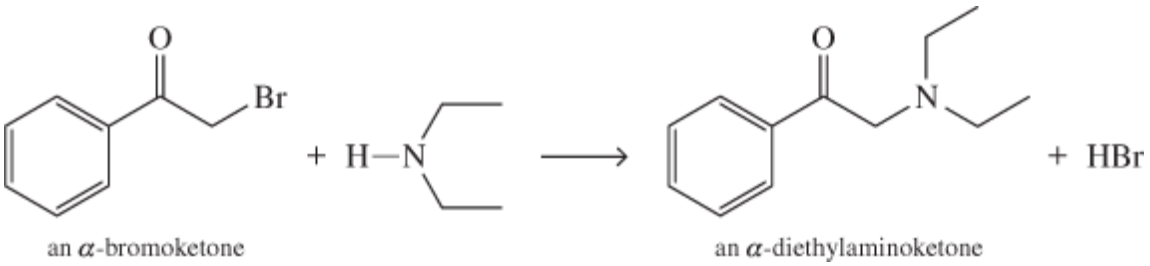
Step 1: Acid-catalysed keto–enol tautomerism gives the enol.



Step 2: Nucleophilic attack of the enol on the halogen molecule gives the α-haloketone.



The value of α-halogenation is that it converts an α-carbon atom into a centre that has a good leaving group and is therefore susceptible to substitution by a variety of good nucleophiles. In the following example, diethylamine (a nucleophile) reacts with the α-bromoketone to give an α-diethylaminoketone.



an α-bromoketone

an α-diethylaminoketone

In practice, this type of nucleophilic substitution is generally carried out in the presence of a weak base, such as potassium carbonate, to neutralise the HX as it is formed.

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SUMMARY

Structure and Bonding

An aldehyde contains a carbonyl group bonded to a hydrogen atom and a carbon atom. A ketone contains a carbonyl group bonded to two carbon atoms.

Nomenclature

An aldehyde is named by changing the *-e* suffix of the parent alkane to *-al*. A—CHO group bonded to a ring is indicated by the suffix *-carbaldehyde*. A ketone is named by changing the *-e* suffix of the parent alkane to *-one* and using a number to locate the carbonyl group. In naming compounds that contain more than one functional group, the IUPAC system has established an order of precedence of functional groups. If the carbonyl group of an aldehyde or a ketone is lower in precedence than other functional groups in the molecule, it is indicated by the infix *-oxo-*.

Physical Properties

Aldehydes and ketones are polar compounds and interact in the pure state by dipole–dipole interactions; they have higher boiling points and are more soluble in water than nonpolar compounds of similar molar mass and similar number of electrons.

Preparation of Aldehydes and Ketones

Aldehydes and ketones can be prepared from various functional groups using many different reactions. Friedel–Crafts acylation of aromatic compounds yields ketones (aldehydes can not be obtained by this method). Aldehydes and ketones can be prepared by the oxidation of alcohols; primary alcohols give aldehydes, and secondary alcohols give ketones. Ozonolysis of alkenes cleaves the carbon–carbon double bond to produce two carbonyl groups. Ketones can also be prepared by the hydration of alkynes. This process proceeds via an enol, which undergoes tautomerism to give the ketone.

Reactions

Aldehydes and ketones are very reactive groups due to the polarity and structure of the carbonyl group. Aldehydes are usually more reactive than ketones because access to the carbonyl group is easier. The most common reaction of the carbonyl group is the addition of a nucleophile to form a tetrahedral carbonyl addition intermediate.

Alkyl, aryl and vinylic halides react with certain metals to form organometallic compounds. Organomagnesium compounds are commonly called Grignard reagents. The carbon–metal bond in Grignard reagents has a partial ionic character. Grignard reagents behave as carbanions and are both strong bases and good nucleophiles.

Treatment of aldehydes and some ketones with sodium cyanide and dilute acid produces cyanohydrins, compounds with an —OH and a —CN bonded to the same carbon atom.

The addition of an alcohol molecule to the carbonyl group of an aldehyde or ketone forms a hemiacetal. The hemiacetal functional group is a carbon atom bonded to an —OH group and an —OR or —OAr group. Hemiacetals can react further with alcohols to form acetals plus a molecule of water. The acetal functional group is a carbon atom bonded to two —OR or —OAr groups.

Ammonia, primary aliphatic amines, RNH_2, and primary aromatic amines, $ArNH_2$, react with the carbonyl group of aldehydes and ketones in the presence of an acid catalyst to give imines (compounds that contain a carbon–nitrogen double bond). When aldehydes and ketones react with hydroxylamine, H_2NOH, they form oximes (compounds containing a C═NOH group). A primary amine is converted

to a secondary amine by way of an imine in a two-step reaction called reductive amination.

Aldehydes are reduced to primary alcohols. Ketones are reduced to secondary alcohols. Sodium borohydride and lithium aluminium hydride are the most common laboratory reagents used to reduce the carbonyl group of an aldehyde or ketone. Each acts as a source of a hydride ion, which is a very strong nucleophile.

Aldehydes are one of the most easily oxidised of all functional groups. They oxidise to carboxylic acids. The addition of Tollens' reagent oxidises an aldehyde to a carboxylate anion and silver ions are reduced to metallic silver. Silver from this reaction precipitates as a smooth, mirror-like deposit, and the reaction is known as the silver-mirror test.

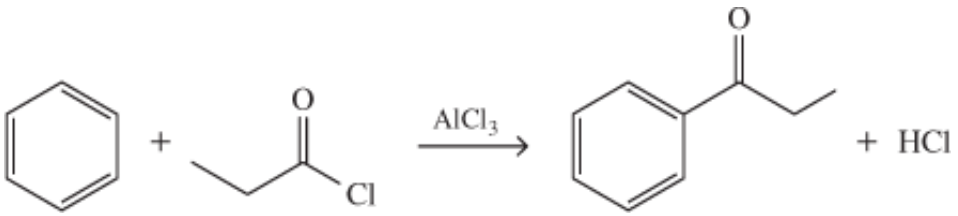
Keto–enol Tautomerism

A carbon atom adjacent to a carbonyl group is called an α-carbon, and a hydrogen attached to it is called an α-hydrogen. An aldehyde or ketone that has at least one α-hydrogen atom is in equilibrium with a constitutional isomer called an enol. Constitutional isomers in equilibrium with each other that differ in the location of a hydrogen atom and a double bond relative to a heteroatom are called tautomers, and this type of isomerism is called tautomerism.

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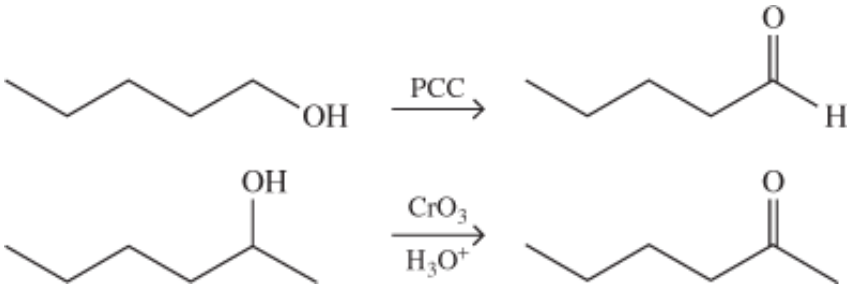
Preparation of ketones by Freidel–Crafts acylation *(section 21.4)*

Ketones can be prepared by Friedel–Crafts acylation of aromatic compounds.



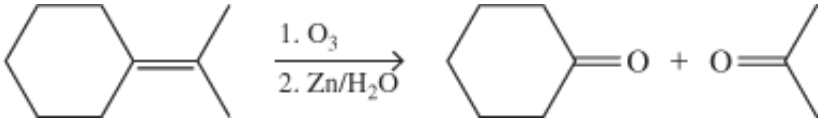
Preparation of aldehydes and ketones by oxidation of alcohols *(section 21.4)*

Primary alcohols can be oxidised under mild conditions to give aldehydes, and secondary alcohols can be oxidised to give ketones.



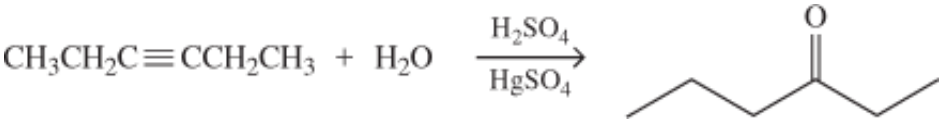
Preparation of aldehydes and ketones by ozonolysis of alkenes *(section 21.4)*

Alkenes are readily cleaved by ozone, which when followed by reductive hydrolysis gives aldehydes and/or ketones.



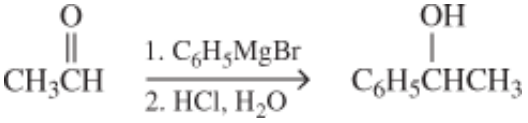
Preparation of ketones by hydration of alkynes *(section 21.4)*

Hydration of alkynes yields ketones.



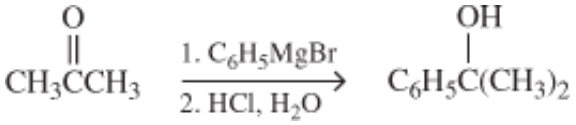
Reaction with Grignard reagents *(section 21.5)*

Treatment of formaldehyde with a Grignard reagent, followed by hydrolysis in aqueous acid, gives a primary alcohol. Similar treatment of any other aldehyde gives a secondary alcohol.

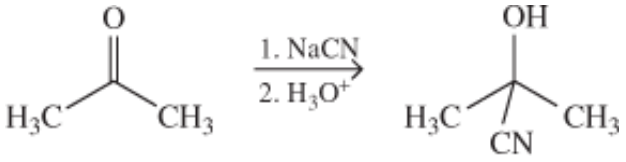


Addition of other carbon nucleophiles *(section 21.5)*

Treatment of a ketone with a Grignard reagent gives a tertiary alcohol.

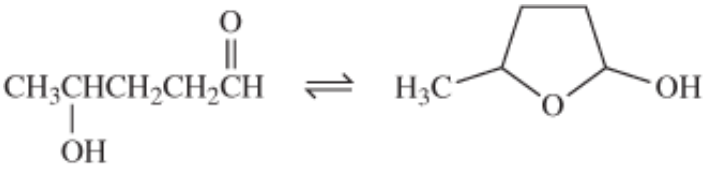


Aldehydes and ketones will react with cyanide ions to form cyanohydrins.



Addition of alcohols to form hemiacetals *(section 21.5)*

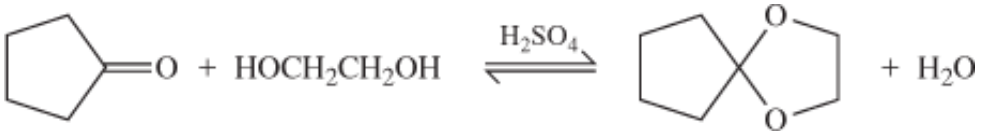
Hemiacetals are only minor components of an equilibrium mixture of an aldehyde or a ketone, and an alcohol, except where the —OH and C═O groups are parts of the same molecule and a five- or six-membered ring can form.



4-hydroxypentanal — a cyclic hemiacetal

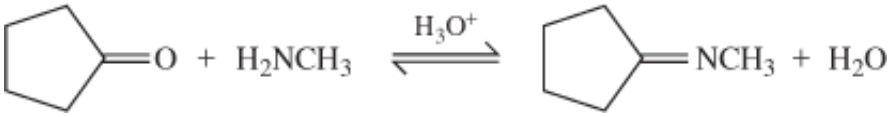
Addition of alcohols to form acetals *(section 21.5)*

The formation of acetals is catalysed by acid.



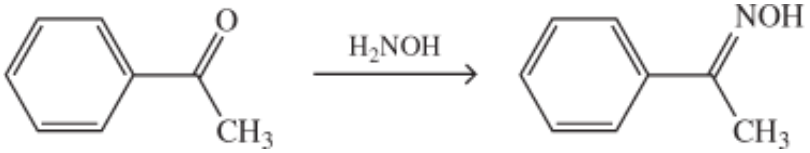
Addition of ammonia and amines *(section 21.5)*

The addition of ammonia or a primary amine to the carbonyl group of an aldehyde or a ketone forms a tetrahedral carbonyl addition intermediate. Loss of water from this intermediate gives an imine.



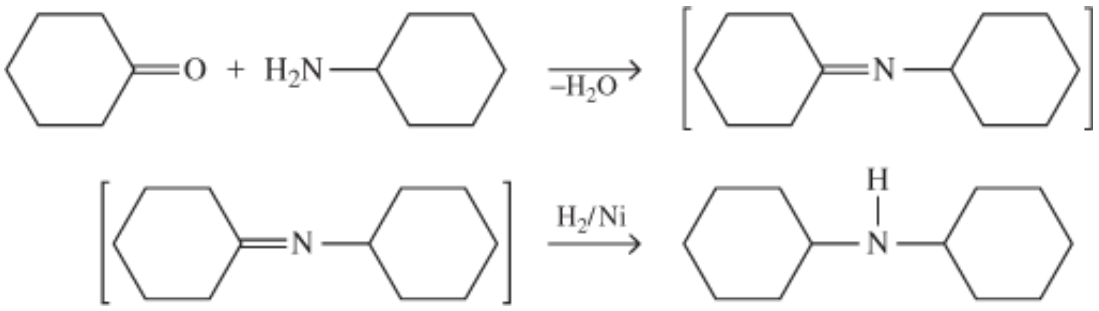
Formation of oximes *(section 21.5)*

The condensation of aldehydes and ketones with hydroxylamine gives oximes.



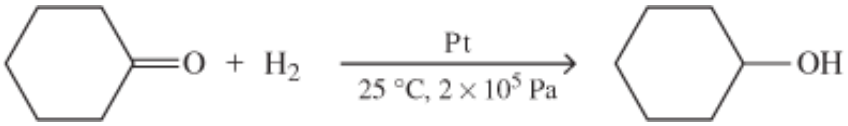
Reductive amination to amines *(section 21.5)*

The carbon–nitrogen double bond of an imine can be reduced by hydrogen in the presence of a transition metal catalyst to a carbon–nitrogen single bond.



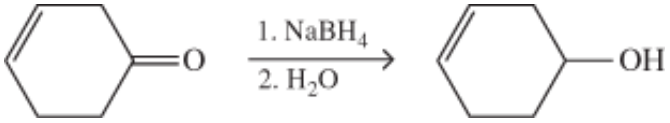
Catalytic reduction *(section 21.5)*

Catalytic reduction of the carbonyl group of an aldehyde or a ketone to a hydroxyl group can be achieved in high yields. However, this occurs much more slowly than the reaction of alkenes and requires more vigorous conditions.



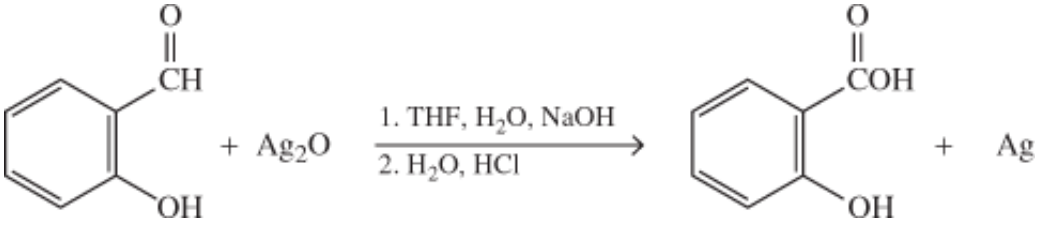
Metal hydride reduction *(section 21.5)*

Both $LiAlH_4$ and $NaBH_4$ reduce the carbonyl group of an aldehyde or a ketone to a hydroxyl group. They are selective in that neither reduces isolated carbon–carbon double bonds.



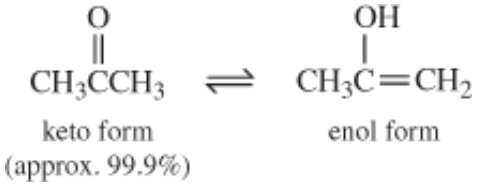
Oxidation of an aldehyde to a carboxylic acid *(section 21.5)*

The aldehyde group is among the most easily oxidised functional groups. Oxidising agents include H_2CrO_4, silver(I) ions including Tollens' reagent, and O_2.



Keto–enol tautomerism *(section 21.6)*

The keto form of an aldehyde or a ketone generally predominates over the enol form at equilibrium.



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REVIEW QUESTIONS

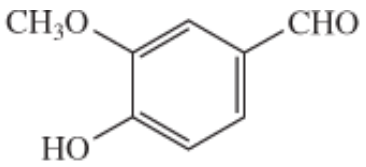
Structure and bonding

21.1 Draw structural formulae for the one ketone and two aldehydes with the molecular formula C_4H_8O.

21.2 Draw structural formulae for the four aldehydes with the molecular formula $C_5H_{10}O$. Which of these aldehydes are chiral?

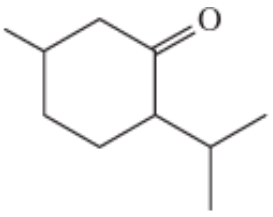
21.3 Use the δ+ and δ - notation to show the polarity of the following carbonyl compounds.

(a)



vanillin
4-hydroxy-3-methoxybenzaldehyde

(b)



menthone
2-isopropyl-5-methylcyclohexanone

21.4 Compare and contrast the bonding in a carbonyl group (C═O) and an alkene group (C═C). What are the similarities and what are the differences?

Nomenclature

21.5 Draw structural formulae corresponding to the following compound names.

(a) bromoacetone
(b) methylbutanone
(c) 3,5-dinitrobenzaldehyde
(d) 3,5-dimethylcyclohexanone
(e) tetramethylpentan-3-one
(f) butandial
(g) 3-hydroxybutanone
(h) 3-phenylpropenal

21.6 Draw structural formulae corresponding to the following compound names.

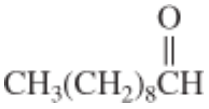
(a) chloropropanone
(b) 3-hydroxybutanal
(c) 4-hydroxy-4-methylpentan-2-one
(d) 3-methyl-3-phenylbutanal
(e) (*S*)-3-bromocyclohexanone
(f) 3-methylbut-3-enone
(g) 5-oxohexanal

(h) 2,2-dimethylcyclohexanecarbaldehyde

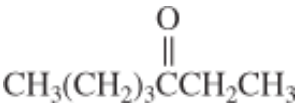
(i) 3-oxobutanoic acid

21.7 Name the following compounds using the IUPAC system of nomenclature.

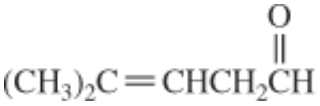
(a)



(b)



(c)



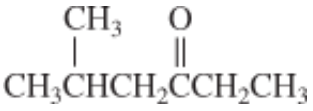
(d)



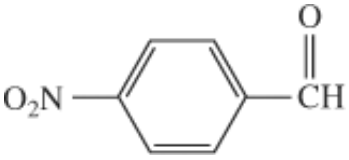
(e)



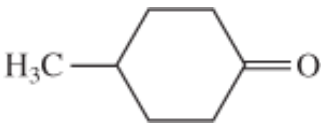
(f)



(g)

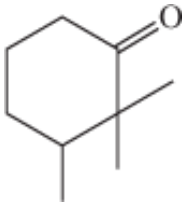


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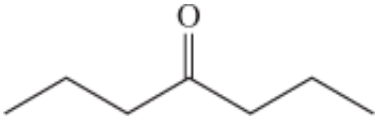


21.8 Name the following compounds using the IUPAC system of nomenclature.

(a)

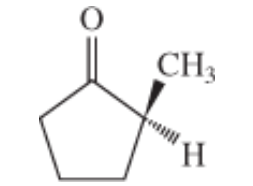


(b)

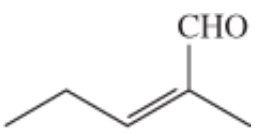


(c)

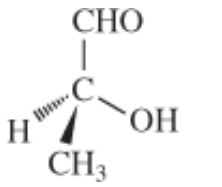
(d)



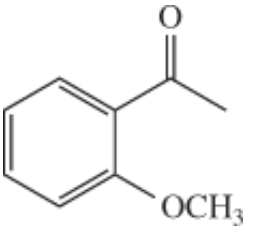
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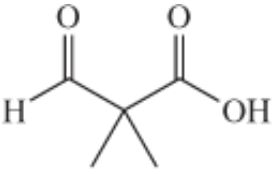
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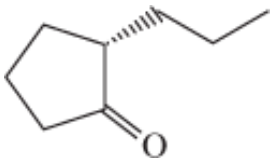


(g)



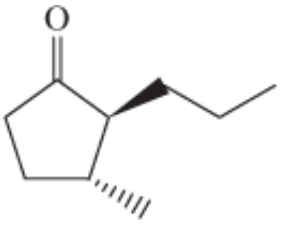
(h)



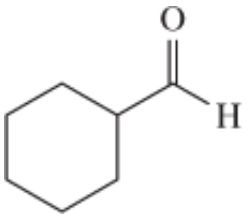


21.9 Provide a systematic (IUPAC) name for each of the following compounds.

(a)

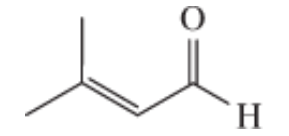


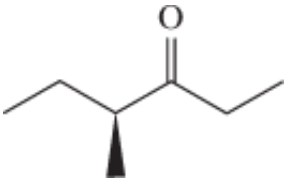
(b)



(c)

(d)



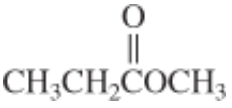


21.10 Name the family to which each of the following compounds belongs.

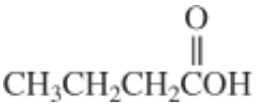
(a) $CH_3CH{=}CH_2$

(b) CH_3CH_2OH

(c)



(d)



(e) $CH_3CH_2CH_2NH_2$

(f) $HOCH_2CH_2CH_3$

21.11 To which organic family does each of the following compounds belong?

(a) $CH_3C{\equiv}CH$

(b)



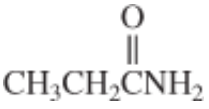
(c)



(d) $CH_3{-}O{-}CH_2CH_3$

(e) $CH_3CH_2NH_2$

(f)



Physical Properties

21.12 Why do aldehydes and ketones have boiling points that are lower than those of their corresponding alcohols?

21.13 Explain why aldehydes and ketones have higher boiling points than alkanes of similar molar mass and similar number of electrons.

21.14 Which would you expect to be more soluble in water, acetaldehyde (ethanal) or hexanal? Explain your answer.

21.15 Which would you expect to be more soluble in water, acetone (propanone) or hexan-3-one?

Explain your answer.

21.16 With the aid of a sketch, show the hydrogen bonding between water and propanal.

21.17 Use a sketch to show the hydrogen bonding between methanol and butanone.

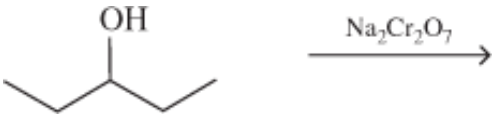
Preparation of Aldehydes and Ketones

21.18 Complete the following reactions.

(a) $H_3CC{\equiv}CCH_3 + H_2O \xrightarrow[HgSO_4]{H_2SO_4}$

(b) $H_3CC(CH_3)=CHCH_3 \xrightarrow[2.\ Zn/H_2O]{1.\ O_3}$

(c) 

(d) 

21.19 Give the structural formulae of the aldehyde or ketone obtained by the PCC oxidation of the following alcohols.

(a) 1-phenylethanol

(b) 2-phenylethanol

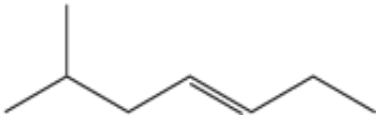
21.20 Give the structural formulae of the ketone(s) obtained by the hydration of the following alkynes.

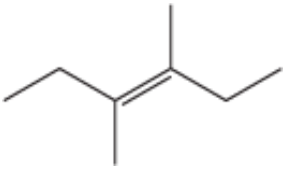
(a) hex-1-yne

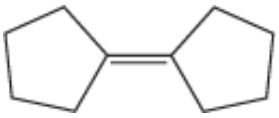
(b) hex-2-yne

(c) hex-3-yne

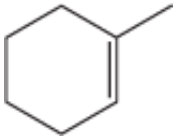
21.21 Give the structural formulae of the carbonyl compounds obtained by ozonolysis and reductive hydrolysis of the following alkenes.

(a) 

(b) 

(c) 

(d)



Reactions

21.22 Write the structures of the isomeric alcohols with the formula $C_4H_{10}O$ that could be oxidised to aldehydes. Write the structure of the isomer that could be oxidised to a ketone.

21.23 Which isomer of butan-1-ol cannot be oxidised by dichromate ions? Write its structure and IUPAC name.

21.24 Write the structure of the principal organic product of each of the following reactions:

(a) magnesium with 2-iodopropane in diethyl ether

(b) the product of (a) with formaldehyde in ether, followed by dilute acid

(c) the product of (a) with cyclopentanone in ether, followed by dilute acid

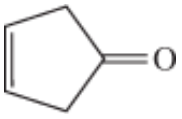
(d) the product of (a) with benzaldehyde in ether, followed by dilute acid.

21.25 Write an equation for the acid–base reaction between phenylmagnesium iodide and a carboxylic acid. Use curved arrows to show the bond-breaking and bond-forming steps in this reaction. In addition, show that the reaction is an example of a stronger acid and stronger base reacting to form a weaker acid and weaker base.

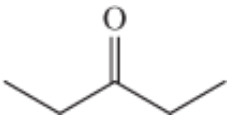
21.26 Draw structural formulae for the product formed by treating each of the following compounds with propylmagnesium bromide, followed by hydrolysis in aqueous acid.

(a) CH_2O

(b)

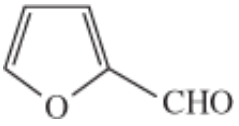


(c)

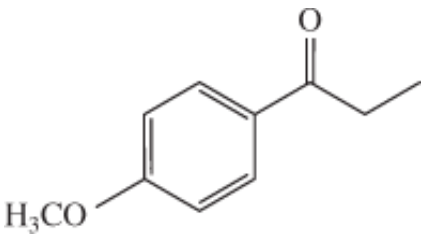


21.27 Draw structural formulae for the product formed by treating each of the following compounds with propylmagnesium bromide, followed by hydrolysis in aqueous acid.

(a)



(b)



21.28 Predict the product of the reaction of propanal with each of the following reagents.

(a) lithium aluminium hydride, followed by treatment with water

(b) sodium borohydride in methanol

(c) hydrogen with a nickel catalyst

(d) methylmagnesium iodide, followed by dilute acid

(e) aniline ($PhNH_2$)

(f) 4-nitrophenylhydrazine

(g) sodium cyanide with addition of sulfuric acid

(h) silver–ammonia complex (Tollens' reagent)

(i) acidified potassium dichromate solution

21.29 Repeat question 21.28 with cyclopentanone as the reactant.

Keto–enol Tautomerism

21.30 Write the structural formulae for all possible enols of:

(a) pentanal

(b) pentan-2-one

(c) pentan-3-one.

21.31 Write the structural formulae of all possible products resulting from the α-bromination of the following ketones:

(a) pentan-2-one

(b) pentan-3-one

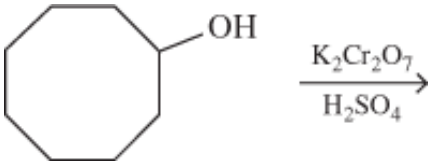
(c) cyclopentanone.

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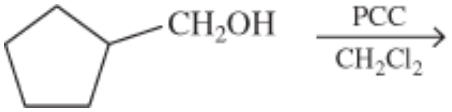
REVIEW PROBLEMS

21.32 Complete the following reactions.

(a)



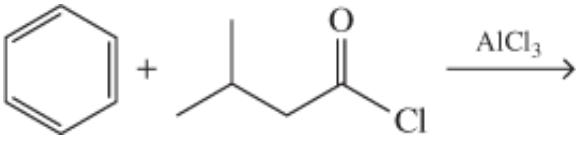
(b)



(c)

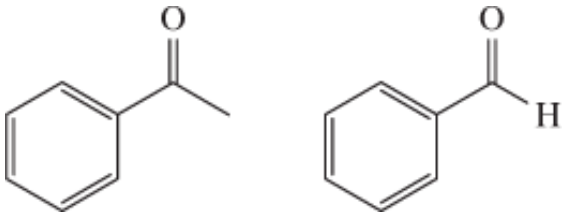


(d)



21.33 For each of the following pairs, identify which compound would be expected to react more rapidly with a nucleophile.

(a)



(b)

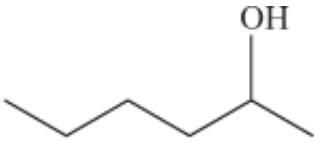


21.34 How can the following conversions be carried out?

(a) pentan-1-ol to pentanal
(b) pentan-1-ol to pentanoic acid
(c) pentan-2-ol to pentan-2-one
(d) pent-1-ene to pentan-2-one
(e) benzene to acetophenone
(f) styrene to acetophenone
(g) cyclohexanol to cyclohexanone
(h) cyclohexene to cyclohexanone

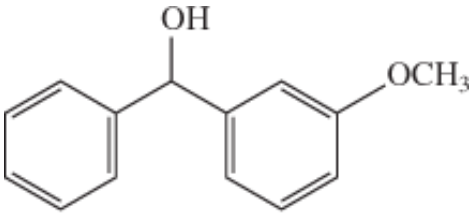
21.35 Suggest a synthesis for each of the following alcohols, starting from an aldehyde or ketone and an appropriate Grignard reagent. (The number of combinations of Grignard reagent and aldehyde or ketone that might be used is shown in parentheses below each target molecule.)

(a)



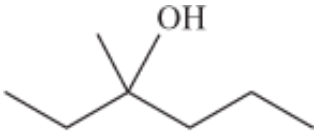
(2 combinations)

(b)



(2 combinations)

(c)



(3 combinations)

21.36 Choose a Grignard reagent and a ketone that can be used to produce each of the following compounds.

(a) 3-methyl-3-pentanol

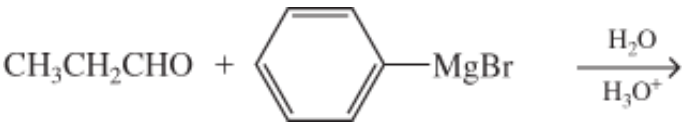
(b) 1-ethylcyclohexanol

(c) triphenylmethanol

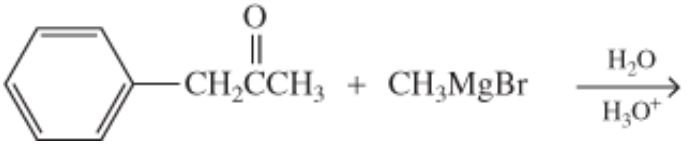
(d) 5-phenyl-5-nonanol

21.37 Complete the following reactions to show the major organic product.

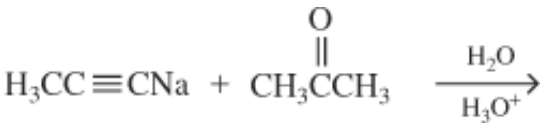
(a)



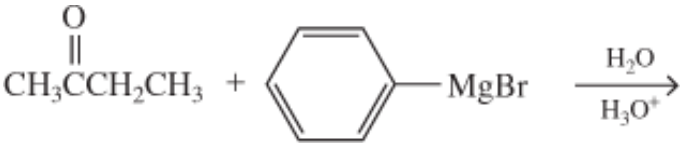
(b)



(c)

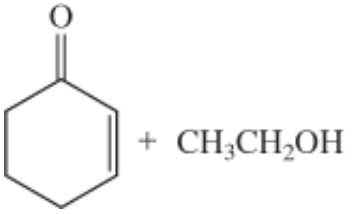


(d)

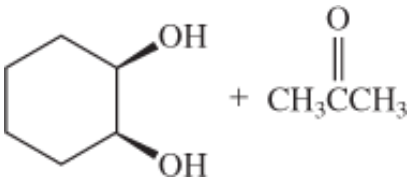


21.38 Draw structural formulae for the hemiacetal and then the acetal formed from each of the following pairs of reactants in the presence of an acid catalyst.

(a)



(b)

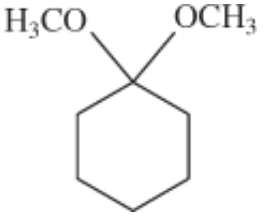


(c)

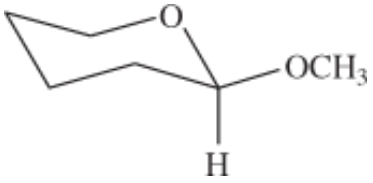


21.39 Draw structural formulae for the products of hydrolysis of each of the following acetals and ketals in aqueous acid.

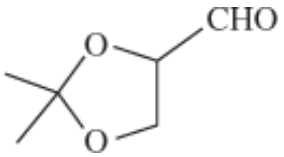
(a)



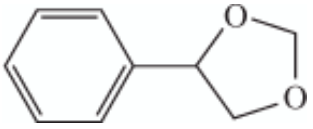
(b)



(c)



21.40 The following compound is a component of the fragrance of jasmine. From what carbonyl-containing compound and alcohol is it derived?

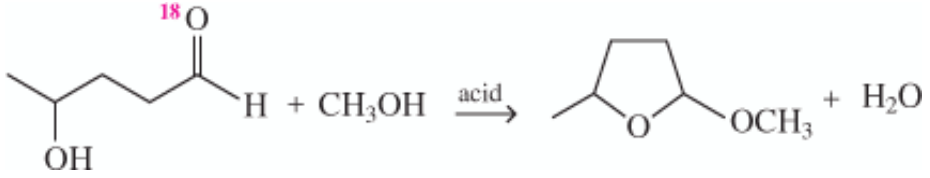


21.41 Propose a mechanism for the formation of the following cyclic acetal by treating acetone with ethylene glycol in the presence of an acid catalyst. Make sure that your mechanism is consistent with the fact that the oxygen atom of the water molecule is derived from the carbonyl oxygen atom of acetone.

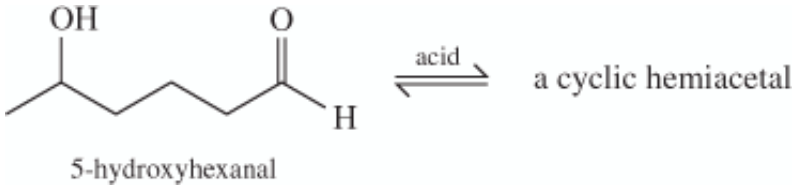


acetone ethylene glycol

21.42 Propose a mechanism for the formation of a cyclic acetal from 4-hydroxypentanal and one equivalent of methanol. If the carbonyl oxygen atom of 4-hydroxypentanal is enriched with oxygen-18, does your mechanism predict that the oxygen label appears in the cyclic acetal or in the water? Explain.



21.43 5-hydroxyhexanal forms a six-membered cyclic hemiacetal that predominates at equilibrium in acidic aqueous solution.

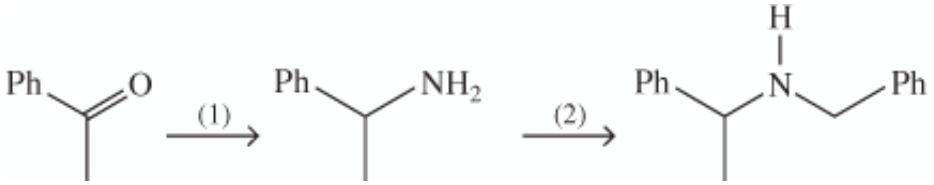


(a) Draw a structural formula for this cyclic hemiacetal.

(b) How many stereoisomers are possible for 5-hydroxyhexanal?

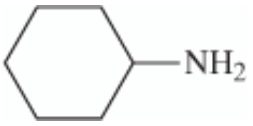
(c) How many stereoisomers are possible for the cyclic hemiacetal?

21.44 Show how the secondary amine below can be prepared by two successive reductive aminations.

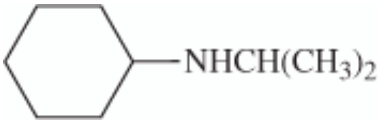


21.45 Show how to convert cyclohexanone to each of the following amines.

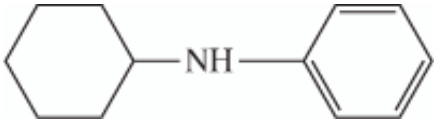
(a)



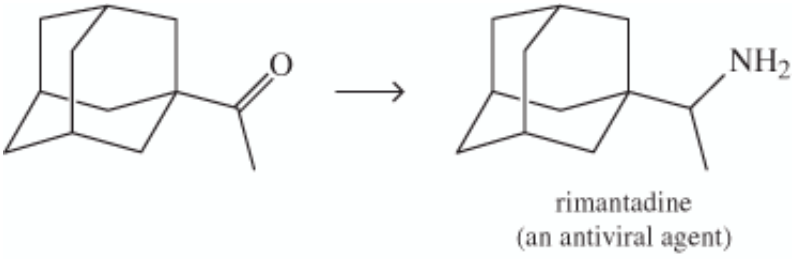
(b)



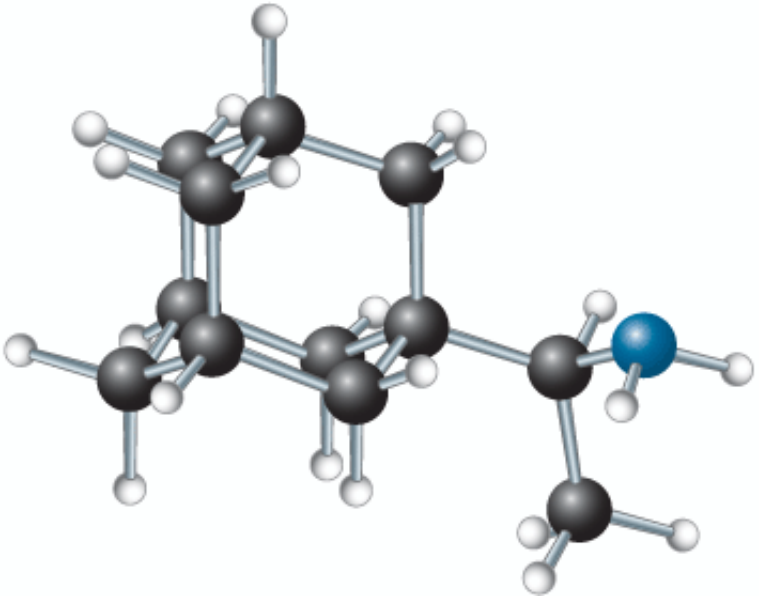
(c)



21.46 Rimantadine is effective in preventing infections caused by the influenza A virus and in treating the established illness. The drug is thought to exert its antiviral effect by blocking a late stage in the assembly of the virus. The following is the final step in the synthesis of rimantadine.



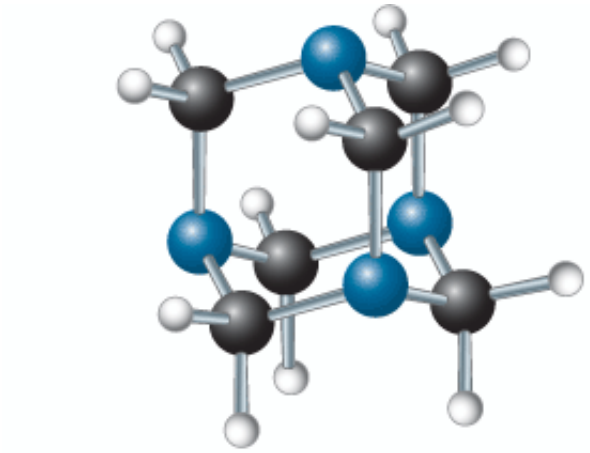
rimantadine
(an antiviral agent)

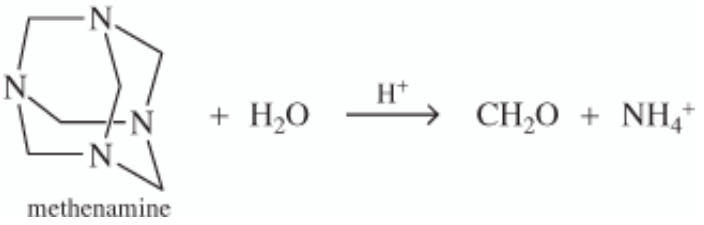


(a) Describe the experimental conditions which bring about this conversion.

(b) Is rimantadine chiral?

21.47 Methenamine, a product of the reaction of formaldehyde and ammonia, is a *prodrug* — a compound that is inactive by itself but is converted to an active drug in the body by a biochemical transformation. The strategy behind the use of methenamine as a prodrug is that nearly all bacteria are sensitive to formaldehyde at concentrations of 20 mg mL^{-1} or higher. Formaldehyde cannot be used directly in medicine because an effective concentration in plasma cannot be achieved with safe doses. Methenamine is stable at pH 7.4 (the pH of blood plasma) but undergoes acid-catalysed hydrolysis to formaldehyde and ammonium ions under the acidic conditions of the kidneys and the urinary tract.





Thus, methenamine can be used as a site-specific drug to treat urinary infections.

(a) Balance the equation for the hydrolysis of methenamine to formaldehyde and ammonium ions.

(b) Does the pH of an aqueous solution of methenamine increase, remain the same or decrease as a result of the hydrolysis of the compound? Explain.

(c) Explain the meaning of the following statement: 'The functional group in methenamine is the nitrogen analogue of an acetal.'

(d) Account for the observation that methenamine is stable in blood plasma but undergoes hydrolysis in the urinary tract.

21.48 Draw a structural formula for the product formed by treating butanal with each of the following sets of reagents.

(a) $LiAlH_4$ followed by H_2O

(b) $NaBH_4$ in CH_3OH/H_2O

(c) H_2/Pt

(d) $[Ag(NH_3)_2]^+$ in NH_3/H_2O and then HCl/H_2O

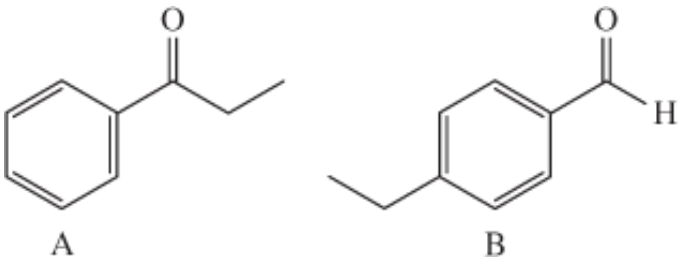
(e) H_2CrO_4

(f) $C_6H_5NH_2$ in the presence of H_2/Ni

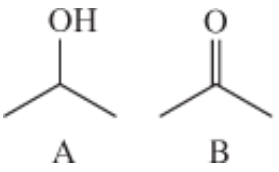
21.49 Draw a structural formula for the product of the reaction of *p*-bromoacetophenone with each set of reagents in question 21.48.

21.50 Show how you would chemically distinguish between the compounds in the following sets. Describe any observations and give equations where applicable.

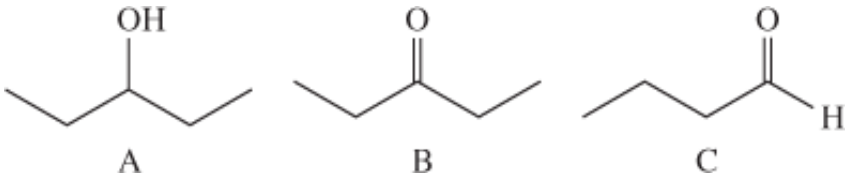
(a)



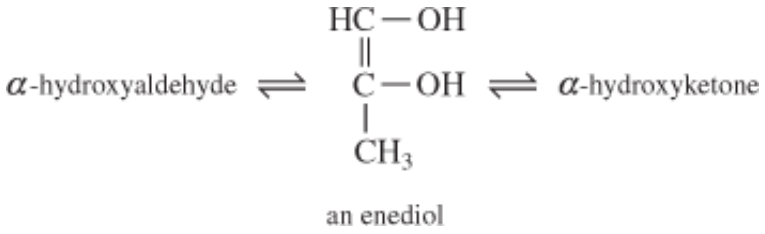
(b)



21.51 Show how you would chemically distinguish between the following compounds. Describe any observations and give equations where applicable.

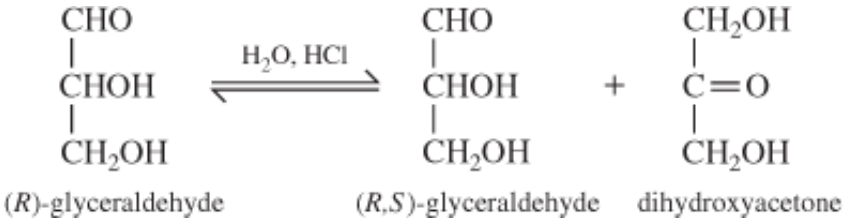


21.52 The following molecule belongs to a class of compounds called enediols. Each carbon atom of the double bond in an enediol carries an —OH group.



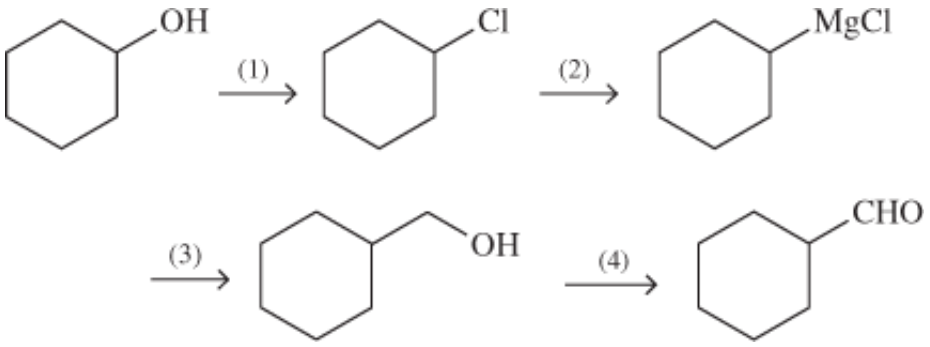
Draw structural formulae for the α-hydroxyketone and the α-hydroxyaldehyde with which this enediol is in equilibrium.

21.53 In dilute aqueous acid, (*R*)-glyceraldehyde is converted into an equilibrium mixture of (*R*,*S*)-glyceraldehyde and dihydroxyacetone.



Propose a mechanism for this isomerisation.

21.54 Show the reagents and conditions that will cause the conversion of cyclohexanol to cyclohexanecarbaldehyde.



21.55 Starting with cyclohexanone, show how to prepare the following compounds (in addition to the given starting material, use any other organic or inorganic reagents, as necessary).

(a) cyclohexanol

(b) cyclohexene

(c) 1-methylcyclohexanol

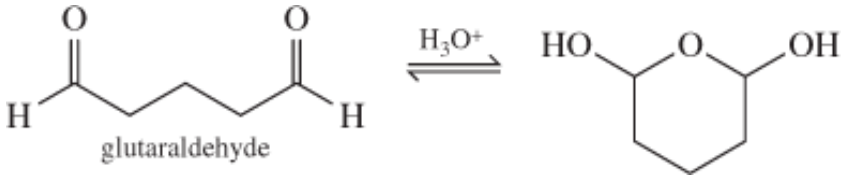
21.56 Starting with cyclohexanone, show how to prepare the following compounds (in addition to the given starting material, use any other organic or inorganic reagents, as necessary).

(a) 1-methylcyclohexene

(b) 1-phenylcyclohexanol

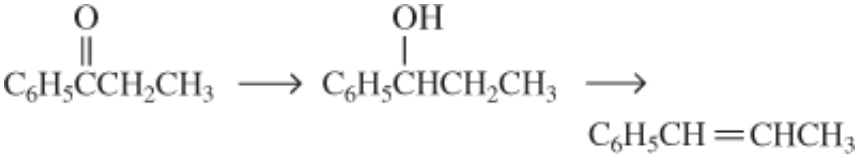
(c) 1-phenylcyclohexene

21.57 Glutaraldehyde is a germicidal agent that is sometimes used to sterilise medical equipment that is too sensitive to be heated in an autoclave. In midly acidic conditions, glutaraldehyde exists in a cyclic form (below right). Draw a plausible mechanism for this transformation.

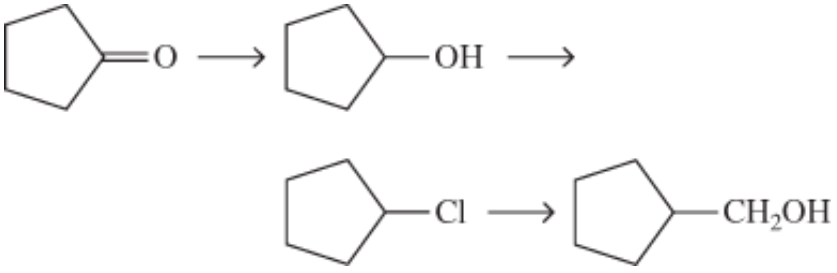


21.58 Show how to bring about the following conversions (in addition to the given starting material, use any other organic or inorganic reagents, as necessary).

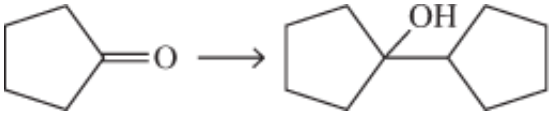
(a)



(b)

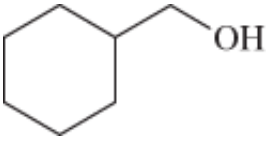


(c)

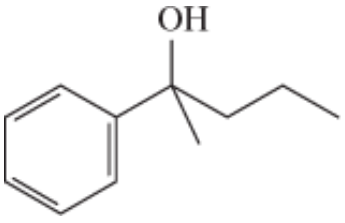


21.59 Using a Grignard reaction, show how you could prepare each of the following alcohols.

(a)

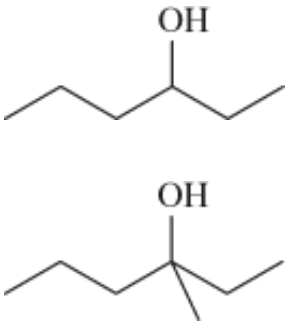


(b)



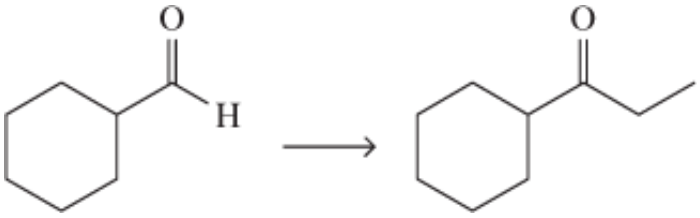
(c)

(d)

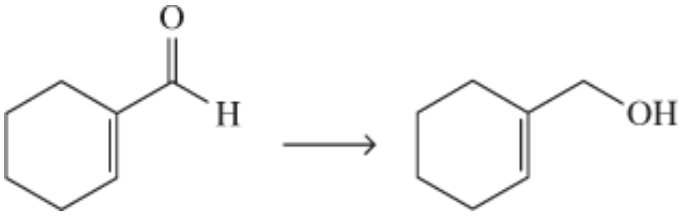


21.60 What reagents would you use to perform each of the following transformations?

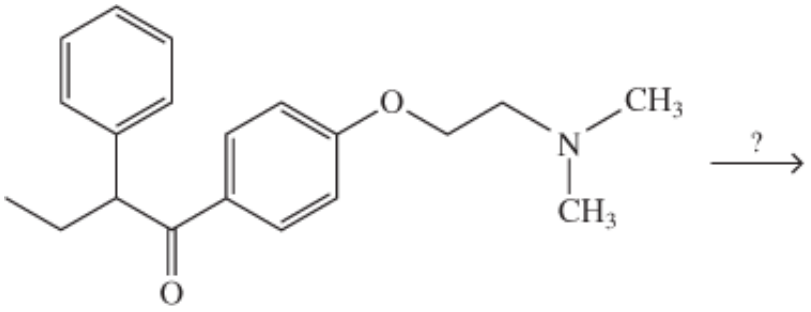
(a)

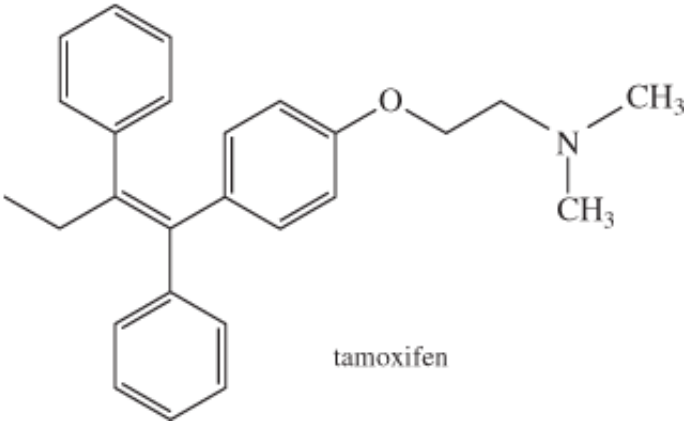


(b)



21.61 Many tumours of the breast are oestrogen dependent. Drugs that interfere with oestrogen binding have antitumour activity and may even help prevent the occurrence of tumours. A widely used antioestrogen drug is tamoxifen.





tamoxifen

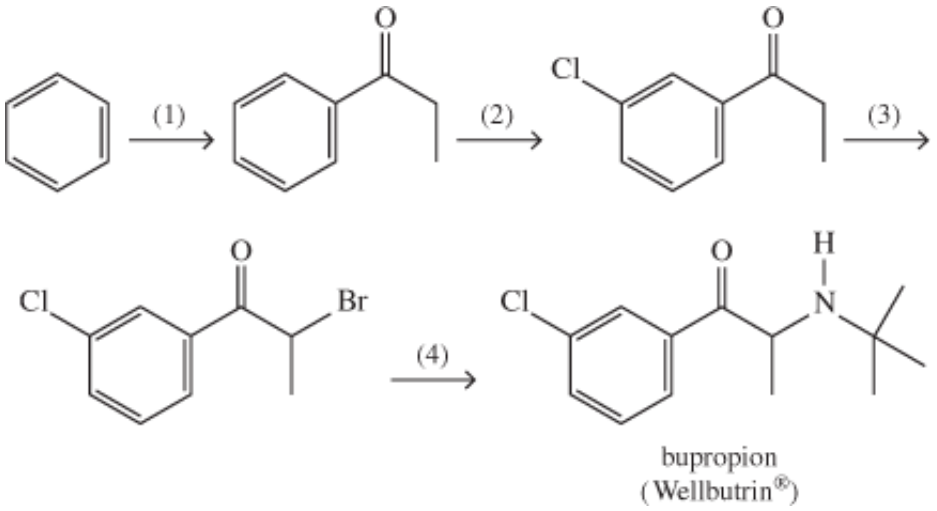
(a) How many stereoisomers are possible for tamoxifen?

(b) Specify the configuration of the stereoisomer shown here.

(c) Show how tamoxifen can be synthesised from the given ketone using a Grignard reaction,

followed by dehydration.

21.62 The following is a possible synthesis of the antidepressant bupropion (Wellbutrin®).



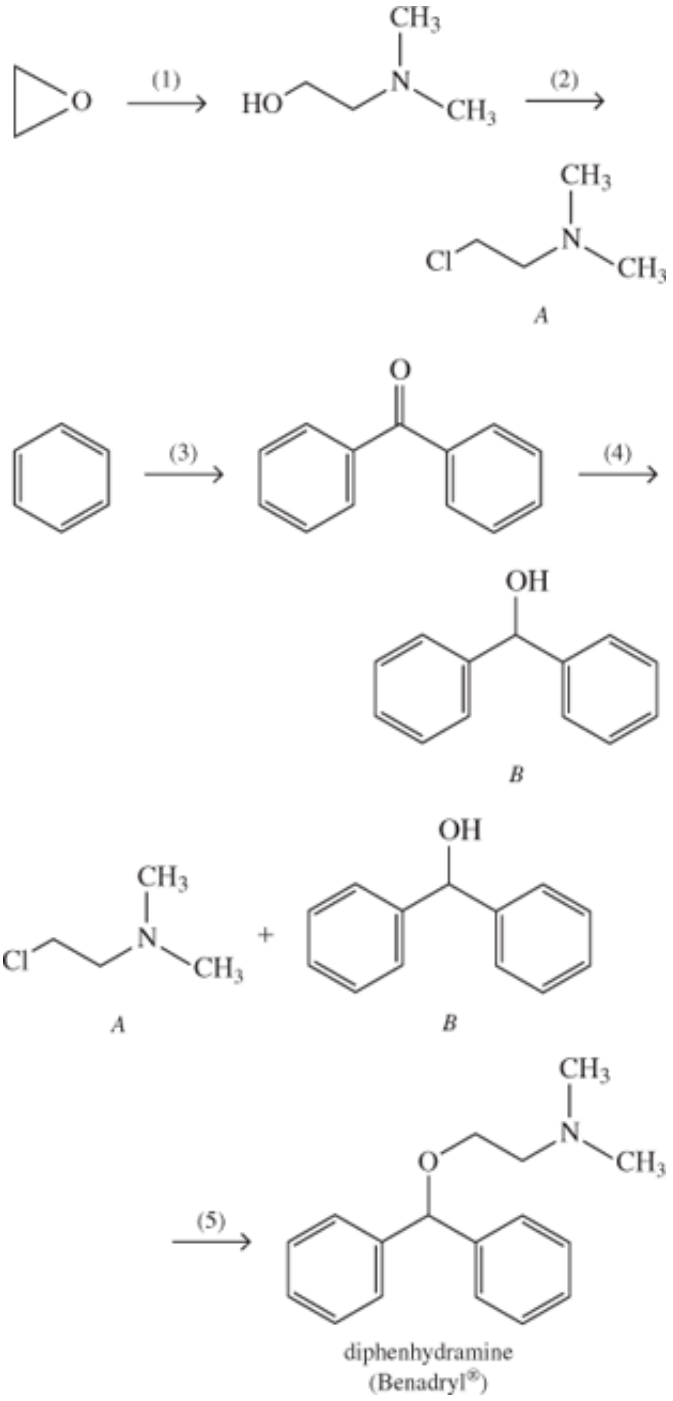
bupropion
(Wellbutrin®)

Show the reagents that will bring about each step in this synthesis.

21.63 An unknown compound *A* gave a positive silver-mirror test. Reaction of *A* with ethylmagnesium bromide followed by treatment with a dilute acid gave compound *B*, $C_6H_{14}O$. Compound *B*, upon treatment with concentrated sulfuric acid, gave compound *C*, C_6H_{12}. Reaction of *C* with ozone followed by zinc in water gave two products, propanal and acetone. Identify each of the compounds *A*, *B* and *C*, based on the chemical information given. Write an equation for each reaction described in the question.

21.64 Compound *A*, $C_5H_{10}O$, is used as a flavouring agent for many foods that possess a chocolate or peach flavour. Its common name is isovaleraldehyde and it gives ^{13}C-NMR peaks at δ 202.7, 52.7, 23.6 and 22.6. Provide a structural formula for isovaleraldehyde and give its IUPAC name.

21.65 The following is a synthesis for diphenhydramine.



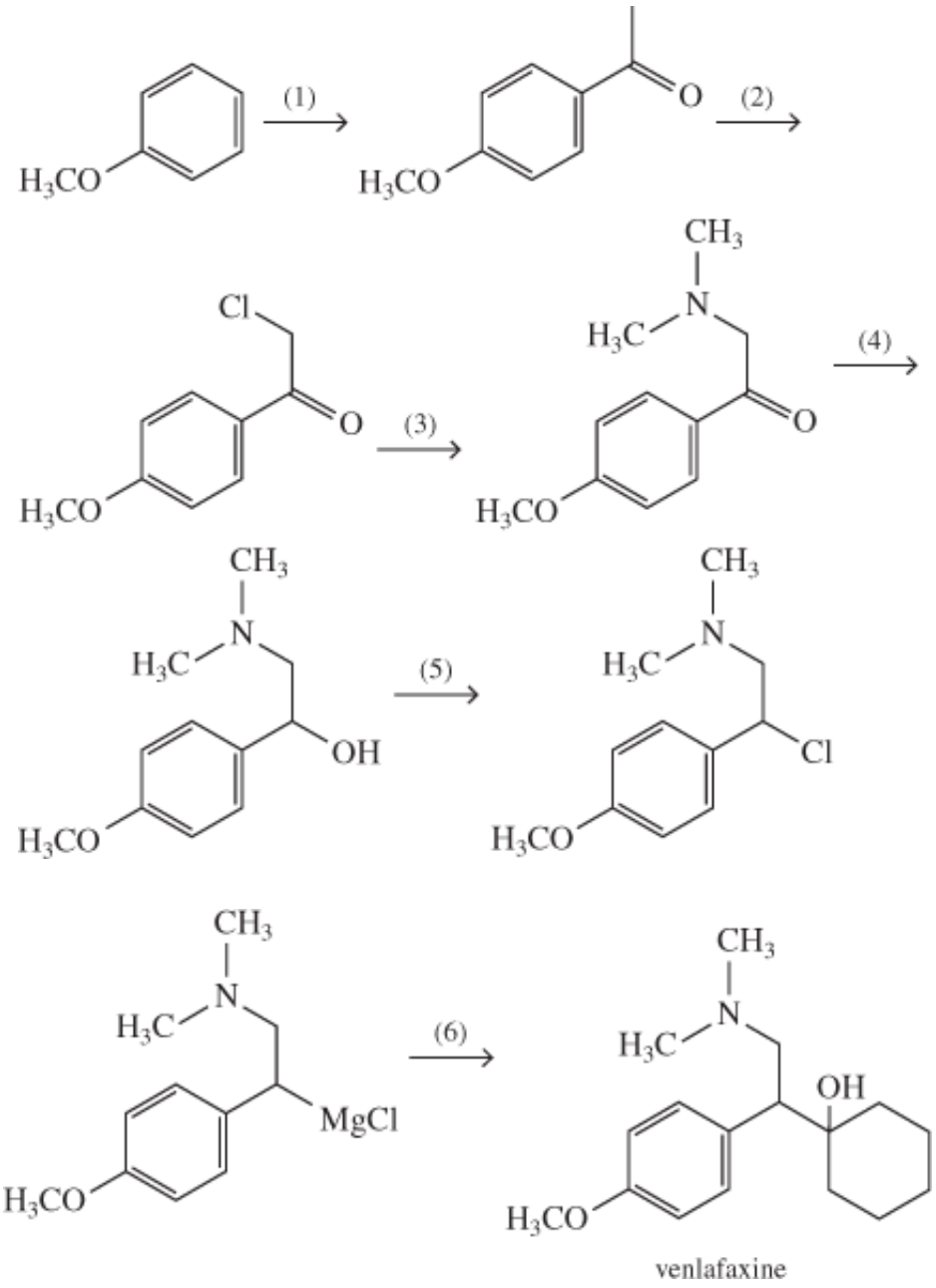
The hydrochloride salt of this compound, best known by its trade name, Benadryl®, is an antihistamine.

(a) Propose reagents for steps 1 and 2.

(b) Propose reagents for steps 3 and 4.

(c) Show that step 5 is an example of nucleophilic aliphatic substitution. What type of mechanism, S_N1 or S_N2, is more likely for this reaction? Explain.

21.66 The following is a synthesis for the antidepressant venlafaxine.



(a) Propose a reagent for step 1, and name the type of reaction that takes place.

(b) Propose reagents for steps 2 and 3.

(c) Propose reagents for steps 4 and 5.

(d) Propose a reagent for step 6, and name the type of reaction that takes place.

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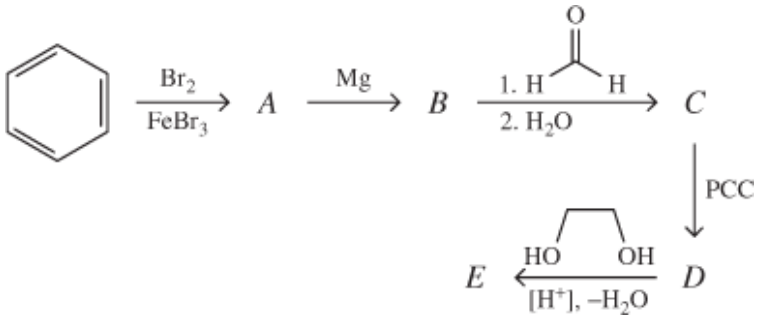
ADDITIONAL EXERCISES

21.67 Diethyl ether is prepared on an industrial scale by the acid catalysed dehydration of ethanol.

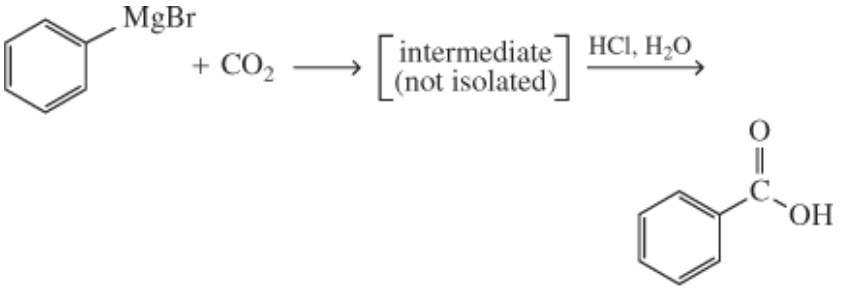
$$2CH_3CH_2OH \xrightarrow[180\,^{\circ}C]{H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

Explain why diethyl ether used in the preparation of Grignard reagents must be carefully purified to remove all traces of ethanol and water.

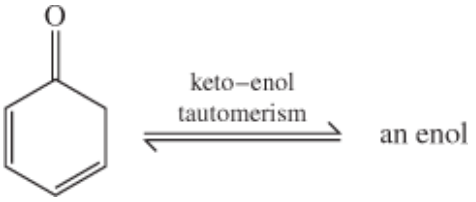
21.68 Identify the structures of compounds *A* to *E* below.



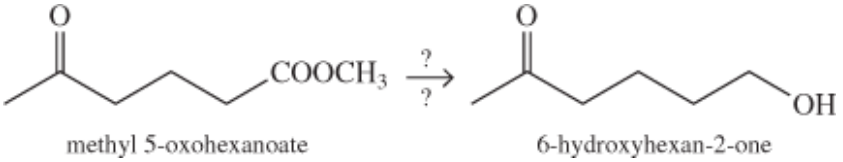
21.69 Reaction of a Grignard reagent with carbon dioxide, followed by treatment with aqueous HCl, gives a carboxylic acid. Propose a structural formula for the bracketed intermediate formed by the reaction of phenylmagnesium bromide with CO_2, and propose a mechanism for the formation of this intermediate.



21.70 Provide the enol form of the ketone below and predict the position of equilibrium.

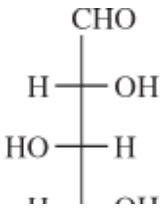


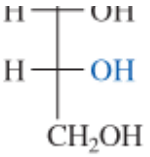
21.71 How would you prepare 6-hydroxyhexan-2-one from methyl 5-oxohexanoate? Esters are readily reduced to primary alcohols with lithium aluminium hydride. More than one step is required.



21.72 Draw the cyclic hemiacetal formed by reaction of the highlighted—OH group with the aldehyde group.

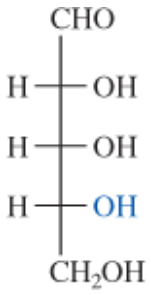
(a)





glucose

(b)



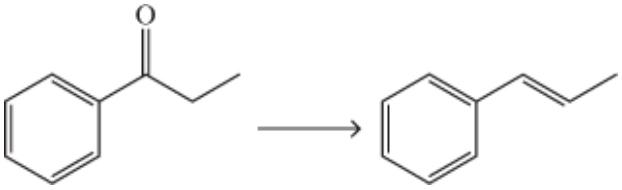
ribose

21.73 Show how the following transformations can be carried out. Give the reagents required and the structure of any intermediate compounds. More than one step is required in all cases and more than one method may be possible.

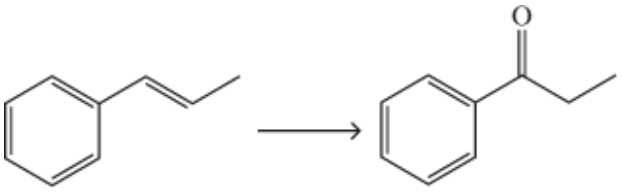
(a)



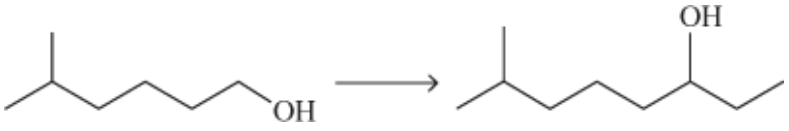
(b)



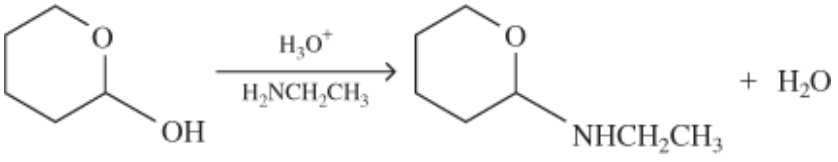
(c)



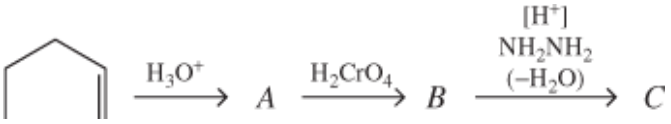
(d)



21.74 Propose a mechanism for the acid-catalysed reaction of the following hemiacetal, with an amine acting as a nucleophile.



21.75 Identify the structures of compounds *A* to *C* below, and then identify the reagents that can be used to convert cyclohexene into compound *C* in just one step.

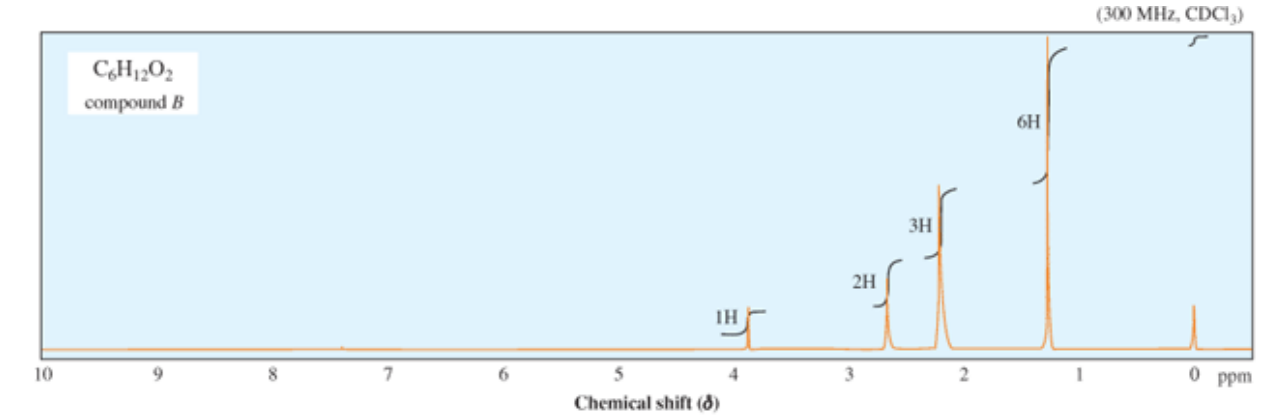


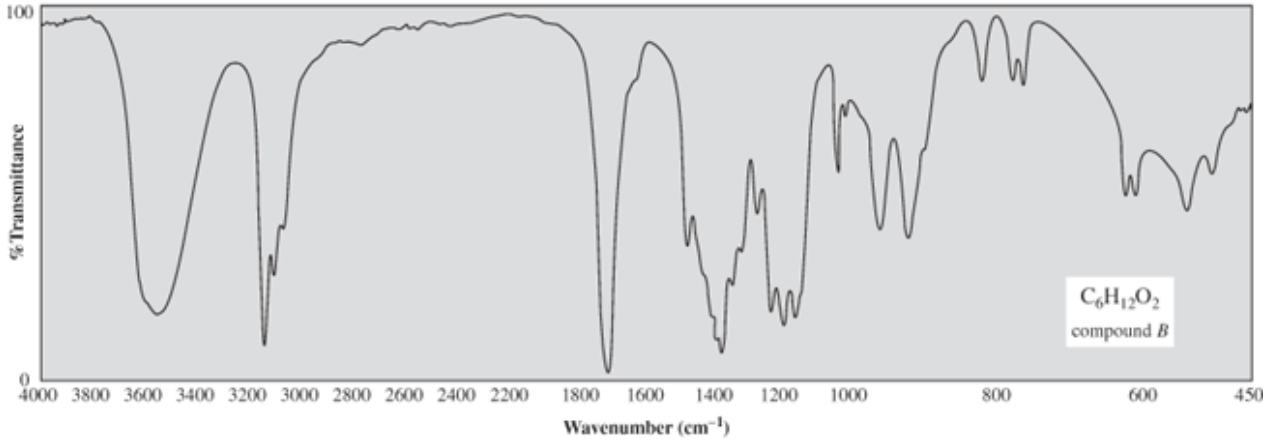
21.76 An aldehyde with the molecular formula C_4H_6O exhibits an IR signal at 1715 cm^{-1}.

(a) Propose two possible structures that are consistent with this information.

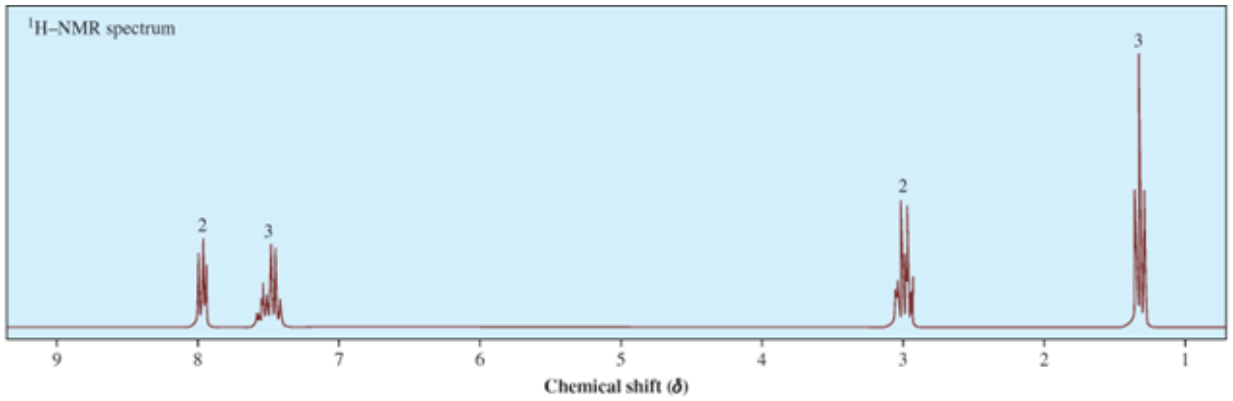
(b) Describe how you could use ^{13}C-NMR spectroscopy to determine which of the two possible structures is correct.

21.77 The following are ^{1}H-NMR and IR spectra (see chapter 20) of compound *B*, $C_6H_{12}O_2$. Propose a structural formula for compound *B*.

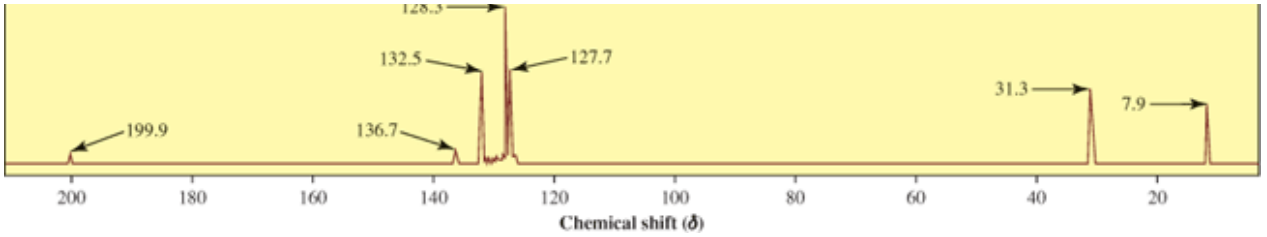




21.78 A compound with the molecular formula $C_9H_{10}O$ exhibits a strong signal at 1687 cm^{-1} in its IR spectrum. The ^{1}H- and ^{13}C-NMR spectra of the compound are shown below. Identify the structure of this compound.







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KEY TERMS

α-carbon
α-hydrogens
acetal
aldehyde
carbanion
cyanohydrins
enol
Grignard reagent
hemiacetal
hydride ion
ketal
ketone
order of precedence of functional groups
organometallic compounds
oximes
reductive amination
silver-mirror test
tautomerism
tautomers
tetrahedral carbonyl addition intermediate
Tollens' reagent

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CHAPTER

22 Carbohydrates

Carbohydrates is a chemical term that almost everybody knows and uses, perhaps without a full understanding of its meaning. Carbohydrates represent a major class of organic molecules that are important in areas ranging from food to materials and medications. They are some of the most abundant and important compounds in the plant and animal world. Carbohydrates give plant cell walls the strength and rigidity they need, and they account for approximately three-quarters of the dry weight of the plant. Animal cells are covered in a dense array of carbohydrate chains that are critical for a cell's survival and healthy function. Carbohydrates act as storehouses of chemical energy (glucose, starch, glycogen) and are components of supportive structures in plants (cellulose), crustacean shells (chitin) and connective tissues in animals (polysaccharides). Animals (including humans) get their carbohydrates from eating plants, but they do not store much of what they consume, with less than one per cent of the body weight of an animal being made of carbohydrates. However, their crucial role in biological chemistry is far greater than this implies. They are essential components in the nucleic acids RNA (D-ribose) and DNA (2-deoxy-D-ribose), and they play crucial roles in cell surface and membrane recognition necessary for cell function. Small carbohydrate molecules, such as glucose, are readily soluble in water and so can be transported through the vascular system to meet a plant's or animal's energy needs.



Our society is also integrally linked to carbohydrates, not only for food but also as key drivers in our economy. For example Australia's wheat (starch) and sugar cane (sucrose) industries alone are worth more than $7.5 billion per year. Equally important in New Zealand, agriculture represents three-quarters of the economy, with New Zealand exporting more than $1 billion of fruit each year, including supplying one-quarter of the world's kiwifruit.





KEY TOPICS

22.1 Introduction to carbohydrates
22.2 Monosaccharides
22.3 The cyclic structure of monosaccharides
22.4 Reactions of monosaccharides
22.5 Disaccharides and oligosaccharides
22.6 Polysaccharides

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22.1 Introduction to Carbohydrates

Carbohydrates possess many functional groups, which leads to some interesting properties. They are also of fundamental importance as biochemicals. In chapters 19 and 21 we dealt with the individual functional groups found in carbohydrates (alcohols, aldehydes and ketones), so many of the properties, reactivities and concepts will be familiar. The range and variety of carbo hydrate chemistry are immense and we will cover only the simplest forms. However, it is crucial to remember that all carbohydrates, no matter how complex, are governed by the properties of the individual chemical groups from which they are constructed.

The word ‘carbohydrate’ means ‘hydrate of carbon’ and derives from the formula $C_n(H_2O)_m$. Two examples of carbohydrates with molecular formulae that can be written as hydrates of carbon are:

- glucose (blood sugar), $C_6H_{12}O_6$, which can be written as $C_6(H_2O)_6$
- sucrose (table sugar), $C_{12}H_{22}O_{11}$, which can be written as $C_{12}(H_2O)_{11}$.

However, not all carbohydrates have this general formula. Some contain too few oxygen atoms, and some contain too many. Some also contain nitrogen. But the term ‘carbohydrate’ has become firmly rooted in chemical nomenclature and, although not completely accurate, it persists as the name for this class of compounds.

At the molecular level, most **carbohydrates** are polyhydroxyaldehydes, polyhydroxyketones or compounds that yield them after hydrolysis. Therefore, the chemistry of carbohydrates is essentially the chemistry of hydroxyl and carbonyl groups, and of the acetal bonds (section 21.5) formed between these two functional groups.

Almost all carbohydrates are chiral. This means that they interact with plane-polarised light (see chapter 17). Chirality is significant for their biological activity as many cellular interactions are controlled by specific carbohydrate stereoisomers. This is also why blood transfusions require specific matching blood types, the different blood types arise from different carbohydrates present on the surface of cells. Another important factor governed by the different structures of carbohydrates is their perceived sweetness. One carbohydrate may be very sweet while another with only a minor structural difference may have little apparent sweetness. Notably, all of the various carbohydrates — from the simplest through to the most complex stereoisomers important in biological activity — have ultimately arisen from the simple nonchiral CO_2 molecule via plant photosynthesis.

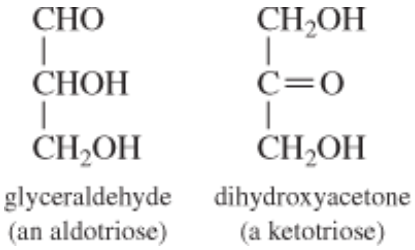
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22.2 Monosaccharides

The word ‘saccharide’ comes from the ancient Latin word for ‘sweet’ and monosaccharides are the simplest forms of carbohydrate, unable to be hydrolysed to anything smaller.

Monosaccharides have the general formula $C_nH_{2n}O_n$, with one of the carbon atoms being part of a carbonyl group of either an aldehyde or a ketone. The most common monosaccharides contain from three to nine carbon atoms. There is a common naming system where the suffix *-ose* indicates that a molecule is a carbohydrate, and the prefixes *tri-*, *tetr-*, *pent-*, and so on, indicate the number of carbon atoms in the chain. Monosaccharides containing an aldehyde group are classified as **aldoses**; those containing a ketone group are classified as **ketoses**.

There are only two trioses — glyceraldehyde, which is an aldotriose, and dihydroxyacetone, which is a ketotriose.



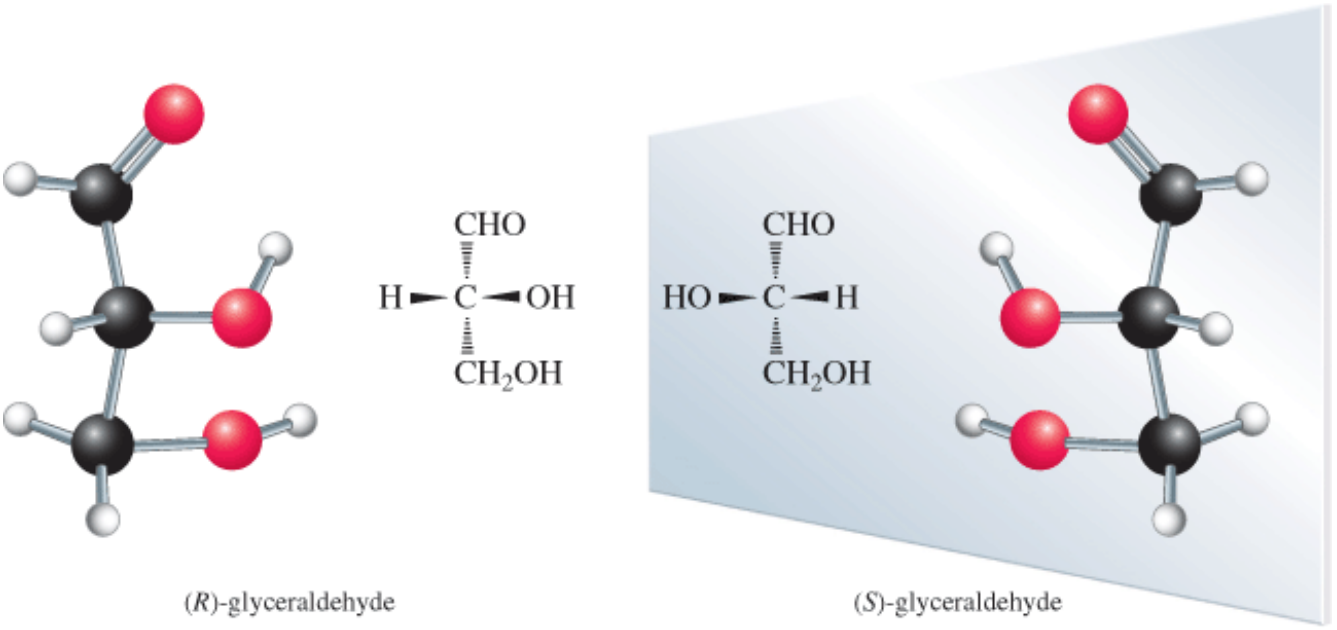
glyceraldehyde (an aldotriose) dihydroxyacetone (a ketotriose)

Often the designations *aldo-* and *keto-* are omitted, and these molecules are referred to simply as trioses, tetroses etc. Although these names do not describe the nature of the carbonyl group, they do indicate that the monosaccharide contains three and four carbon atoms, respectively.

Remember that these molecules can also be named using the IUPAC nomenclature system (see chapter 2). For example, the correct IUPAC name for glyceraldehyde is 2,3-dihydroxypropanal, and dihydroxyacetone is more correctly called 1,3-dihydroxypropanone.

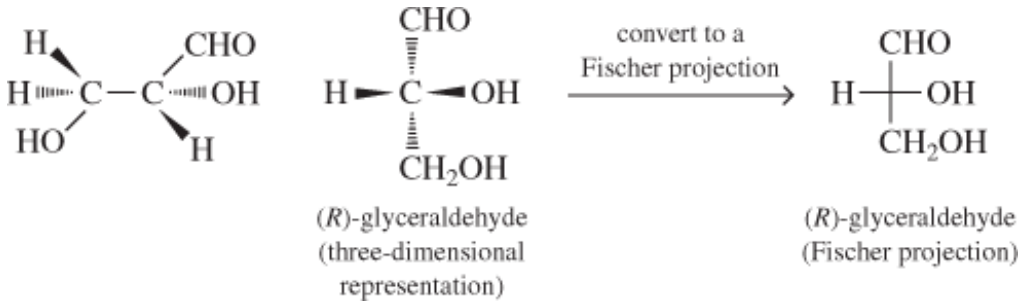
Stereoisomerism

Glyceraldehyde contains one stereocentre and exists as a pair of enantiomers (see chapter 17). The stereoisomer shown at the top left on the next page has the *R* configuration and is named (*R*)-glyceraldehyde, while its enantiomer, shown at the top right on the next page, is named (*S*)-glyceraldehyde.



Fischer Projections

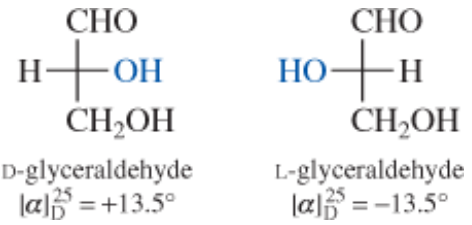
Chemists commonly use two-dimensional representations called **Fischer projections** to show the three-dimensional configuration of carbohydrates. To draw a Fischer projection, draw a three-dimensional representation with the most oxidised carbon atom towards the top and the molecule oriented so that the vertical bonds from each stereocentre are directed away from you and the horizontal bonds are directed towards you. Then write the molecule as a two-dimensional figure with each stereocentre indicated by the point at which the bonds cross. You now have a Fischer projection.



The two horizontal segments of this Fischer projection represent bonds directed towards you, and the two vertical segments represent bonds directed away from you. The only atom in the plane of the paper is the stereocentre. Note that you cannot treat a Fischer projection as a 3-D object as you can with the structure on the left. The horizontal and vertical lines in a Fischer projection have structural implications. If you rotate a Fischer projection by 90° then you create a new 3-D structure.

D- and L-monosaccharides

Even though the *R*, *S* system is widely accepted as a standard for designating the configuration of stereocentres, we still commonly indicate the configuration of carbohydrates using the D, L system proposed by Emil Fischer in 1891. He assigned the dextrorotatory and levorotary enantiomers of glyceraldehyde the following configurations and named them D-glyceraldehyde and L-glyceraldehyde, respectively.



The monosaccharides D-glyceraldehyde and L-glyceraldehyde serve as reference points for the assignment of relative configurations for all other aldoses and ketoses. The reference point is the stereocentre furthest from the carbonyl group. Because this stereocentre is the next-to-the-last carbon atom on the chain, it is called the **penultimate carbon**. A **D-monosaccharide** is a monosaccharide that has the same configuration at its penultimate carbon atom as D-glyceraldehyde (its —OH is on the right in a Fischer projection). (Note that the D used in $[\alpha]_D^{25}$ refers to the sodium D line (see chapter 17) and is unrelated to the D in D-glyceraldehyde.) An **L-monosaccharide** has the same configuration at its penultimate carbon atom as L-glyceraldehyde (its —OH is on the left in a Fischer projection). Almost all monosaccharides in the biological world belong to the D series, and the majority of them are either hexoses or pentoses.

Figure 22.1 shows the names and Fischer projections for all D-aldotrioses, tetroses, pentoses and hexoses. Each name consists of three parts. The letter d specifies the configuration at the stereocentre furthest from the carbonyl group. Prefixes, such as *rib-*, *arabin-* and *gluc-*, specify the configurations of all other stereocentres relative to one another. The suffix *-ose* shows that the compound is a carbohydrate.

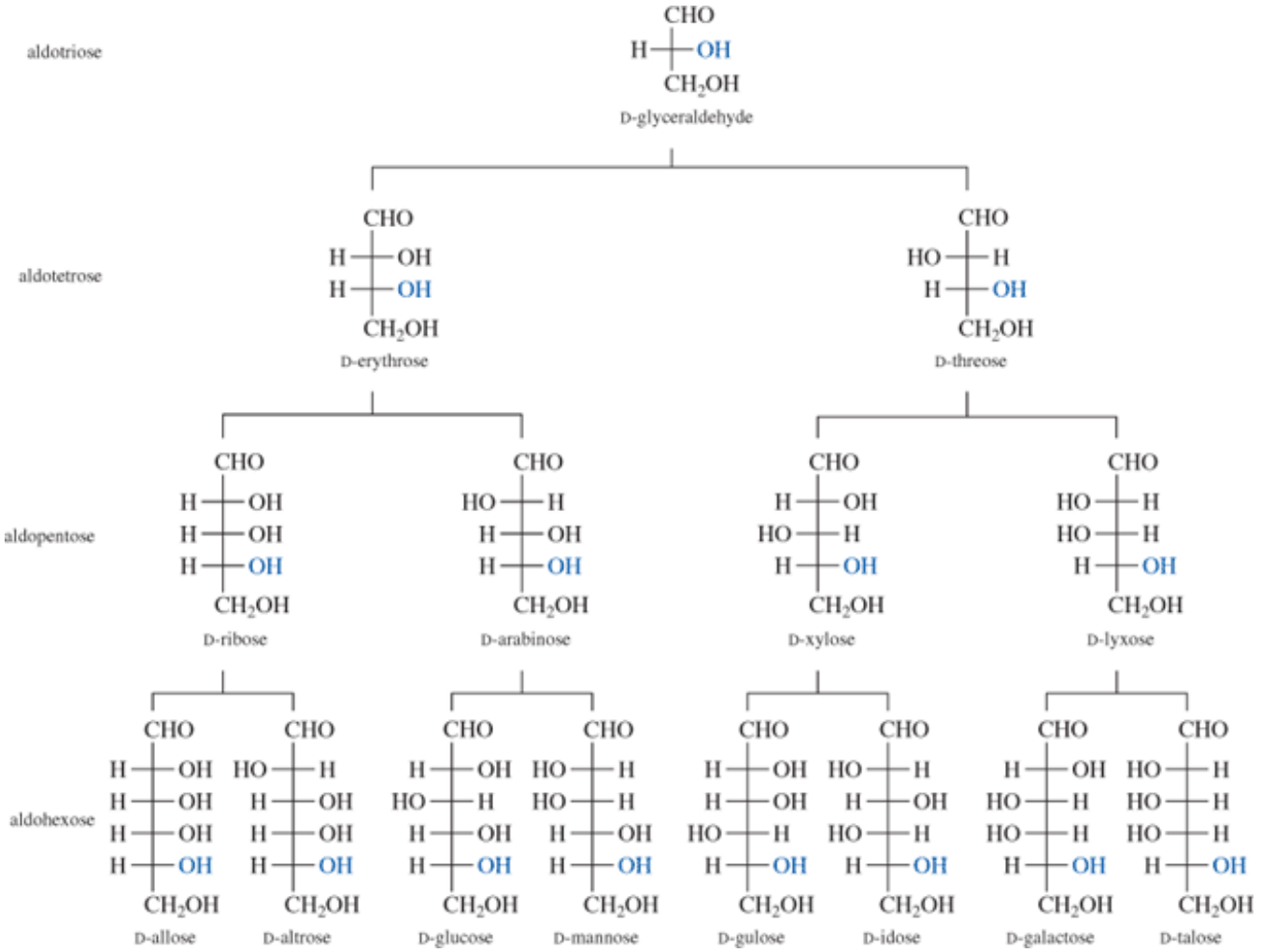
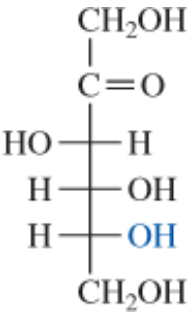


FIGURE 22.1 Configurational relationships among the isomeric D-aldotetroses, D-aldopentoses and D-aldohexoses. The configuration of the reference —OH on the penultimate carbon atom is shown in blue.

The three most abundant hexoses in the biological world are D-glucose, D-galactose and D-fructose. The first

two are D-aldohexoses while the third, fructose, is a D-2-ketohexose. Glucose, by far the most abundant of the three, is also known as dextrose because it is dextrorotatory. Other names for this monosaccharide include *grape sugar* and *blood sugar*. Human blood normally contains 65–110 mg of glucose/100 mL of blood. D-fructose is one of the two monosaccharide building blocks of sucrose (table sugar, section 22.5).



WORKED EXAMPLE 22.1

Naming and Drawing Simple Carbohydrates

(a) Draw Fischer projections for the four aldotetroses.

(b) Which of the four aldotetroses are D-monosaccharides, which are L-monosaccharides and which are enantiomers?

(c) Refer to Figure 22.1, and name each aldotetrose you have drawn.

Analysis

One way of approaching this question is to build chemical models of the aldotetroses and compare the relationships of the atoms and bonds in three-dimensional space. However, if you do not have a chemical model kit, you can draw and name the structures in order to properly visualise the relationships between the atoms and bonds involved in these molecules.

Solution

The Fischer projections for the four aldotetroses are:



Note that in the Fischer projection of a D-aldotetrose the —OH on C(3) is on the right and in an L-aldotetrose it is on the left.

Is our answer reasonable?

The most common mistake with Fischer projections is incorrectly counting the number of carbon atoms in the chain. Remember to put the most oxidised carbon atom at the top of the chain and put the (nonchiral) terminal CH_2OH at the bottom. Every intersection of vertical and horizontal

lines represents a carbon atom.

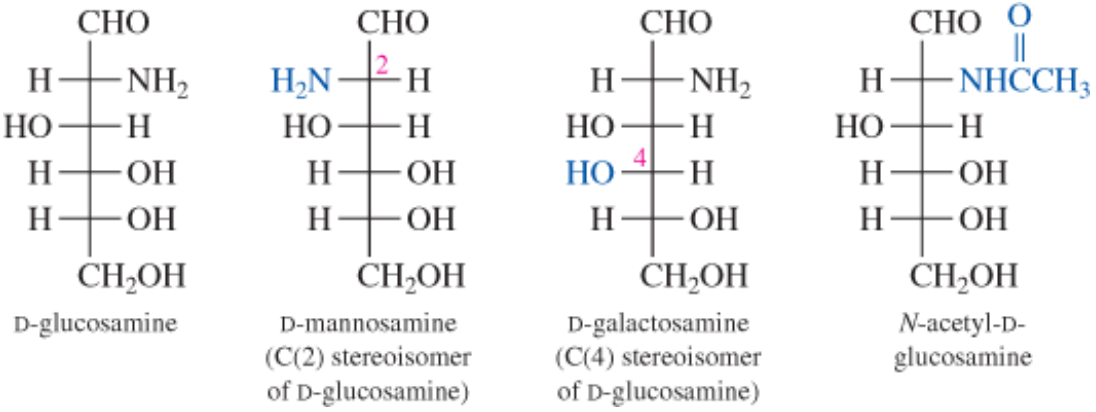
PRACTICE EXERCISE 22.1

(a) Draw Fischer projections for all 2-ketopentoses.

(b) Which of the 2-ketopentoses are D-ketopentoses, which are L-ketopentoses, and which are enantiomers?

Amino Sugars

Amino sugars contain an —NH_2 group in place of an —OH group. Only three amino sugars are common in nature: D-glucosamine, D-mannosamine and D-galactosamine. *N*-acetyl-D-glucosamine, a derivative of D-glucosamine, is a component of many polysaccharides, including connective tissue such as cartilage. It is also a component of chitin, the hard shell-like exoskeleton of lobsters, crabs, prawns and other shellfish. Several other amino sugars are components of naturally occurring antibiotics.



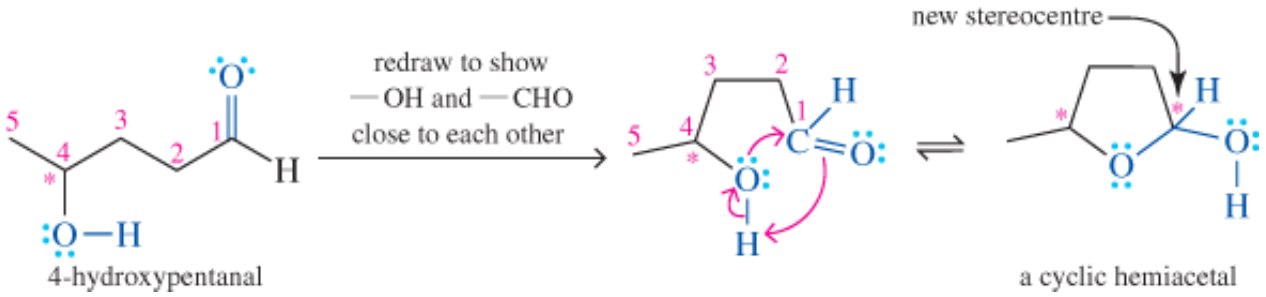
Physical Properties

Monosaccharides are colourless, crystalline solids. Because hydrogen bonding is possible between their polar —OH groups and water, all monosaccharides are very soluble in water. They are only slightly soluble in ethanol and are insoluble in nonpolar solvents such as diethyl ether, dichloromethane and benzene.

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22.3 The Cyclic Structure of Monosaccharides

In section 21.5, we saw that aldehydes and ketones react with alcohols to form **hemiacetals**, sometimes referred to as hemiketals when derived from a ketone. We also saw that cyclic hemi acetals form readily when hydroxyl and carbonyl groups are parts of the same molecule and their interaction can form a five- or six-membered ring. For example, 4-hydroxypentanal forms a five-membered cyclic hemiacetal as shown on the next page. Note that 4-hydroxypentanal contains one stereocentre and that a second stereocentre is generated at C(1) by hemiacetal formation.



Monosaccharides contain hydroxyl and carbonyl groups in the same molecule, and they exist almost exclusively as five- and six-membered cyclic hemiacetals.

Haworth Projections

A common way of representing the cyclic structure of monosaccharides is the **Haworth projection**, which is named after the English chemist Sir Walter Norman Haworth (Nobel Prize in chemistry, 1937). In a Haworth projection, a five- or six-membered cyclic hemiacetal is represented as a planar pentagon or hexagon lying roughly perpendicular to the plane of the paper. Groups bonded to the carbon atoms of the ring then lie either above or below the plane of the ring. The new stereocentre created in forming the cyclic structure is called the **anomeric carbon**. Stereoisomers that differ in configuration only at the anomeric carbon atom are called **anomers**. The anomeric carbon atom of an aldose is C(1); in D-fructose, the most common ketose, it is C(2).

Typically, Haworth projections are written with the anomeric carbon atom at the right and the hemiacetal oxygen atom at the back right (figure 22.2).

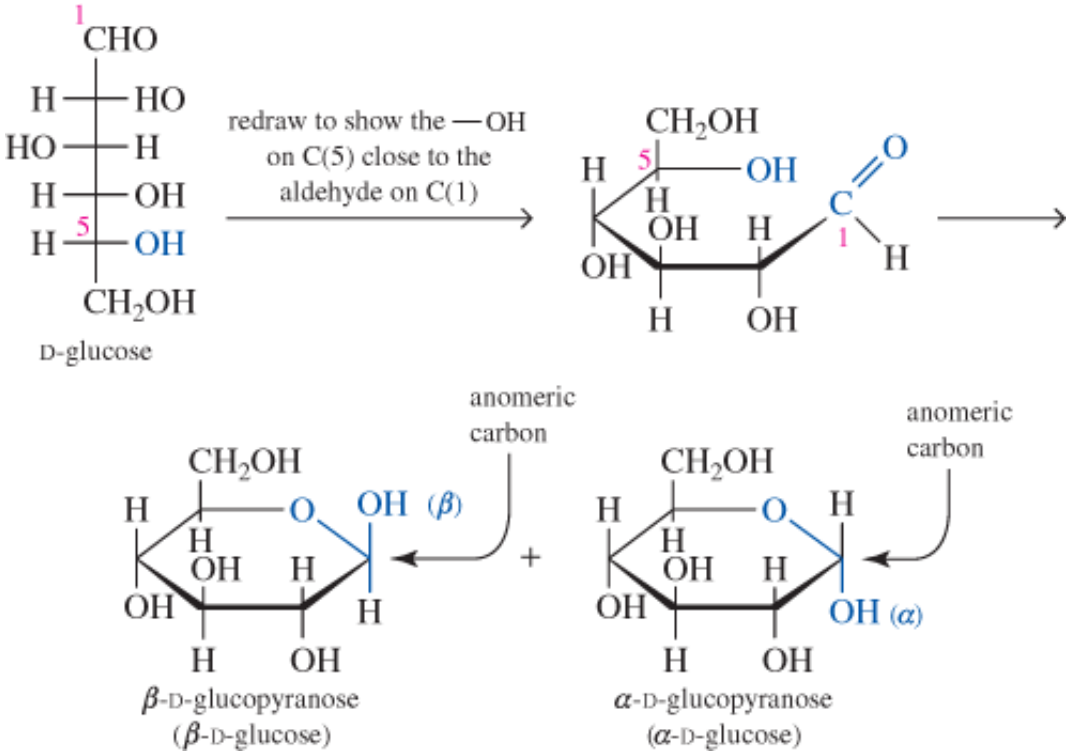
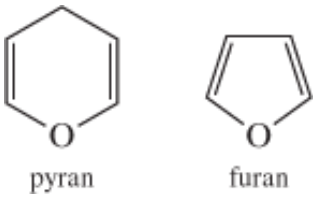


FIGURE 22.2 Haworth projections for β-D-glucopyranose and α-D-glucopyranose.

As you study the open-chain and cyclic hemiacetal forms of D-glucose, note that in converting from a Fischer projection to a Haworth structure:

- groups on the right in the Fischer projection point down in the Haworth projection
- groups on the left in the Fischer projection point up in the Haworth projection
- for a D-monosaccharide, the terminal —CH_2OH points up in the Haworth projection
- the configuration of the anomeric —OH group is relative to the terminal —CH_2OH group: if the anomeric —OH group is on the same side as the terminal —CH_2OH, its configuration is β; if the anomeric —OH group is on the opposite side, it is α.



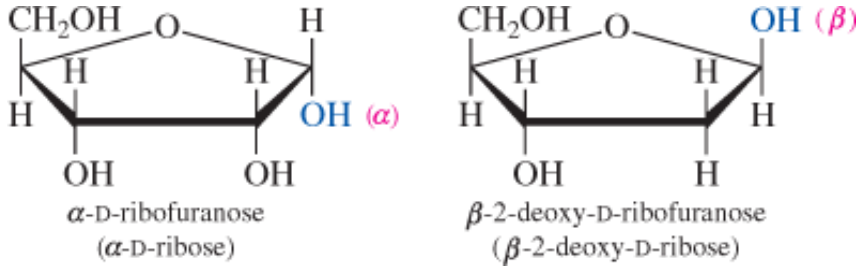
A six-membered hemiacetal ring is named with the component *-pyran-*, and a five-membered hemiacetal ring is named with the component *-furan-*. The terms **furanose** and **pyranose** are used because monosaccharide five- and six-membered rings correspond to the heterocyclic compounds pyran and furan.

A furanose is a five-membered cyclic hemiacetal form of a monosaccharide. A pyranose is a six-membered cyclic hemiacetal form of a monosaccharide.

Because the α and β forms of glucose are six-membered cyclic hemiacetals, they are named α-D-glucopyranose and β-D-glucopyranose, respectively. However, the designations *-furan-* and *-pyran-* are not always used in the names of monosaccharides. Thus, the glucopyranoses are often named simply α-D-glucose and β-D-glucose.

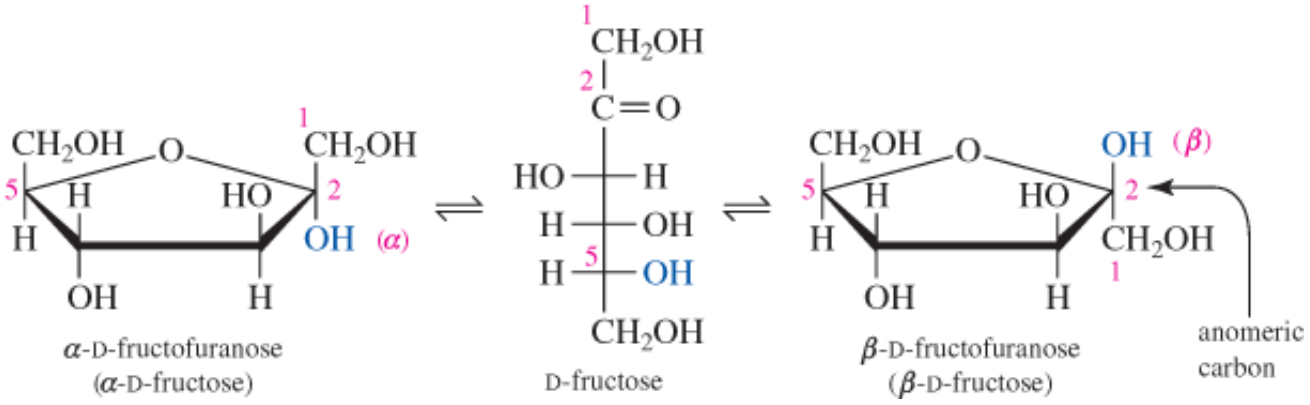
Aldopentoses also form cyclic hemiacetals. The most prevalent forms of D-ribose and other pentoses in

the biological world are furanoses. Haworth projections for α-D-ribofuranose (α-D-ribose) and β-2-deoxy-D-ribofuranose (β-2-deoxy-D-ribose) are shown on the next page.



The prefix '2-deoxy' indicates the absence of oxygen at C(2). Units of D-ribose and 2-deoxy-D-ribose in nucleic acids and most other biological molecules are found almost exclusively in the β-configuration.

Fructose also forms five-membered cyclic hemiacetals. β-D-fructofuranose, for example, is found in the carbohydrate sucrose (section 22.5).



Conformation Representations

A five-membered ring is so close to being planar that Haworth projections are adequate to represent furanoses. For pyranoses, however, the six-membered ring is more accurately represented by what is known as a **chair conformation**, so-called because the molecule looks like a chair. The chair conformation allows all of the carbon atoms to have bond angles that are very close to the optimal tetrahedral bond angle and the strain in the molecule is therefore minimal. Figure 22.3 shows structural formulae for α-D-glucopyranose and β-D-glucopyranose, both drawn as chair conformations. The figure also shows the open-chain, or free, aldehyde form with which the cyclic hemiacetal forms are in equilibrium in aqueous solution. Notice that each group, including the anomeric —OH, in the chair conformation of β-D-glucopyranose is equatorial. Notice also that the —OH group on the anomeric carbon atom in α-D-glucopyranose is axial. Because of the equatorial orientation of the —OH on its anomeric carbon atom, β-D-glucopyranose is more stable and predominates in aqueous solution.

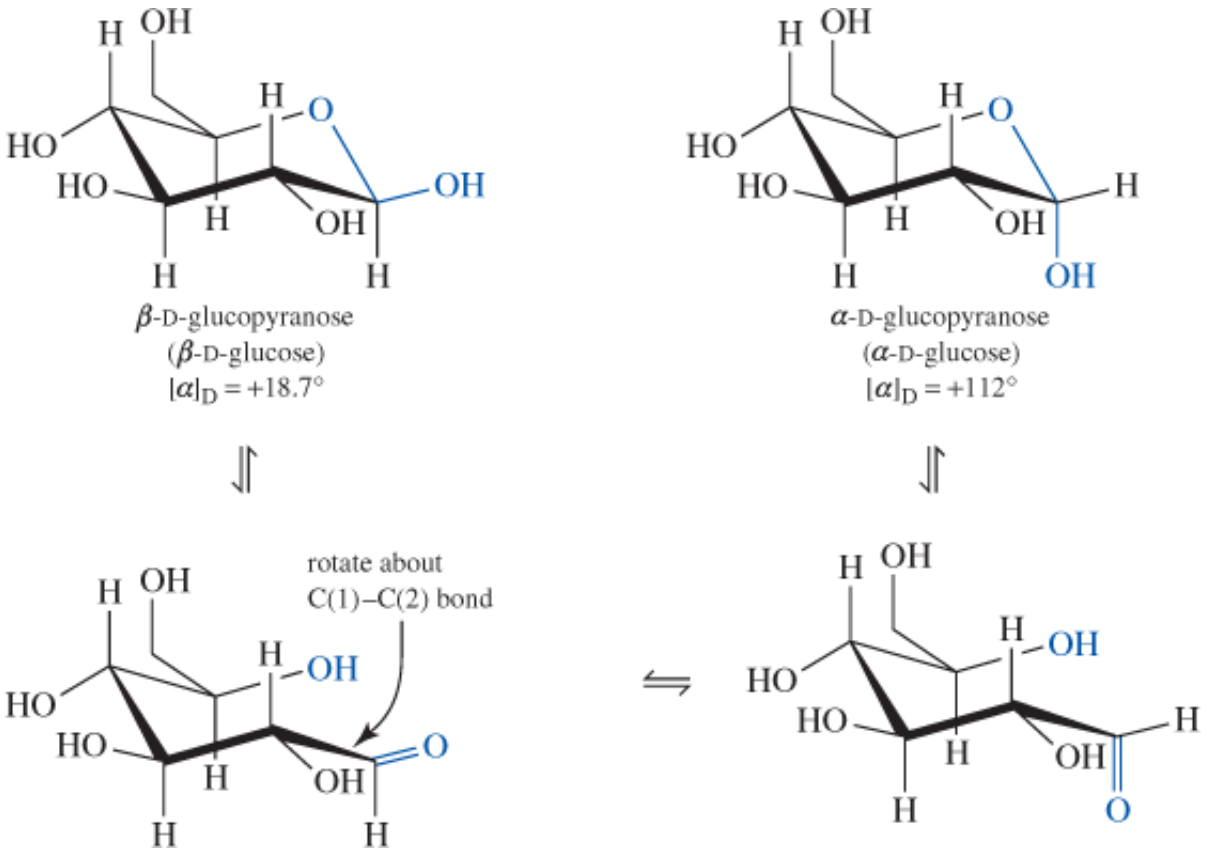
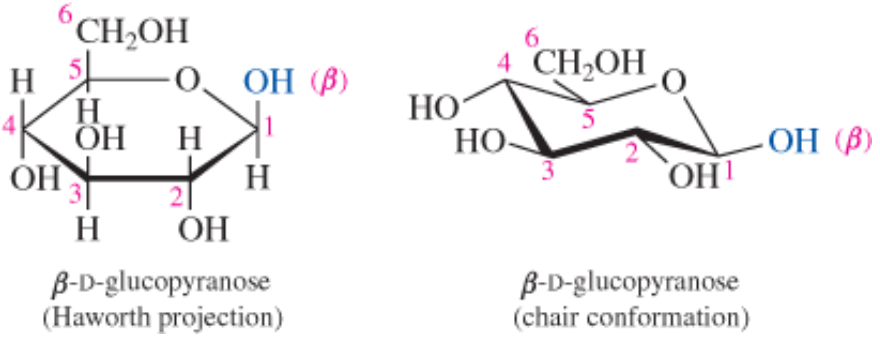


FIGURE 22.3 Chair conformations of α-D-glucopyranose and β-D-glucopyranose. Because α-D-glucose and β-D-glucose are different compounds (they are anomers), they have different specific rotations.

At this point, you should compare the relative orientations of groups on the D-glucopyranose ring in the Haworth projection and chair conformation.



Notice that the orientations of the groups on C(1) to C(5) in the Haworth projection of β-D-glucopyranose are up, down, up, down and up, respectively. The same is the case in the chair conformation, which has been drawn without showing the hydrogen atoms, for clarity.

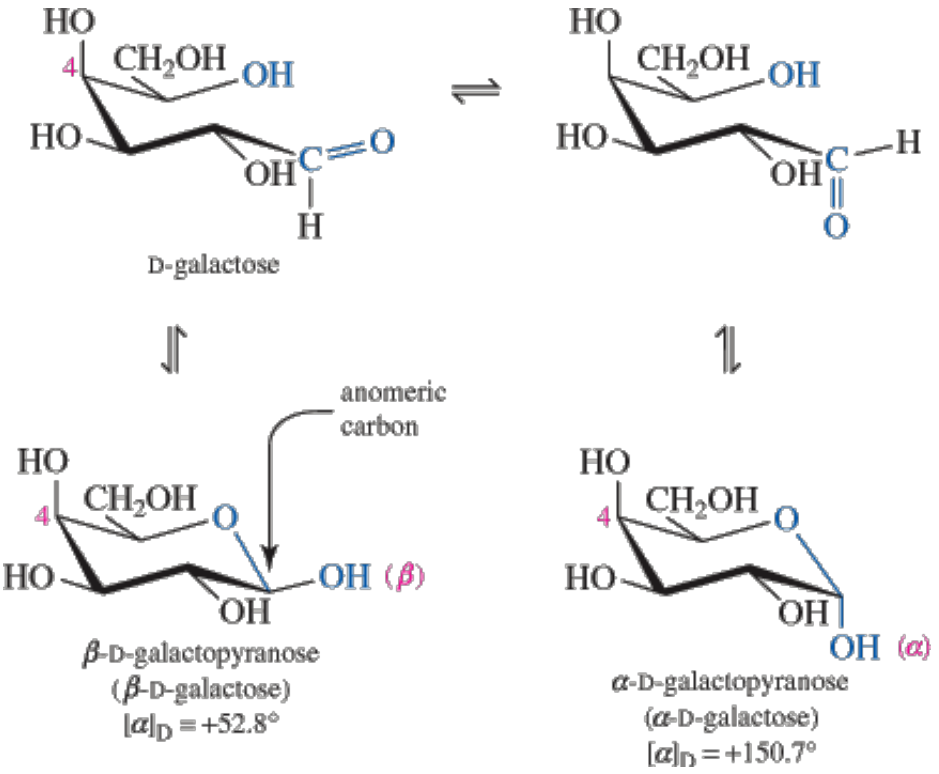
WORKED EXAMPLE 22.2

Representing Carbohydrates in the Chair Conformation

Draw chair conformations for α-D-galactopyranose and β-D-galactopyranose. Label the anomeric carbon atom in each cyclic hemiacetal.

Analysis and solution

D-galactose differs in configuration from D-glucose only at C(4). Therefore, to represent D-galactose, simply draw the α and β forms of D-glucopyranose and then interchange the positions of the —OH and —H groups on C(4). The specific rotations of each anomer are shown and you will note the impact on the optical rotation of the inversion of one stereocentre.



Is our answer reasonable?

Remember that the α and β anomers differ only in the orientation of the groups on the carbon atom of the hemiacetal group. Therefore, the structures of the α and β forms of the molecule should be the same in all aspects except for the stereochemistry of this carbon atom.

PRACTICE EXERCISE 22.2

Draw chair conformations for α-D-mannopyranose and β-D-mannopyranose. Label the anomeric carbon atom in each.

Mutarotation

Mutarotation is the change in specific rotation that accompanies the interconversion of α and β anomers in aqueous solution. As an example, a solution prepared by dissolving crystalline α-D-glucopyranose in water shows an initial rotation of +112° (figure 22.3), which gradually decreases to an equilibrium value of +52.7° as α-D-glucopyranose reaches an equilibrium with β-D-glucopyranose. A solution of β-D-glucopyranose also undergoes mutarotation, during which the specific rotation changes from an initial value of +18.7° to the same equilibrium value of +52.7°. The equilibrium mixture

consists of 64% β-D-glucopyranose and 36% α-D-glucopyranose and only traces (0.003%) of the open-chain form. Mutarotation occurs in all carbohydrates that exist in hemiacetal forms.

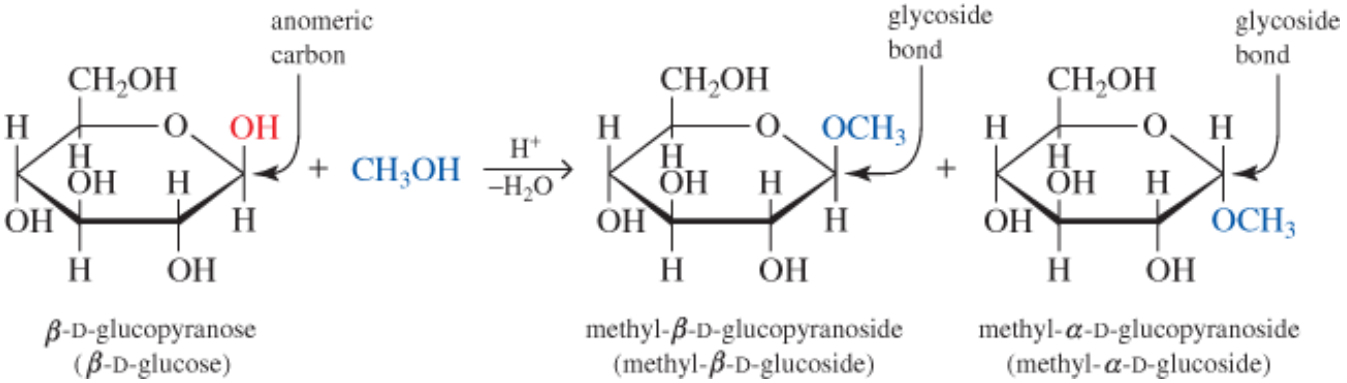
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22.4 Reactions of Monosaccharides

In this section, we discuss the reactions of monosaccharides with alcohols, reducing agents and oxidising agents. We also examine how these reactions are useful in our everyday lives.

Formation of Glycosides (Acetals)

As we saw in section 21.5, treating an aldehyde or ketone with one molecule of an alcohol yields a hemiacetal, and treating the hemiacetal with a molecule of an alcohol yields an acetal. Treating a monosaccharide, all of which exist as cyclic hemiacetals, with an alcohol gives an acetal, as illustrated by the reaction of methanol with β-D-glucopyranose (β-D-glucose) drawn in the Haworth projection to emphasise the differences in the structures of the two products.



A cyclic acetal derived from a monosaccharide is called a **glycoside**, and the bond from the anomeric carbon to the —OR group is called a **glycosidic bond**. Unlike a hemiacetal, an acetal is no longer in equilibrium with the open-chain carbonyl-containing compound in neutral or alkaline solutions. Like other acetals (section 21.5), glycosides are stable in water and aqueous base, but undergo hydrolysis in aqueous acid to form an alcohol and a monosaccharide.

We name glycosides by listing the alkyl or aryl group bonded to oxygen, followed by the name of the carbohydrate with the ending *-e* replaced with *-ide*. For example, glycosides derived from β-D-glucopyranose are named β-D-glucopyranosides; those derived from β-D-ribofuranose are named β-D-ribofuranosides.

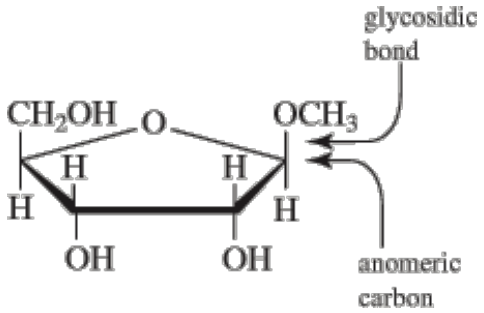
WORKED EXAMPLE 22.3

Understanding the Structures of Glycosides

Draw a structural formula for methyl-β-D-ribofuranoside (methyl-β-D-riboside). Label the anomeric carbon atom and the glycosidic bond.

Analysis By drawing a precise representation of the structure of a glycoside from its name you will gain an appreciation of how the atoms are arranged to give rise to this functional group.

Solution



Is our answer reasonable?

Glycosides are acetals, so, unlike hemiacetals, they are always locked into a cyclic form. Consequently, you cannot use a Fischer projection — only a Haworth projection or perhaps a full structural representation. For simple glycosides, a Haworth projection clearly shows the relative arrangement of the —OH groups, which is crucial for determining which of the many mono saccharides is involved (figure 22.1).

PRACTICE EXERCISE 22.3

Draw a structural formula for the chair conformation of methyl-α-D-mannopyranoside (methyl-α-D-mannoside). Label the anomeric carbon atom and the glycosidic bond.

Just as the anomeric carbon atom of a cyclic hemiacetal reacts with the —OH group of an alcohol to form a glycoside, it can also react with the —NH group of an amine to form an *N*-glycoside. Especially important in the biological world are the *N*-glycosides formed between D-ribose and 2-deoxy-D-ribose (each as a furanose), and the heterocyclic aromatic amines uracil, cytosine, thymine, adenine and guanine (figure 22.4). *N*-glycosides of these compounds are the structural units of nucleic acids (chapter 25).

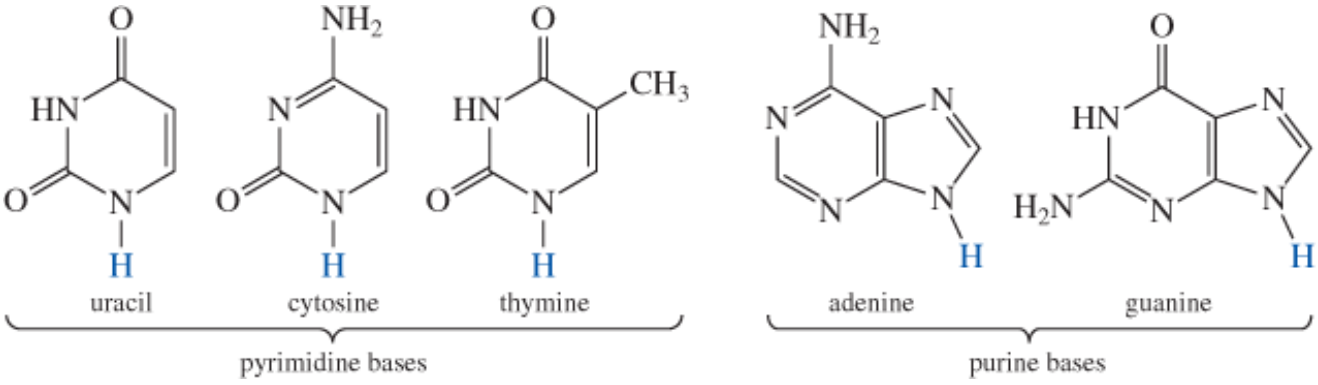


FIGURE 22.4 Structural formulae of the five most important purine and pyrimidine bases found in DNA and RNA. The hydrogen atom shown in colour is lost in the formation of an *N*-glycoside.

WORKED EXAMPLE 22.4

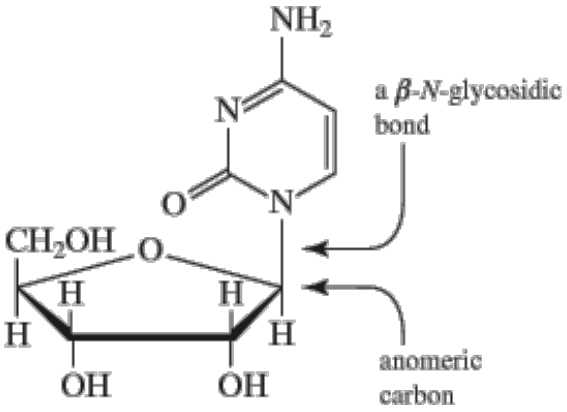
Understanding the Structures of More Complicated,

Biologically Relevant Glycosides

Draw a structural formula for the β-*N*-glycoside formed between D-ribofuranose and cytosine. Label the anomeric carbon atom and the *N*-glycosidic bond.

Analysis Putting together the structural representations we have made for simple functional groups allows us to begin to build up representations of even the most complicated biological molecules, such as DNA. An *N*-glycoside contains an N atom bonded to the anomeric carbon atom of the carbohydrate. The β designation means that the N atom will lie on the same side of the ring as the CH_2OH group.

Solution



Is our answer reasonable?

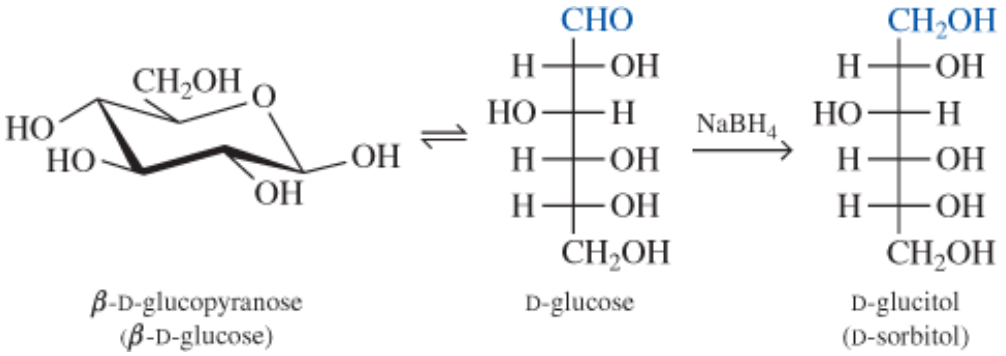
The basis to the structure has to be the Haworth projection, so first check to ensure that it is correctly drawn. The acetal oxygen that forms the ring should be at the rear of the structure and the terminal —CH_2OH should also be to the rear, pointing up. Then check that the bond between D-ribofuranose and cytosine is correct. The bond is drawn upwards from the anomeric carbon atom to the nitrogen atom of cytosine and is therefore a β-*N*-glycosidic bond.

PRACTICE EXERCISE 22.4

Draw a structural formula for the β-*N*-glycoside formed between β-D-ribofuranose and adenine.

Reduction to Alditols

The carbonyl group of a monosaccharide can be reduced to a hydroxyl group by a variety of reducing agents, including $NaBH_4$ (section 21.5, p. 957). The reduction products are known as **alditols**. Reduction of D-glucose gives D-glucitol, more commonly known as D-sorbitol. D-glucose is shown below in the open-chain form, only a small amount of which is present in solution. However, as it is reduced, the equilibrium between the cyclic hemiacetal form and the open-chain form shifts to replace the D-glucose. Note that D-glucose has also been represented in a chair conformation, which more realistically represents the reality of its shape.



Chemistry Research

Combatting Flu with Glycomics

Professor Mark von Itzstein, Institute for Glycomics, Griffith University

The important and sometimes essential roles of carbohydrates in biological processes, particularly in a number of disease-related processes, have become better defined. Understanding how carbohydrates, and proteins that recognise them, are involved in disease provides exciting opportunities for drug discovery. For example, influenza virus uses its membrane-associated carbohydrate-recognising protein, haemagglutinin (HA), to target specific host cell-bound carbohydrates in the respiratory tract and initiate infection. The virus also has a membrane-associated, carbohydrate-recognising enzyme known as sialidase (neuraminidase, NA) that acts as a pair of biological scissors; it clips carbohydrates away from the infected cell surface and enables the virion progeny to move on and infect new cells. Clearly both of these influenza virus surface proteins are possible drug design targets as they are both essential in the lifecycle of the virus.

In 1993, the Australian-based von Itzstein group reported the first designer anti-influenza drug now known as Relenza® (figure 22.5). This carbohydrate-based drug blocks the action of the enzyme sialidase, leaving the virion progeny clumped at the infected cell surface. The clumped virion progeny are then readily cleaned up by the immune system and the spread of infection is halted. Relenza is synthesised from a naturally occurring and widely distributed, negatively charged carbohydrate known as *N*-acetylneuraminic acid.

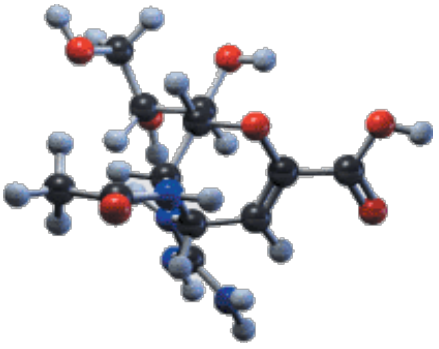
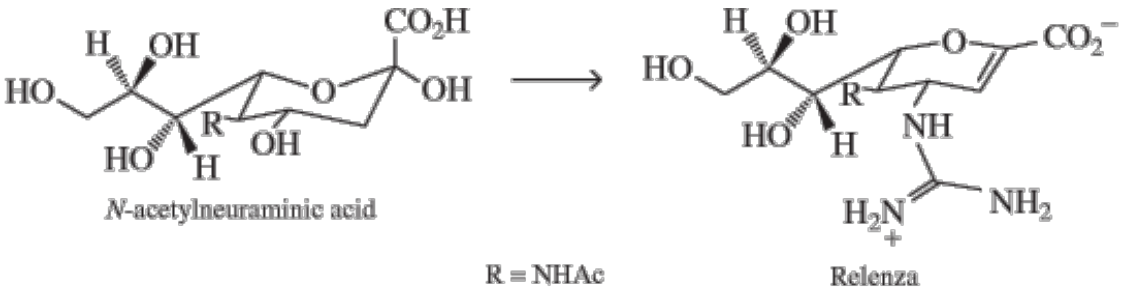
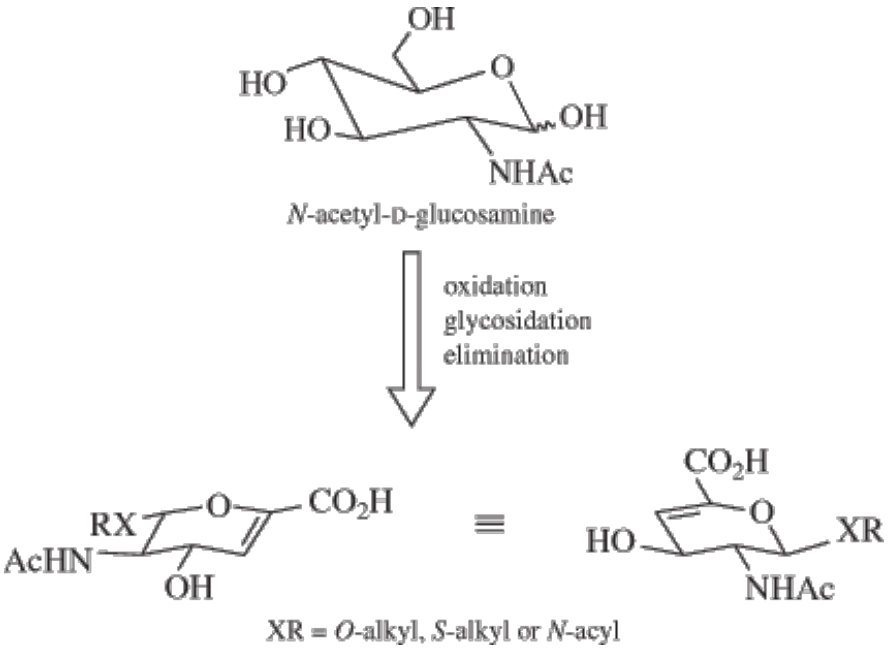


FIGURE 22.5 Structure of Relenza.



Importantly, the drug is active against *all* strains of influenza virus. von Itzstein and his group continue their efforts towards the development of next generation anti-influenza drugs that are based on relatively inexpensive simple carbohydrates such as *N*-acetyl-D-glucosamine (shown below). Such compounds mimic the drug Relenza and show potent activity in *in vitro* enzyme and cell culture-based assays. In a recent publication in *Nature Communications*, the von Itzstein group and researchers from Institut Pasteur in Paris and the University of St Andrews in Scotland described the development of a series of inhibitors for the design of next-generation anti-influenza drugs.

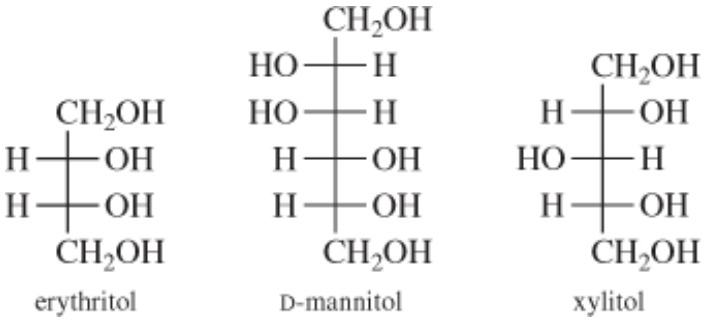


Glycomics, the study of the chemistry and biology of carbohydrates, promises to provide new opportunities for the discovery of clinically useful medicines. Griffith University's Institute for Glycomics, one of only six dedicated glycomics research facilities in the world, is a leader in the field of carbohydrate science and has made significant breakthroughs in the role that carbohydrates play in disease and the ageing process.

Alditols are named by replacing the *-ose* in the name of the monosaccharide with *-itol*. Sorbitol is found in the plant world in many berries and in cherries, plums, pears, apples, seaweed and algae. It is about 60 per cent as sweet as sucrose (table sugar) and is used in the manufacture of lollies and as a sugar substitute for diabetics. Among other alditols common in the biological world are erythritol, D-mannitol and xylitol, the last of which is used as a sweetening agent in ‘sugarless’ gum, confectionery and sweet cereals (figure 22.6).



FIGURE 22.6 Many 'sugar free' products contain sugar alcohols, such as D-sorbitol and xylitol.



WORKED EXAMPLE 22.5

Determining the Structure of Monosaccharide Reaction Products

Sodium borohydride, $NaBH_4$, reduces D-glucose to D-glucitol. Do you expect the alditol formed under these conditions to be optically active or optically inactive? Explain.

Analysis

Understanding how a functional group transformation can control a molecule's properties is best achieved by drawing the precise structure of the product.

Solution

Optical activity requires a chiral molecule, and D-glucitol is chiral. Reduction by $NaBH_4$ does not affect any of the four stereocentres in D-glucose, and the product does not have an internal plane of symmetry, so it is not a *meso* isomer. Therefore, we can predict that the product is optically active.

Is our answer reasonable?

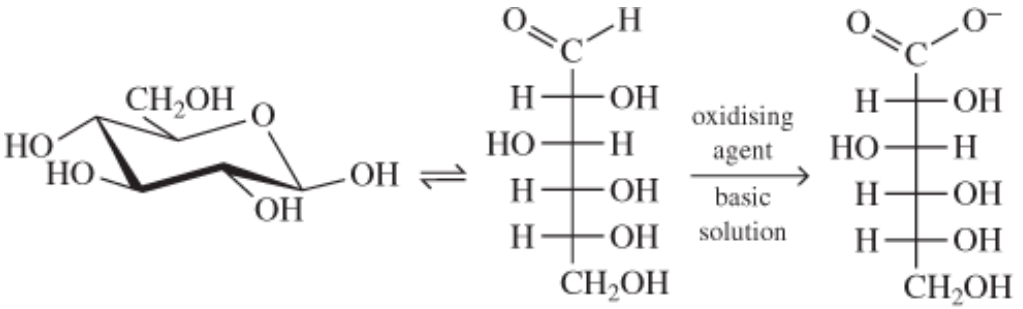
Reduction using $NaBH_4$ removes the aldehyde functional group and therefore prevents hemiacetal formation. The generation of a hemiacetal creates a new chiral carbon atom, so this possibility is prevented. However, the other chiral carbon atoms are unaffected, so the product molecule still retains optical activity.

PRACTICE EXERCISE 22.5

Sodium borohydride, $NaBH_4$, reduces D-erythrose to erythritol. Do you expect the alditol formed under these conditions to be optically active or optically inactive? Explain.

Oxidation to Aldonic Acids (Reducing Sugars)

We saw in section 21.5 that several agents, including O_2, oxidise aldehydes (RCHO) to carboxylic acids (RCOOH). The ease of oxidation of aldehydes leads to a specific test for this functional group called the Tollens' test (chapter 21, p. 959), which is also relevant for monosaccharides. Similarly, under basic conditions, the aldehyde group of an aldose can be oxidised to a carboxylate group. Under these conditions, the cyclic form of the aldose is in equilibrium with the open-chain form, which is then oxidised by a mild oxidising agent. D-glucose, for example, is oxidised to D-gluconate (the anion of D-gluconic acid).

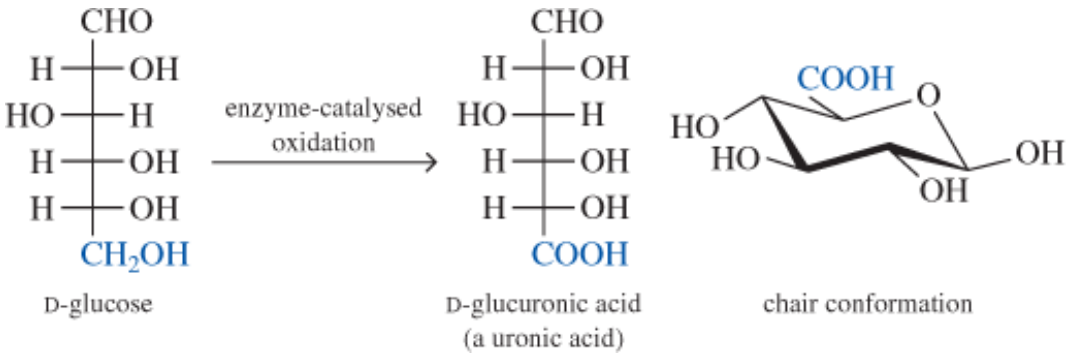


β-D-glucopyranose (β-D-glucose) | D-glucose | D-gluconate

Any carbohydrate that reacts with an oxidising agent to form an aldonic acid is classified as a **reducing sugar**. (It reduces the oxidising agent.)

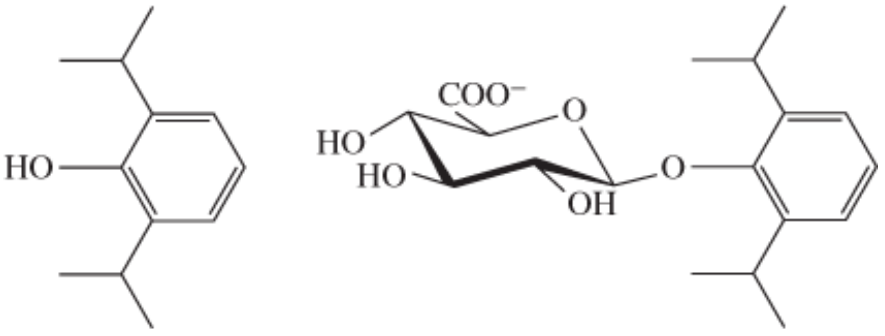
Oxidation to Uronic Acids

Enzyme-catalysed oxidation of the primary alcohol at C(6) of a hexose yields a uronic acid. Enzyme-catalysed oxidation of D-glucose, for example, yields D-glucuronic acid, shown here in both its open-chain and cyclic hemiacetal forms (only the β form is shown).



D-glucose | D-glucuronic acid (a uronic acid) | chair conformation

D-glucuronic acid is widely distributed in both the plant and animal worlds. In humans, it is an important component of the acidic polysaccharides of connective tissues. The body also uses it to detoxify foreign phenols and alcohols. In the liver, these compounds are converted to glycosides of glucuronic acid (glucuronides), to be excreted in urine. The intravenous anaesthetic propofol, for example, is converted to the following water-soluble glucuronide and then excreted in urine.



propofol urine-soluble glucuronide

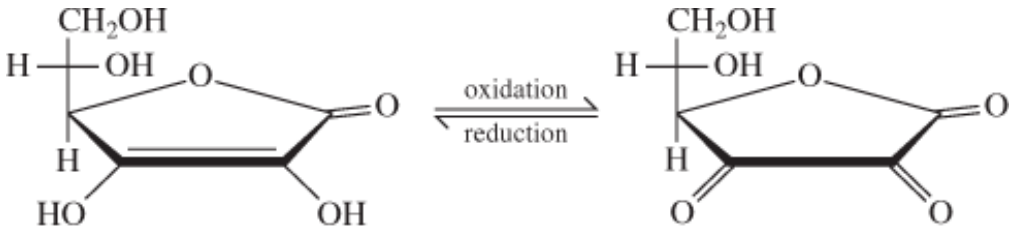
L-ascorbic Acid (Vitamin C)

One of the most important reactions of glucose is its conversion to L-ascorbic acid (vitamin C). This vitamin is synthesised biochemically by plants and some animals from D-glucose. Humans, however, do not have the enzyme systems required for this synthesis and so for us L-ascorbic acid is a vitamin, i.e. an essential component of our diet. Captain Cook insisted that his crew consume sauerkraut and lime juice on the long voyages from England when he mapped the east coast of Australia and circumnavigated New Zealand. Limes are rich in vitamin C and so his crew did not suffer from scurvy, a vitamin C deficiency that was common among sailors of the time. Today, vitamin C is one of the most commonly used dietary supplements as there is a perception that it is an important antioxidant which controls free radicals and ageing (figure 22.7).



FIGURE 22.7 Vitamin C in an orange is identical to its synthetic tablet form.

The structural formula of vitamin C (L-ascorbic acid) resembles that of a monosaccharide. L-ascorbic acid is very easily oxidised to L-dehydroascorbic acid, a diketone.



L-ascorbic acid (vitamin C)

L-dehydroascorbic acid

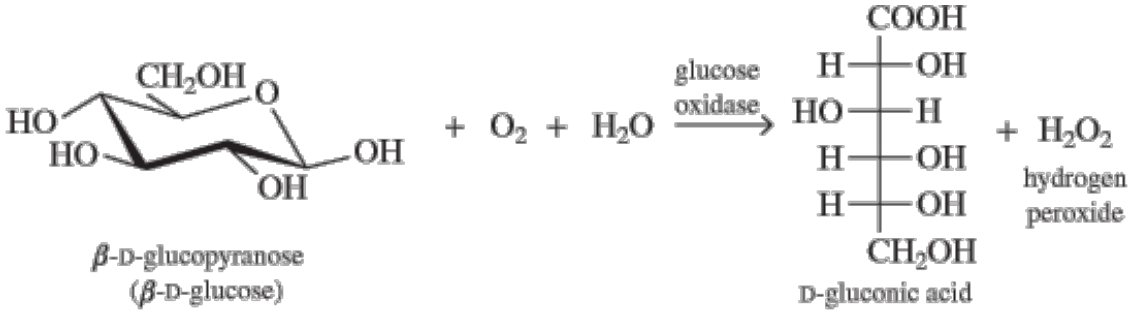
It is this ease of oxidation that makes vitamin C a crucial antioxidant in the body's biological defence mechanisms. Both L-ascorbic acid and L-dehydroascorbic acid are physiologically active and are found together in most body fluids.

Chemical Connections

Measuring Blood Sugar (Glucose) to Manage Diabetes

Almost two million people in Australia and New Zealand suffer from diabetes, and more than 100 000 are diagnosed each year. These people need to closely monitor their blood sugar levels and administer medication to manage their condition. Accurately determining the level of glucose in blood, urine and other biological fluids is one of the most common analytical procedures performed in clinical chemistry laboratories.

Diabetic people and animals produce insufficient levels of the polypeptide hormone insulin (section 24.4). If the blood concentration of insulin is too low, muscle and liver cells do not absorb glucose; this can quickly lead to increased levels of blood glucose (hyperglycaemia), impaired metabolism of fats and proteins, ketosis and, possibly, diabetic coma. Therefore, diabetics need to measure their own blood sugar levels regularly. A rapid procedure for determining blood glucose levels is critical for early diagnosis and effective management of this disease. In addition to being rapid, a test must give an accurate measure of D-glucose; that is, it must be specific for D-glucose and not be affected by other substances present in blood. Modern glucose monitors use technology based on the enzyme glucose oxidase. This enzyme catalyses the oxidation of β-D-glucose to D-gluconic acid.

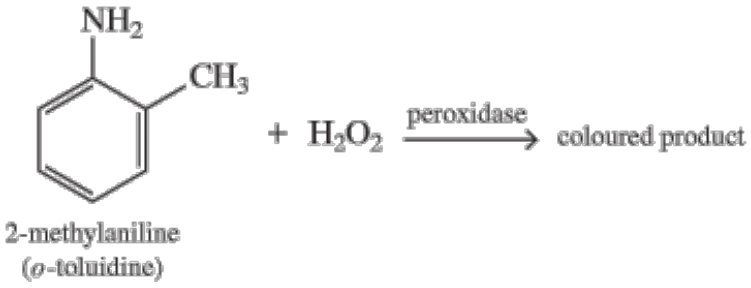


β-D-glucopyranose (β-D-glucose)

D-gluconic acid

Glucose oxidase is specific for β-D-glucose. Therefore, complete oxidation of any sample containing both β-D-glucose and α-D-glucose requires conversion of the α form to the β form.

In the earlier forms of blood glucose monitors, molecular oxygen, O_2, was used as the oxidising agent, producing hydrogen peroxide, H_2O_2, the concentration of which can be detected spectrophotometrically. For example, hydrogen peroxide converts colourless *o*-toluidine to a coloured product in a reaction catalysed by the enzyme peroxidise.



The original test strips used to measure blood sugar levels (see figure 22.8) relied on a colour intensity chart to determine the extent of the reaction and hence the concentration of glucose in the test solution. The first electronic testers used a spectrophotometric approach to determine the concentration of the coloured oxidation product.



FIGURE 22.8 A blood test strip, which uses a colour intensity chart to measure glucose concentration.

Newer devices that do not rely on colour have come onto the market. Instead, an enzyme-linked electrode containing glucose oxidase is exposed to a precise amount of blood. The extent of oxidation of D-glucose is detected by the electrode and a glucose reading is given based on the current generated (figure 22.9).



FIGURE 22.9 A home blood sugar monitor.

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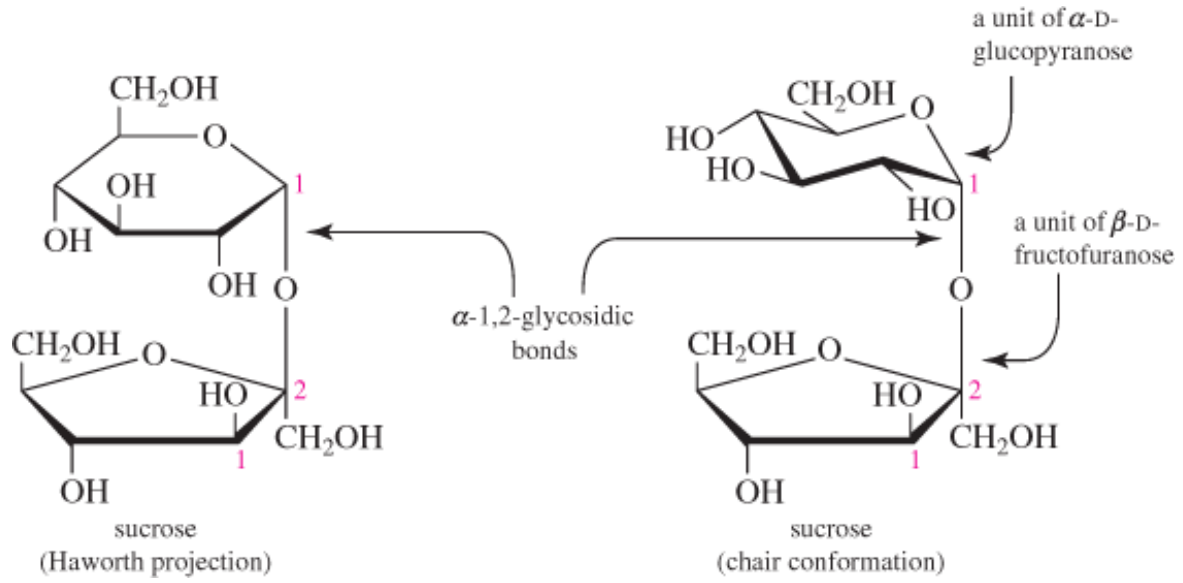
22.5 Disaccharides and Oligosaccharides

Most carbohydrates in nature contain more than one monosaccharide unit. Those which contain two units are called **disaccharides**; those which contain three units are called **trisaccharides**, and so on. The more general term, **oligosaccharide**, is often used for carbohydrates that contain from six to ten monosaccharide units. Carbohydrates containing larger numbers of monosaccharide units are called **polysaccharides**.

In a disaccharide, two monosaccharide units are joined by a glycosidic bond between the anomeric carbon atom of one unit and an —OH of the other. Sucrose, lactose and maltose are important disaccharides.

Sucrose

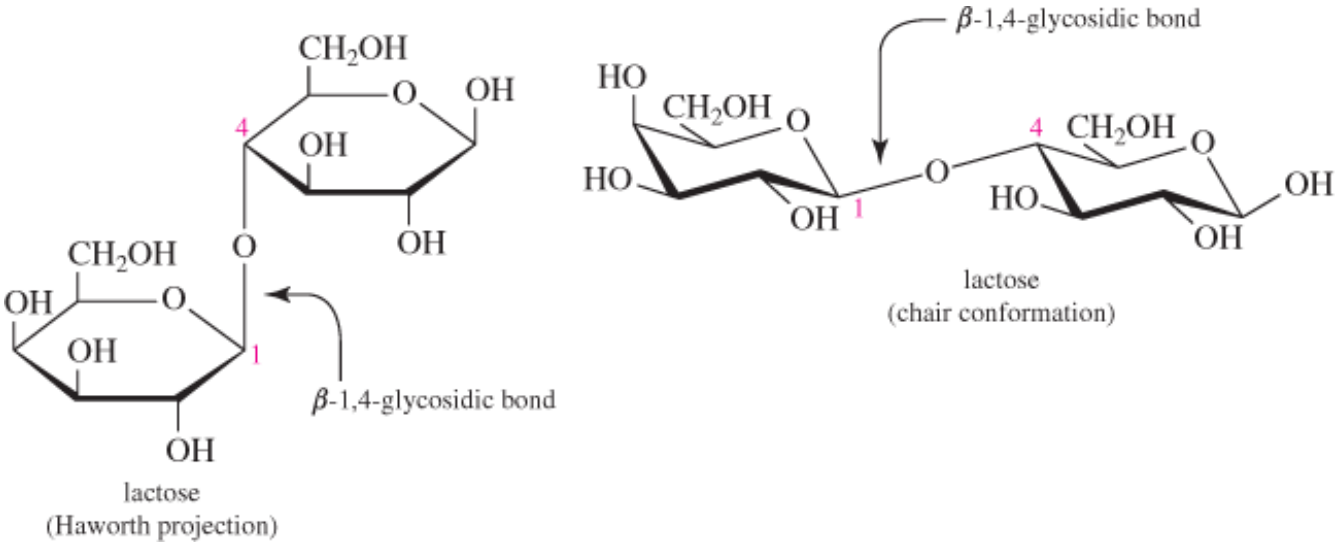
Sucrose (table sugar) is the most abundant disaccharide in the biological world. It is obtained principally from the juice of sugar cane and sugar beets. In sucrose, C(1) of α-D-glucopyranose bonds to C(2) of β-D-fructofuranose through an α-1,2-glycosidic bond.



Because the anomeric carbon atoms of both the glucopyranose and fructofuranose units are involved in formation of the glycosidic bond, neither monosaccharide unit is in equilibrium with its open-chain form. Thus, sucrose is a nonreducing sugar.

Lactose

Lactose, the principal sugar in milk, accounts for 5 to 8 per cent of human milk and 4 to 6 per cent of cow's milk. This disaccharide consists of D-galactopyranose, bonded by a β-1,4-glycosidic bond to C(4) of D-glucopyranose.



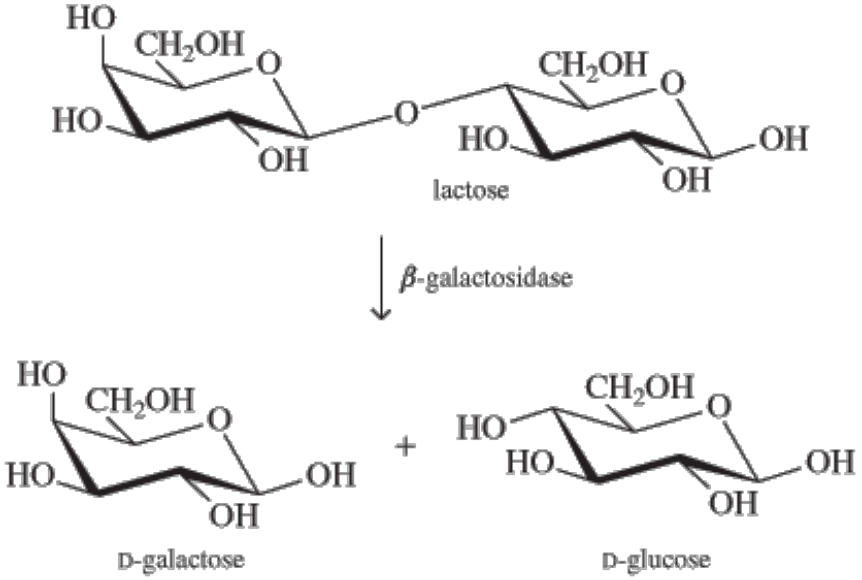
Lactose is a reducing sugar, because the cyclic hemiacetal of the D-glucopyranose unit is in equilibrium with its open-chain form and can be oxidised to a carboxyl group.

It has been estimated that 1 in 10 Australians and New Zealanders experience some degree of lactose intolerance. Lactose intolerance is an especially important health issue for Indigenous Australians and Maori among whom the incidence is much higher. People with lactose intolerance may suffer from calcium deficiencies unless their diet includes non-dairy sources of calcium.

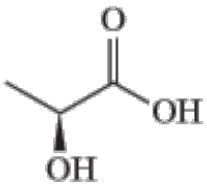
Chemical Connections

Lactose Intolerance

In our bodies, an enzyme called lactase (β-galactosidase) catalyses the hydrolysis of lactose to form glucose and galactose.



The galactose produced in this process is subsequently converted by the liver into additional glucose, which is then further metabolised to produce energy. Many people do not produce a sufficient amount of lactase and are incapable of hydrolysing large quantities of lactose. Instead, lactose accumulates and is ultimately broken down into CO_2 and H_2 by bacteria present in the intestines. Bacterial degradation of lactose produces several by-products, including lactic acid.



lactic acid

The build-up of lactic acid and other acidic by-products causes cramps, nausea and diarrhoea. This condition is called lactose intolerance, and it is estimated that over 10% of the population is lactose intolerant and so are unable to enjoy even a glass of milk (figure 22.10). Different ethnic and racial groups are affected to different extents, wih the highest incidence of lactose intolerance occurring among Asians and the lowest incidence occurring among Europeans.



FIGURE 22.10 Some people lack the enzymes needed to metabolise dairy products.

Lactose intolerance develops with time. Lactose production begins to decline for most children at about age two, although many people do not experience symptoms of lactose intolerance until later in life. It is estimated that 75% of the adult population worldwide will develop lactose intolerance at some stage in their life. This condition also affects other species, including dogs and cats, both of which are particularly susceptible to developing lactose intolerance.

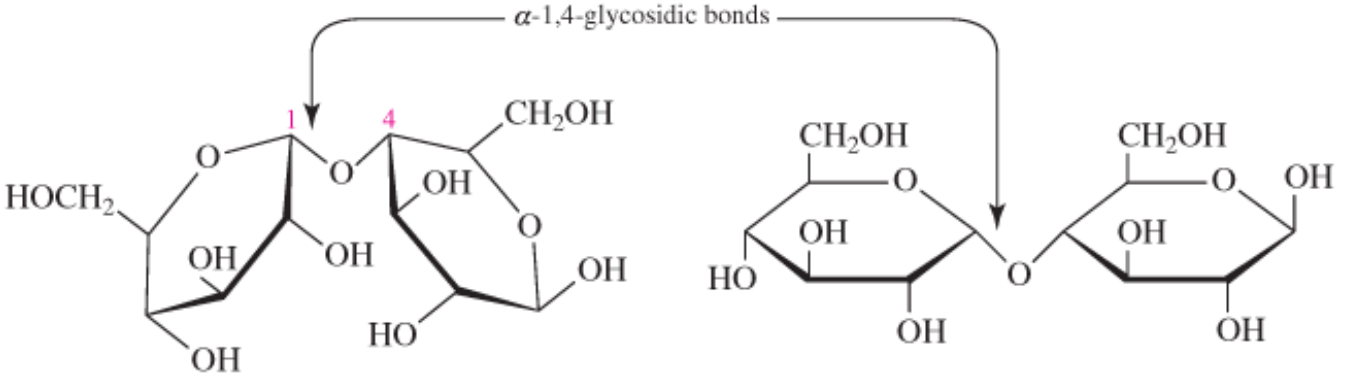
Lactose intolerance is easily treated through a controlled diet that minimises the intake of food products containing lactose. Several dairy products are produced via processes that remove the lactose, and these products are marketed as being ‘lactose free’. In addition, the enzyme lactase is available in tablet or liquid and can be taken prior to eating products containing lactose.

Maltose

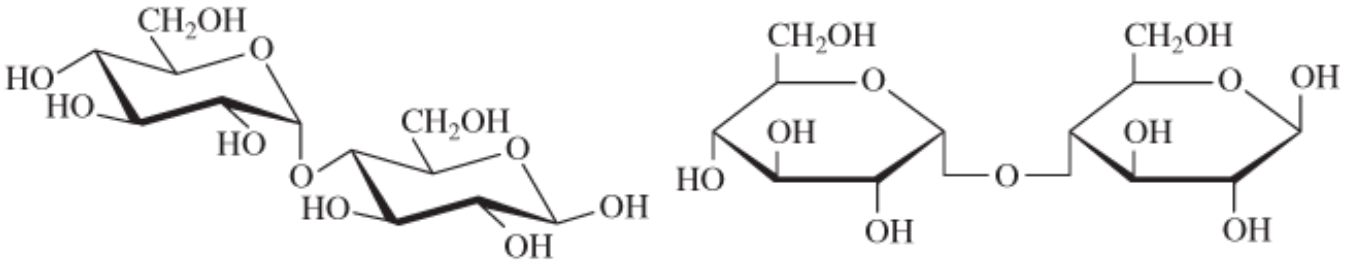
Maltose derives its name from its presence in malt, the juice from sprouted barley and other cereal grains. Maltose consists of two units of D-glucopyranose, joined by a glycosidic bond between C(1) (the anomeric carbon atom) of one unit and C(4) of the other unit. Because the oxygen atom on the anomeric carbon atom of the first glucopyranose unit is α, the bond joining the two units is called an α-1,4-glycosidic bond.

You might like to consider how you could best represent the structure of the carbohydrate rings and the α-

disaccharide linkage that is present in maltose. Shown below are Haworth projections and a chair conformation for β-maltose, so named because the —OH group on the anomeric carbon atom of the glucose unit on the right is β. Remember that the protocol for Haworth projections is that the bonds coming from the rings are drawn vertically to the plane of the ring. This would mean that two Haworth projections linked together would require that the rings are oriented at an angle to each other. Perhaps a better representation keeps the rings in the horizontal plane orientation but shows the glycoside bond as not being vertical.



two ways of showing the glycoside link between Haworth projections of glucose present in β-maltose



β-maltose preferred structural representation

β-maltose non-preferred structural representation

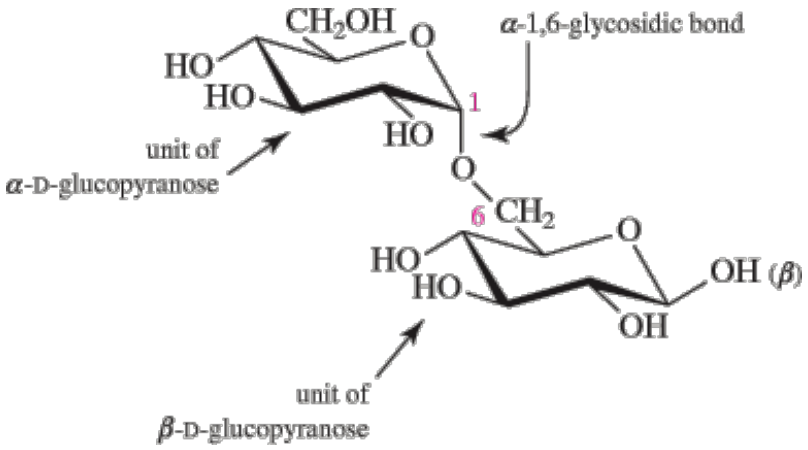
In reality the structure of disaccharides is best represented by the actual chair conformation, which more clearly shows the real bond angles and distances, as discussed in chapter 17 (p. 691). In some texts you might see the glycoside linkage drawn as a U-shaped connection. This is not a very good representation, as the method for drawing structures outlined in chapter 17 (p. 687) suggests that two lines meeting at an angle indicate the presence of a carbon atom, and this is clearly not the case with a glycosidic bond.

WORKED EXAMPLE 22.6

Understanding the 3-D Structure of Disaccharides

Draw a chair conformation for the β anomer of a disaccharide in which two units of D-glucopyranose are joined by an α-1,6-glycosidic bond.

Analysis and solution First draw a chair conformation of α-D-glucopyranose. Then connect the anomeric carbon atom of this monosaccharide to C(6) of a second D-glucopyranose unit by an α-glycosidic bond. The resulting molecule is either α or β depending on the orientation of the —OH group on the reducing end of the disaccharide. The disaccharide shown here is β.



Is our answer reasonable?

Look closely at the drawing of the molecule. For a 1,6-connection, the first carbon atom of one ring, C(1), connects to the last carbon atom of the second ring, C(6). An α connection is oriented downwards from the first ring.

PRACTICE EXERCISE 22.6

Draw a Haworth projection and a chair conformation for the α form of a disaccharide in which two units of D-glucopyranose are joined by a β-1,3-glycosidic bond.

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22.6 Polysaccharides

Polysaccharides consist of a large number of monosaccharide units joined together by glycosidic bonds. Three important polysaccharides, all made up of glucose units, are starch, glycogen and cellulose.

Starch: Amylose and Amylopectin

Starch is found in all plant seeds and tubers, and it is the form in which glucose is stored for later use. Starch can be separated into two principal polysaccharides: amylose and amylopectin. Although the starch from each plant is unique, most starches contain 20 to 25 per cent amylose and 75 to 80 per cent amylopectin.

Complete hydrolysis of both amylose and amylopectin yields only D-glucose. Amylose is composed of continuous, unbranched chains of as many as 4000 D-glucose units joined by α-1, 4-glycosidic bonds. Amylopectin contains chains of up to 10 000 D-glucose units, also joined by α-1,4-glycosidic bonds. In addition, amylopectin has considerable branching from this linear network. At branch points, new chains of 24 to 30 units start by α-1,6-glycosidic bonds (figure 22.11).

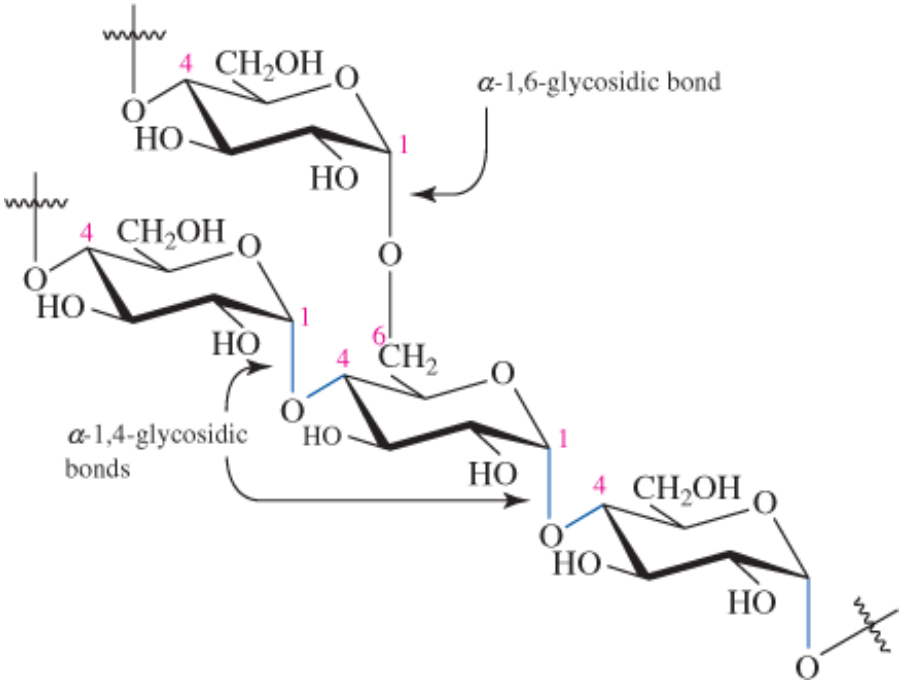


FIGURE 22.11 Amylopectin is a highly-branched polymer of D-glucose. Chains consist of 24 to 30 units of D-glucose, joined by α-1,4-glycosidic bonds, and branches created by α-1,6-glycosidic bonds.

Why are carbohydrates stored in plants as polysaccharides rather than monosaccharides, a more directly usable source of energy? The answer has to do with osmotic pressure, which is proportional to the molar concentration, not the molar mass, of a solute. If 1000 molecules of glucose are assembled into one starch macromolecule, a solution containing 1 g of starch per 10 mL will have only one-thousandth the osmotic pressure relative to a solution of 1 g of glucose in the same volume. This feat of packaging is a tremendous advantage because it reduces the strain on various membranes enclosing solutions of such macromolecules.

Glycogen

Glycogen is the reserve carbohydrate for animals. Like amylopectin, glycogen is a branched polymer of D-glucose. Each branch contains approximately 12–14 glucose units, joined by α-1,4-and α-1,6-glycosidic bonds. The total amount of glycogen in the body of a well-nourished adult human is about 350 g, divided

almost equally between liver and muscle.

Cellulose

Cellulose, the most widely distributed plant skeletal polysaccharide, constitutes almost half of the cell-wall material of wood. Cotton (figure 22.13) is almost pure cellulose.



FIGURE 22.13 Cotton ready to be harvested.

Cellulose, a linear polymer of D-glucose units joined by β-1,4-glycosidic bonds (figure 22.12), has an average molar mass of 400 000 g mol^{-1}, corresponding to approximately 2800 glucose units per molecule.

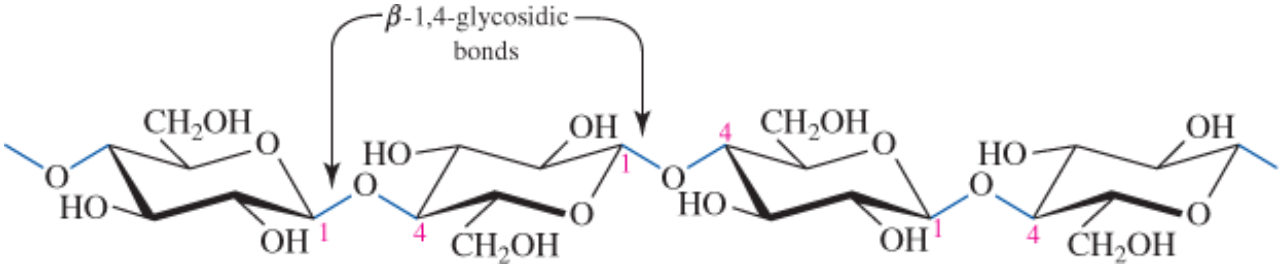


FIGURE 22.12 Cellulose is a linear polymer of D-glucose, joined by β-1,4-glycosidic bonds.

Cellulose molecules act like stiff rods by aligning themselves side-by-side into well-organised, water-insoluble fibres in which the —OH groups form numerous intermolecular hydrogen bonds. This arrangement of bundles of parallel chains gives cellulose fibres their high mechanical strength and explains why cellulose is insoluble in water. When a piece of cellulose-containing material is placed in water, there are not enough —OH groups on the surface of the fibre to pull individual cellulose molecules away from the strongly hydrogen-bonded fibre. At the molecular level, the chains of carbohydrates bind together through hydrogen bonding to form bundles (figure 22.14). These bundles of fibres are called microfibrils. They are glued together by smaller polysaccharide chains, called hemicelluloses, and act as the structural units that give plant walls their strength and rigidity.

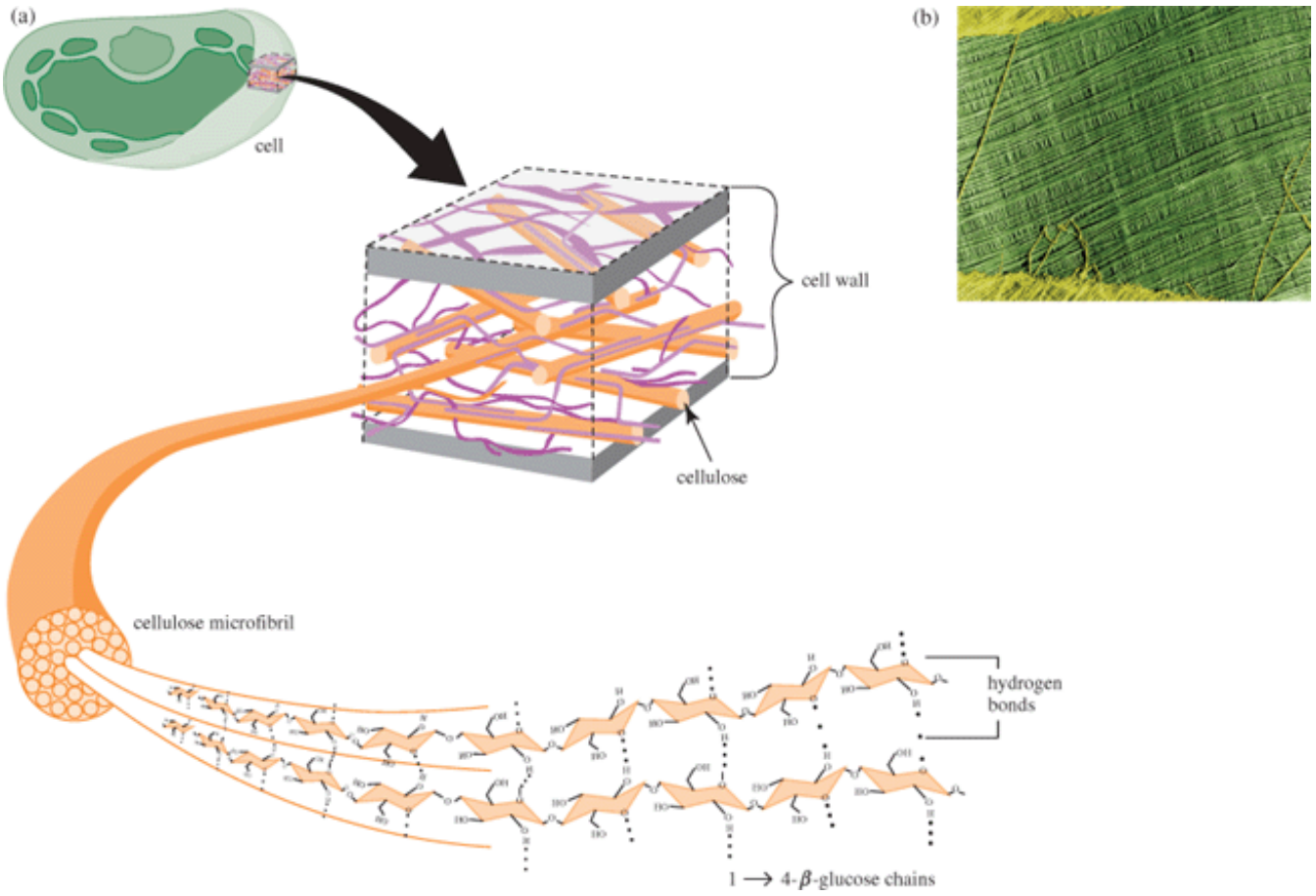


FIGURE 22.14 (a) Principal structures of plant cell walls, which are composed of cross-linked cellulose microfibrils constructed from linked β-glucose chains;
(b) electron micrograph of cell wall showing cross-linked microfibrils.

Humans cannot use cellulose as food because our digestive systems do not contain β-glucosidases, enzymes that catalyse the hydrolysis of β-glycosidic bonds. Instead, we have only α-glucosidases; hence, the polysaccharides we use as sources of glucose are starch and glycogen. By contrast, many bacteria and micro-organisms do contain β-glucosidases and can digest cellulose. Termites are fortunate (much to our regret) to have such bacteria in their intestines and can use wood as their principal food. Ruminants (cud-chewing animals) and horses can also digest grasses and hay, because β-glucosidase-containing micro-organisms are present within their alimentary systems.

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SUMMARY

Introduction to Carbohydrates

Carbohydrates are polyhydroxyaldehydes, polyhydroxyketones or substances that yield these compounds after hydrolysis. Carbohydrates, no matter how complex, are governed by the properties of the individual chemical groups from which they are constructed.

Monosaccharides

Monosaccharides are polyhydroxyaldehydes or polyhydroxyketones. The most common have the general formula $C_nH_{2n}O_n$, where *n* varies from 3 to 9. Their names contain the suffix *-ose*. The prefixes *tri-*, *tetr-*, *pent-* and so on show the number of carbon atoms in the chain. The prefix *aldo-* indicates an aldehyde, the prefix *keto-* designates a ketone. Monosaccharides containing an aldehyde group are classified as aldoses, and those containing a ketone group are ketoses.

In a Fischer projection of a carbohydrate, the carbon chain is written vertically, with the most highly oxidised carbon atom towards the top. Horizontal lines show groups projecting above the plane of the page, vertical lines show groups projecting behind the plane of the page. A monosaccharide that has the same configuration at the penultimate carbon atom as D-glyceraldehyde is called a D-monosaccharide; one that has the same configuration at the penultimate carbon atom as L-glyceraldehyde is called an L-monosaccharide.

An amino sugar contains an —NH_2 group in place of an —OH group.

The Cyclic Structure of Monosaccharides

Monosaccharides exist primarily as cyclic hemiacetals in a chair conformation. The new stereocentre resulting from hemiacetal formation is referred to as an anomeric carbon atom. The stereoi-somers formed this way are called anomers. When an anomer of one form is added to an aqueous solution, it forms an equilibrium with the other anomer in a process called mutarotation, which is detected by the change in the optical rotation of the initial solution.

A six-membered cyclic hemiacetal is called a pyranose, a five membered cyclic hemiacetal is a furanose. The symbol β indicates that the —OH on the anomeric carbon atom is on the same side of the ring as the terminal —CH_2OH. The symbol α indicates that —OH on the anomeric carbon atom is on the opposite side of the ring from the terminal —CH_2OH. Furanoses and pyranoses can be drawn as Haworth projections.

Reactions of Monosaccharides

A glycoside is an acetal derived from a monosaccharide. The bond from the anomeric carbon atom to the —OR group is called a glycosidic bond. The name of the glycoside is composed of the name of the alkyl or aryl group bonded to the acetal oxygen atom, followed by the name of the monosaccharide in which the terminal *-e* has been replaced by *-ide*.

An alditol is a polyhydroxy compound formed by the reduction of the carbonyl group of a monosaccharide. An aldonic acid is a carboxylic acid formed by oxidation of the aldehyde group of an aldose. The aldose reduces the oxidising agent and is therefore called a reducing sugar. Enzyme-catalysed oxidation of the terminal —CH_2OH to a —COOH gives a uronic acid.

The determination of blood glucose levels is an important clinical test for the diagnosis and management of diabetes. The test uses the enzyme glucose oxidase, which catalyses the oxidation of β-D-glucose to D-gluconic acid.

L-ascorbic acid (vitamin C) is synthesised in nature from D-glucose by a series of enzyme-catalysed steps.

Disaccharides and Oligosaccharides

A disaccharide contains two monosaccharide units joined by a glycosidic bond. Terms applied to carbohydrates containing larger numbers of monosaccharides are: trisaccharide, tetrasaccharide, oligosaccharide and polysaccharide.

Sucrose is a disaccharide consisting of D-glucose joined to D-fructose by an α-1,2-glycosidic bond. Lactose is a disaccharide consisting of D-galactose joined to D-glucose by a β-1,4-glycosidic bond. Maltose is a disaccharide of two molecules of D-glucose joined by an α-1,4-glycosidic bond.

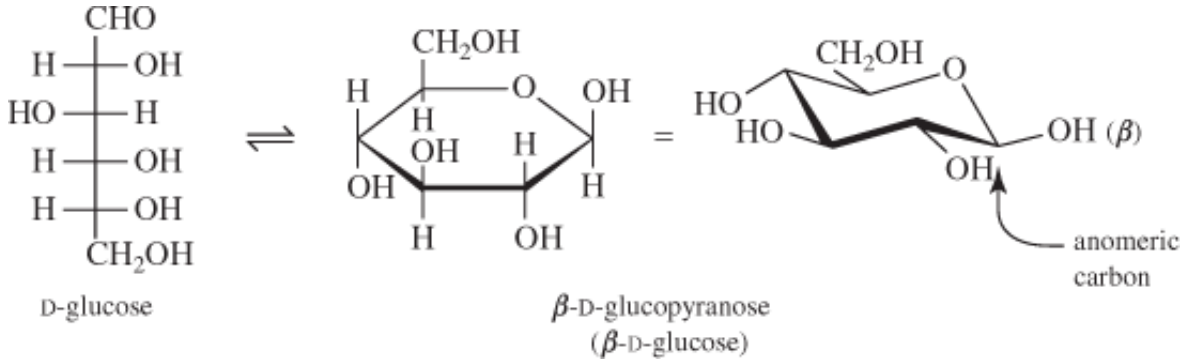
Polysaccharides

Starch can be separated into two fractions called amylose and amylopectin. Amylose is a linear polymer of up to 4000 units of D-glucopyranose joined by α-1,4-glycosidic bonds. Amylopectin is a highly-branched polymer of D-glucose joined by α-1,4-glycosidic bonds and, at branch points, by α-1,6-glycosidic bonds. Glycogen, the reserve carbohydrate of animals, is a highly-branched polymer of D-glucopyranose joined by α-1,4-glycosidic bonds and, at branch points, by α-1,6-glycosidic bonds. Cellulose, the skeletal polysaccharide of plants, is a linear polymer of D-glucopyranose joined by β-1,4-glycosidic bonds.

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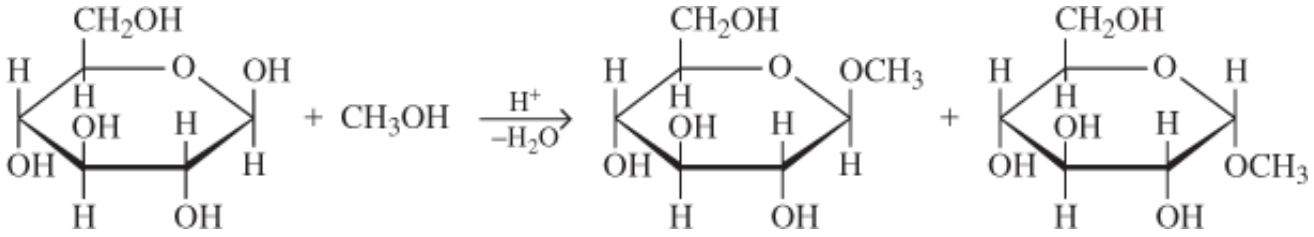
Formation of cyclic hemiacetals *(section 22.3)*

A monosaccharide existing as a five-membered ring is a furanose; one existing as a six-membered ring is a pyranose. A pyranose is most commonly drawn as a Haworth projection or a chair conformation.



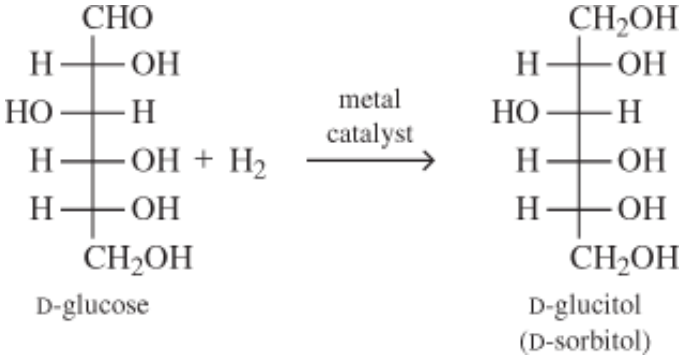
Formation of glycosides *(section 22.4)*

Treatment of a monosaccharide with an alcohol in the presence of an acid catalyst forms a cyclic acetal called a glycoside. The bond to the new —OCH_3 group is called a glycosidic bond.



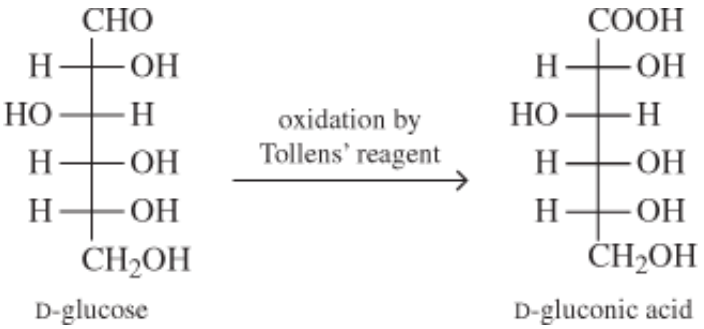
Reduction to alditols *(section 22.4)*

Reduction of the carbonyl group of an aldose or a ketose to a hydroxyl group yields a polyhydroxy compound called an alditol.



Oxidation to an aldonic acid *(section 22.4)*

A mild oxidising agent oxidises the aldehyde group of an aldose to a carboxyl group to give a polyhydroxycarboxylic acid called an aldonic acid.



D-glucose D-gluconic acid

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REVIEW QUESTIONS

Monosaccharides

22.1 What is the difference in structure between:

(a) an aldose and a ketose and

(b) an aldopentose and a ketopentose?

22.2 Which hexose is also known as dextrose?

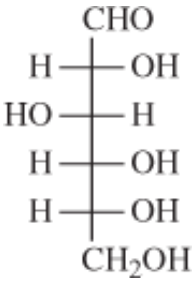
22.3 D- and L-glyceraldehyde are enantiomers. Explain what this means.

22.4 Explain the meaning of the designations d and l as used to specify the configuration of carbohydrates.

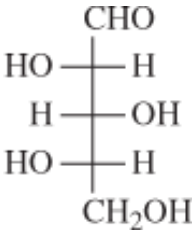
22.5 How many stereocentres are present in D-glucose? How many stereocentres are present in D-ribose? How many stereoisomers are possible for each monosaccharide?

22.6 Which of the following compounds are D-monosaccharides and which are L-monosaccharides?

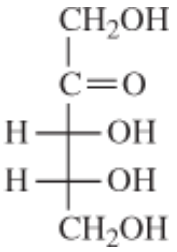
(a)



(b)



(c)



22.7 Explain why all mono- and disaccharides are soluble in water.

22.8 What is an amino sugar? Name the three amino sugars most commonly found in nature.

The Cyclic Structure of Monosaccharides

22.9 Define the term ‘anomeric carbon’.

22.10 Explain the conventions for using α and β to designate the configurations of cyclic forms of monosaccharides.

22.11 Are α-D-glucose and β-D-glucose anomers? Explain. Are they enantiomers? Explain.

22.12 Are α-D-gulose and α-l-gulose anomers? Explain.

22.13 Hexopyranoses are sometimes represented in the chair form. In what way are chair conformations a more accurate representation of molecular shape of hexopyranoses than Haworth projections?

22.14 Explain the phenomenon of mutarotation in carbohydrates. By what means is mutarotation detected?

22.15 α-D-galactopyranose has an $[\alpha]_D = +150.7°$. When it is dissolved in water, however, the specific rotation of the solution after some time is measured as +80.2°. What would be the specific rotation of a solution of β-D-galactopyranose measured under the same conditions?

22.16 The specific rotation of α-D-glucose is +112.2°. What is the specific rotation of α-l-glucose?

22.17 When α-D-glucose is dissolved in water, the specific rotation of the solution changes from +112.2° to +52.7°. Does the specific rotation of α-l-glucose also change when it is dissolved in water? If so, to what value does it change?

Reactions of Monosaccharides

22.18 There are four D-aldopentoses (figure 22.1). If each is reduced with $NaBH_4$, which yield optically active alditols? Which yield optically inactive alditols?

22.19 Account for the observation that the reduction of D-glucose with $NaBH_4$ gives an optically active alditol, whereas the reduction of D-galactose with $NaBH_4$ gives an optically inactive alditol.

22.20 Which two D-aldohexoses give optically inactive (*meso*) alditols on reduction with $NaBH_4$? (*Hint:* See chapter 17.)

22.21 Name the two alditols formed by $NaBH_4$ reduction of D-fructose.

22.22 Is ascorbic acid a biological oxidising agent or a biological reducing agent? Explain.

Disaccharides and Oligosaccharides

22.23 Define the term ‘glycosidic bond’.

22.24 What is the difference in meaning between the terms ‘glycosidic bond’ and ‘glucosidic bond’?

22.25 Do glycosides undergo mutarotation?

22.26 In making lollies or syrup from sugar, sucrose is boiled in water with a little acid, such as lemon juice. Why does the product mixture taste sweeter than the starting sucrose solution?

22.27 Which of the following disaccharides are reduced by $NaBH_4$?

(a) sucrose

(b) lactose

(c) maltose

Polysaccharides

22.28 What is the difference in structure between oligosaccharides and polysaccharides?

22.29 Name three polysaccharides that are composed of units of D-glucose. In which of the three polysaccharides are the glucose units joined by α-glycosidic bonds? In which are they joined by β-glycosidic bonds?

22.30 Starch can be separated into two principal polysaccharides: amylose and amylopectin. What is the major difference in structure between the two?

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22.31 2,6-dideoxy-D-altrose, known alternatively as D-digitoxose, is a monosaccharide obtained from the hydrolysis of digitoxin, a natural product extracted from purple foxglove (*Digitalis purpurea*). Digitoxin has found wide use in cardiology because it reduces the pulse rate, regularises heart rhythm and strengthens the heartbeat. Draw the structural formula of 2,6-dideoxy-D-altrose.



The foxglove plant produces the important cardiac medication digitalis.

22.32 Draw Fischer projections for the monosaccharides L-ribose and L-arabinose.

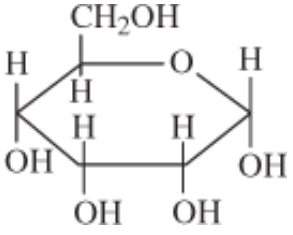
22.33 Draw α-D-glucopyranose (α-D-glucose) as a Haworth projection. Now, using only the following information, draw Haworth projections for the following monosaccharides.

(a) α-D-mannopyranose (α-D-mannose). The configuration of D-mannose differs from that of D-glucose only at C(2).

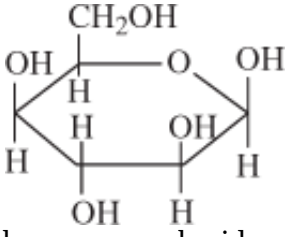
(b) α-D-gulopyranose (α-D-gulose). The configuration of D-gulose differs from that of D-glucose at C(3) and C(4).

22.34 Convert each of the following Haworth projections to an open-chain form and then to a Fischer projection.

(a)

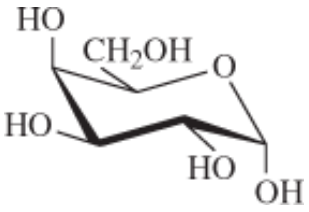


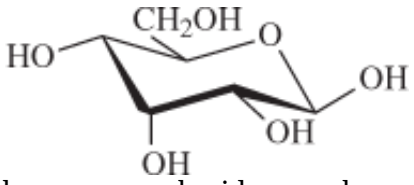
(b)



Name the monosaccharides you have drawn.

22.35 Convert each of the following chair conformations to an open-chain form and then to a Fischer projection.

(a) 

(b) 

Name the monosaccharides you have drawn.

22.36 The configuration of D-arabinose differs from the configuration of D-ribose only at C(2). Using this information, draw a Haworth projection for α-D-arabinofuranose (α-D-arabinose).

22.37 Draw Fischer projections for the product(s) formed by the reaction of D-galactose with the following compounds, and state whether each product is optically active or optically inactive.

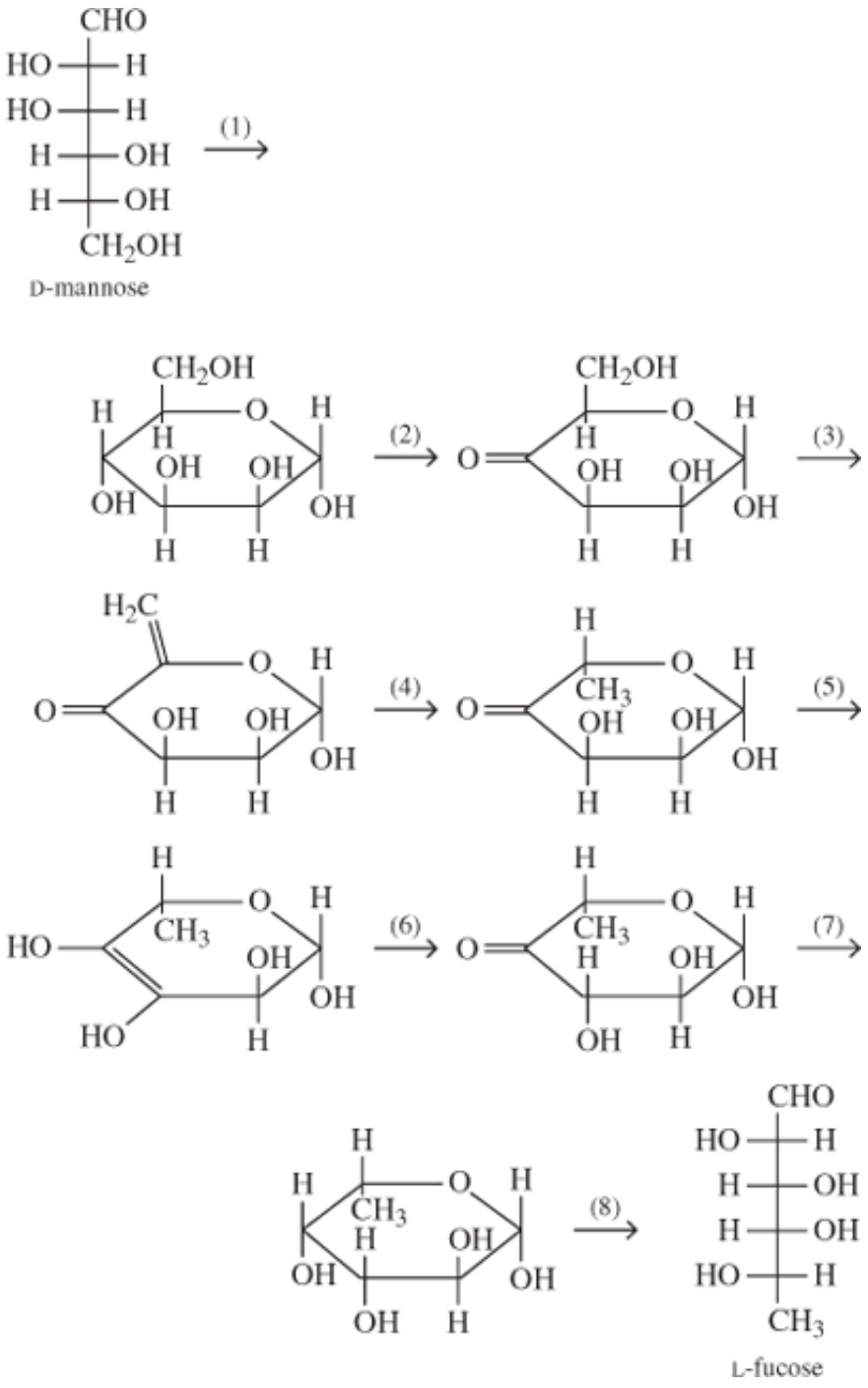
(a) $NaBH_4$ in H_2O

(b) $AgNO_3$ in NH_3, H_2O

22.38 Repeat question 22.37, but use D-ribose in place of D-galactose.

22.39 The reduction of D-fructose by $NaBH_4$ gives two alditols, one of which is D-sorbitol. Name and draw a structural formula for the other alditol.

22.40 L-fucose, one of several monosaccharides commonly found in the surface polysaccharides of animal cells, is synthesised biochemically from D-mannose in the following eight steps.

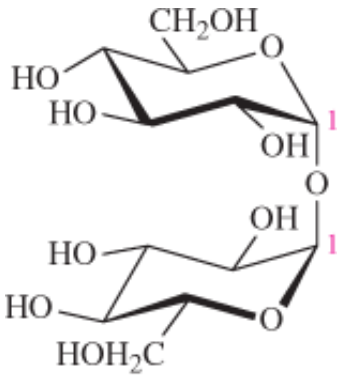


(a) Describe the type of reaction (oxidation, reduction, hydration, dehydration etc.) involved in each step.

(b) Explain why this monosaccharide, which is derived from D-mannose, now belongs to the L series.

22.41 Ascorbic acid is a diprotic acid with the following acid ionisation constants: $pK_{a1} = 4.17$ and $pK_{a2} = 11.57$. The two acidic hydrogen atoms are those connected with the enediol part of the molecule. Which hydrogen atom has which ionisation constant? (*Hint:* Draw separately the anion derived by the loss of one of these hydrogen atoms and that formed by the loss of the other hydrogen atom. Which anion has the greater degree of resonance stabilisation?)

22.42 Trehalose is found in young mushrooms and is the chief carbohydrate in the blood of certain insects. Trehalose is a disaccharide consisting of two D-monosaccharide units, joined by an α-1,1-glycosidic bond.



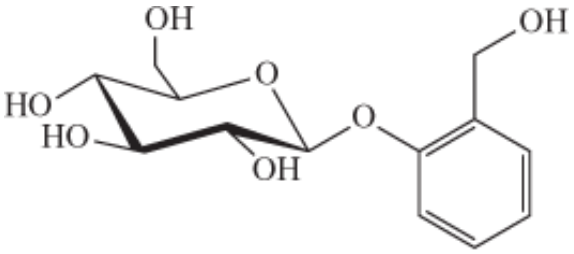
trehalose

(a) Is trehalose a reducing sugar?

(b) Does trehalose undergo mutarotation?

(c) Name the two monosaccharide units of which trehalose is composed.

22.43 Hot-water extracts of ground willow bark are an effective pain reliever. Unfortunately, the liquid is so bitter that most people refuse it. The pain reliever in these infusions is salicin.



salicin

Name the monosaccharide unit in salicin.

22.44 A Fischer projection of *N*-acetyl-D-glucosamine is given on p. 981.

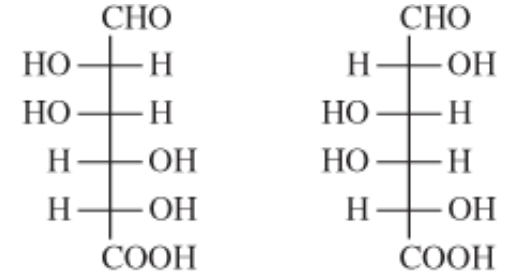
(a) Draw a Haworth projection and a chair conformation for the α- and β-pyranose forms of this monosaccharide.

(b) Draw a Haworth projection and a chair conformation for the disaccharide formed by joining two units of the pyranose form of *N*-acetyl-D-glucosamine by a β-1,4-glucosidic bond. If your drawing is correct, you have the structural formula for the repeating dimer of chitin, the structural polysaccharide component of the shell of lobsters and other crustaceans.

22.45 Propose structural formulae for the repeating disaccharide unit in the following polysaccharides.

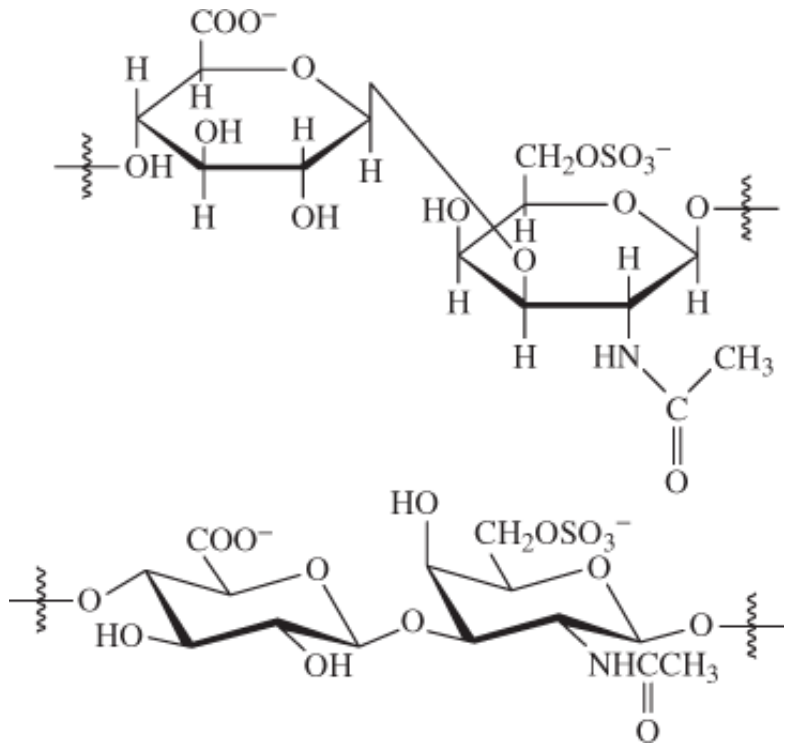
(a) Alginic acid, isolated from seaweed, is used as a thickening agent in ice-cream and other foods. Alginic acid is a polymer of D-mannuronic acid in the pyranose form, joined by β-1,4-glycosidic bonds.

(b) Pectic acid is the main component of pectin, which is responsible for the formation of jellies from fruits and berries. Pectic acid is a polymer of D-galacturonic acid in the pyranose form joined by α-1,4-glycosidic bonds.



D-mannuronic acid D-galacturonic acid

22.46 The following are a Haworth projection and a chair conformation for the repeating disaccharide unit in chondroitin 6-sulfate.



This biopolymer acts as a flexible connecting matrix between the tough protein filaments in cartilage and is available as a dietary supplement, often combined with D-glucosamine sulfate. Some believe that the combination can strengthen and improve joint flexibility.

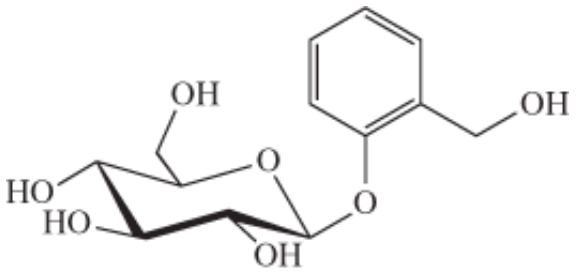
(a) From what two monosaccharide units is the repeating disaccharide unit of chondroitin 6-sulfate derived?

(b) Describe the orientation of the glycosidic bond between the two units.

(c) Which is the better representation of the structure of chondroitin 6-sulfate?

22.47 Trehalose is a naturally occurring disaccharide found in bacteria, insects and many plants. It protects cells from dry conditions because of its ability to retain water, thereby preventing cellular damage from dehydration. This property of trehalose has also been exploited in the preparation of food and cosmetics. Trehalose is not a reducing sugar, it is hydrolysed to yield two equivalents of D-glucose, and it does not have any β-glycoside linkages. Draw the structure of trehalose.

22.48 Salicin is a natural analgesic present in the bark of willow trees, and it has been used for thousands of years to treat pain and reduce fevers.



salicin

(a) Is salicin a reducing sugar?

(b) Identify the products obtained when salicin is hydrolysed in the presence of an acid.

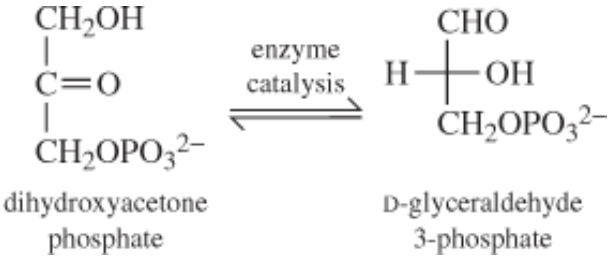
(c) Is salicin an α-glycoside or a β-glycoside?

(d) Draw the major product expected when salicin is treated with excess acetic anhydride in the presence of pyridine.

(e) Would you expect salicin to exhibit mutarotation when dissolved in neutral water?

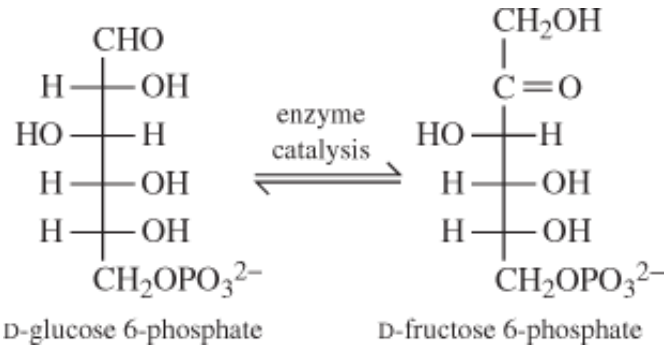
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22.1 One step in glycolysis, the pathway that converts glucose to pyruvate, involves an enzyme-catalysed conversion of dihydroxyacetone phosphate to D-glyceraldehyde 3-phosphate.



Show that this transformation can be regarded as two enzymecatalysed keto–enol tautomerisations (section 21.5).

22.2 One pathway for the metabolism of glucose 6-phosphate is its enzyme-catalysed conversion to fructose 6-phosphate.



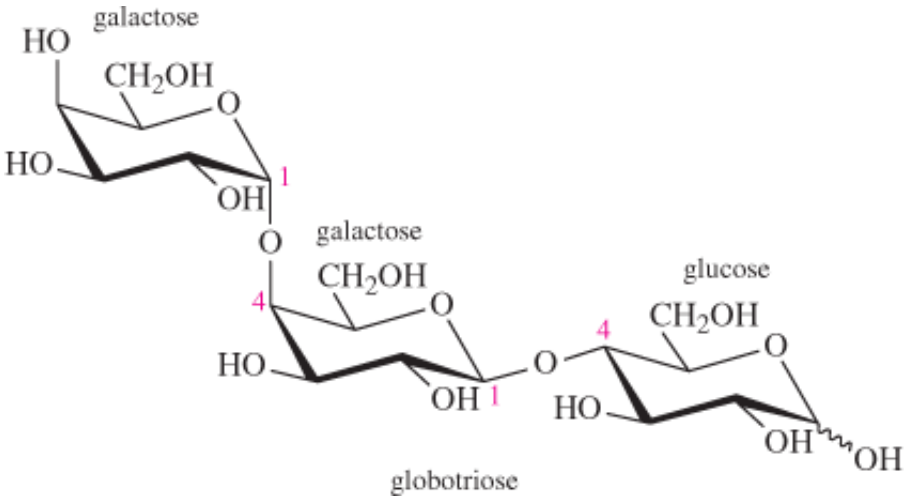
Show that this transformation can be regarded as two enzymecatalysed keto–enol tautomerisations.

22.3 Epimers are carbohydrates that differ in configuration at only one stereocentre.

(a) Which of the aldohexoses are epimers of each other?

(b) Are all anomer pairs also epimers of each other? Explain. Are all epimers also anomers? Explain.

22.4 Oligosaccharides are very valuable therapeutically, but are especially difficult to synthesise, even though the starting materials are readily available. The structure of globotriose is shown below. This molecule is a receptor for a series of toxins synthesised by some strains of *E. coli*.



From left to right, globotriose consists of an α-1,4-linkage of galactose to a galactose that is part of a β-1,4-linkage to glucose. The squiggly line indicates that the configuration at that carbon atom can be α or β. Suggest why it would be difficult to synthesise this trisaccharide, for example, by first forming the galactose–galactose glycosidic bond and then forming the glycosidic bond to

glucose.

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KEY TERMS

alditols
aldoses
anomeric carbon
anomers
carbohydrates
chair conformation
D-monosaccharide
disaccharides
Fischer projections
furanose
glycoside
glycosidic bond
Haworth projection
hemiacetals
ketoses
L-monosaccharide
Monosaccharides
Mutarotation
oligosaccharide
penultimate carbon
polysaccharides
pyranose
reducing sugar
trisaccharides

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CHAPTER

23 Carboxylic Acids and their Derivatives

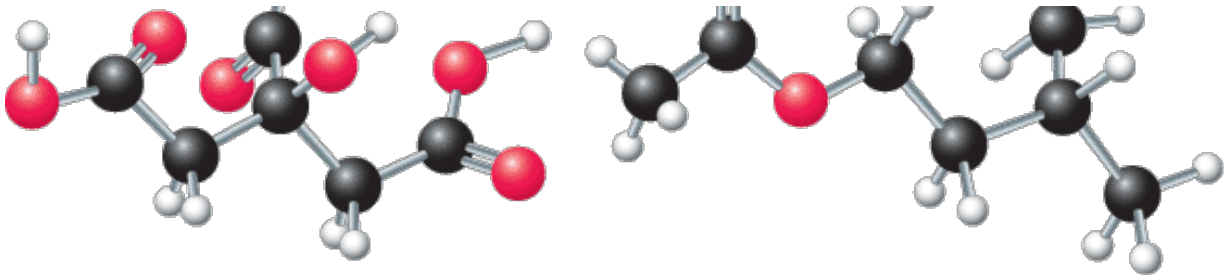
Carboxylic acids and their derivatives are important compounds in our lives because they play a significant role in foods and many biological processes. They also find industrial applications in the form of polyesters, polyamides and more recently as biodiesel fuel. Carboxylic acids are weak acids and are responsible for the sour taste in many foods.

Carboxylic acids and their esters are important flavour components of fruits. Citric acid (below left) is abundant in oranges, lemons, limes, grapefruits and mandarins. Malic acid was so named because it was isolated from apples (apple trees belong to the genus *Malus*). While tartaric acid is found in many fruits, it is an important acid in grapes and a by-product of the wine industry. Carboxylic acids also inhibit or retard microbial growth. This accounts for the use of vinegar (which contains about 5% acetic acid) to pickle (preserve) meats and vegetables. Benzoic acid (additive 210; 211–213 are its sodium, potassium and calcium salts) is commonly used as a food preservative, and citric acid (food acid 330; 331 is its sodium salt) is a common additive in soft drinks. The odour and flavour of fruits are due to a complex mixture of compounds, not just individual esters. However, individual esters can be important contributors to the odour and flavour. For example, the esters of acetic acid are important contributors to the odours of banana (isopentyl acetate, below right, and butyl acetate), pear (pentyl acetate) and orange (octyl acetate). Similarly, the esters of butanoic acid (a very unpleasant smelling acid) are common in apples and pineapples (methyl and ethyl butanoate), pears (pentyl butanoate), and strawberries and apricots (isopentyl butanoate).



In this chapter we will study the chemistry of carboxylic acids and four classes of organic compounds derived from the carboxyl group: acid halides, acid anhydrides, esters and amides.





KEY TOPICS

23.1 Structure and bonding
23.2 Nomenclature
23.3 Physical properties
23.4 Preparation of carboxylic acids
23.5 Reactions of carboxylic acids and derivatives
23.6 Triglycerides

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23.1 Structure and Bonding

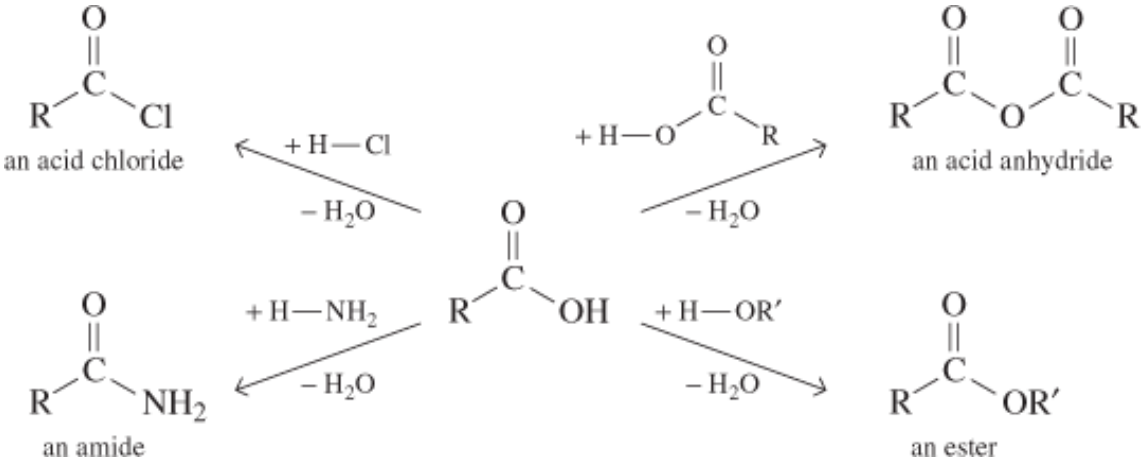
Carboxylic acids and their derivatives have similar structural and bonding features that result in similar reactions. However, their subtle structural differences also lead to quite different reactivities.

Carboxylic Acids

The **carboxylic acid group** comprises the **carboxyl group**, so named because it is made up of a *carbonyl* group and a *hydroxyl* group. The following is a Lewis structure of the carboxyl group, as well as two alternative representations of it:

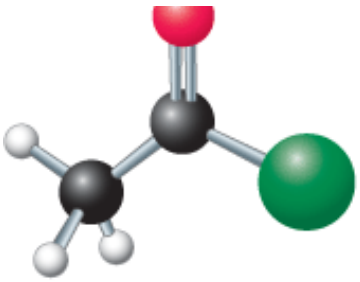


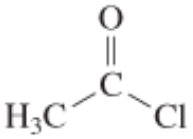
The general formula of an aliphatic carboxylic acid is RCOOH; that of an aromatic carboxylic acid is ArCOOH (Ar = aromatic ring). The general formula for each of the four carboxylic acid derived functional groups is given below, along with a drawing to help you see how the group is formally related to a carboxyl group. In all of these groups, the carbonyl carbon atom is bonded to a hetero atom (an atom other than carbon or hydrogen).



Acid Halides

The **acid halide** (acyl halide) functional group comprises an **acyl group** (RCO—) bonded to a halogen atom. These are sometimes written in abbreviated form as RCOX or ArCOX (where X = halogen). The most common acid halides are the acid chlorides.

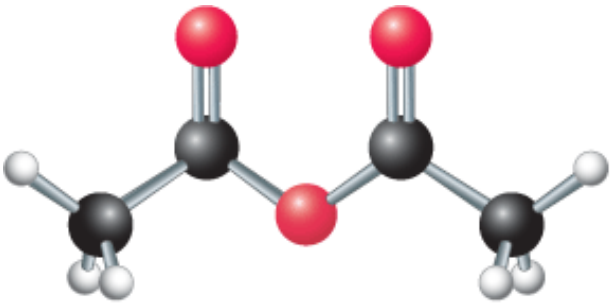


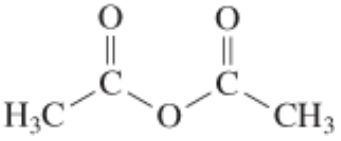


acetyl chloride
(ethanoyl chloride)

Acid Anhydrides

The **acid anhydride** functional group (commonly referred to simply as an anhydride) is two acyl groups bonded to an oxygen atom. The anhydride may be symmetrical (with two identical acyl groups), or it may be mixed (with two different acyl groups).

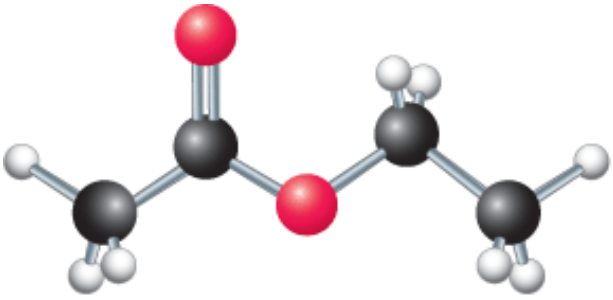


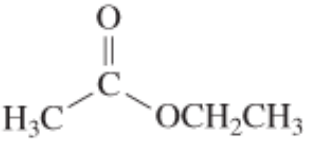


acetic anhydride
(ethanoic anhydride)

Esters of Carboxylic Acids

The **ester** functional group is an acyl group bonded to an —OR or an —OAr group.



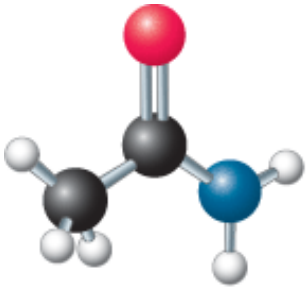


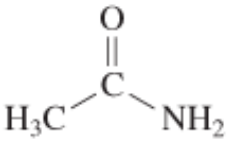
ethyl acetate
(ethyl ethanoate)

When esters are formed between an alcohol and a carboxylic acid group from within the same molecule, they are cyclic and are termed **lactones**.

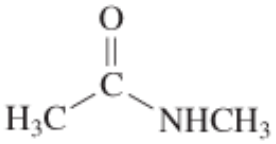
Amides of Carboxylic Acids

The **amide** functional group is an acyl group bonded to a trivalent nitrogen atom. Amides can be classified as primary (N bonded to one carbon atom), secondary (N bonded to two carbon atoms) or tertiary (N bonded to three carbon atoms).

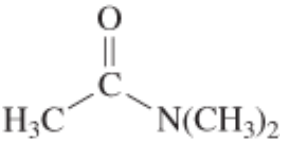




acetamide
(ethanamide)
(a 1° amide)



N-methylacetamide
(*N*-methylethanamide)
(a 2° amide)



N,*N*-dimethylacetamide
(*N*,*N*-dimethylethanamide)
(a 3° amide)

When amides are formed between an amino group and a carboxylic acid group from within the same molecule, they are cyclic and are termed **lactams**. Amide bonds are the key structural feature that joins amino acids together to form polypeptides and proteins (chapter 24).

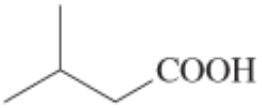
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23.2 Nomenclature

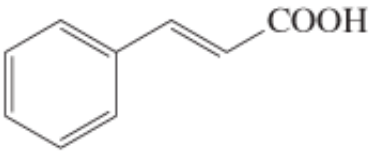
We explained the basic rules of IUPAC nomenclature in chapter 2. Here, we will briefly describe the process for carboxylic acids and their derivatives. We will commence with the carboxylic acids and work progressively through the acid halides, anhydrides, esters and finally the amides.

Carboxylic Acids

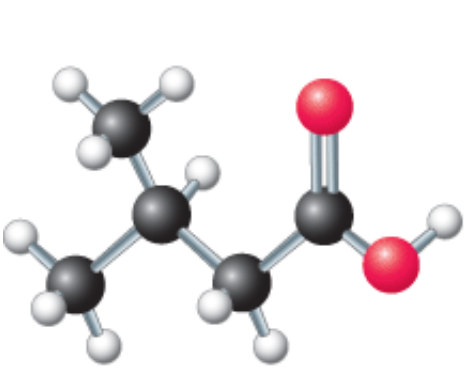
We derive the IUPAC name of a carboxylic acid from that of the longest carbon chain that contains the carboxyl group by dropping the final *e* from the name of the parent alkane and replacing it with *–oic acid*. We number the chain beginning with the carbon atom of the carboxyl group; since it is understood to be C(1), there is no need to give it a number. In the following examples, the common name of each acid is given in parentheses.

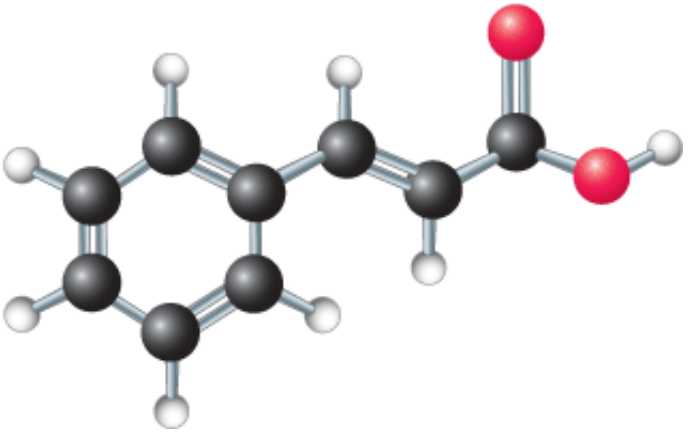


3-methylbutanoic acid
(isovaleric acid)



trans-3-phenylpropenoic acid
(*E*)-3-phenylpropenoic acid
(cinnamic acid)





Many aliphatic carboxylic acids were known long before the development of structural theory and IUPAC nomenclature and were named according to their source or for some characteristic property. Table 23.1 lists several of the unbranched aliphatic carboxylic acids found in the biological world (e.g. figure 23.1), along with the common name of each. Those with 16, 18 and 20 carbon atoms are particularly abundant in fats and oils (section 23.6).

TABLE 23.1 Several aliphatic carboxylic acids and their common names.

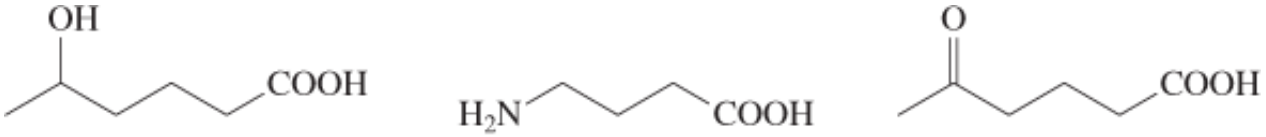
Structure	IUPAC name	Common name	Derivation
HCOOH	methanoic acid	formic acid	Latin: *formica*, ant
CH_3COOH	ethanoic acid	acetic acid	Latin: *acetum*, vinegar
CH_3CH_2COOH	propanoic acid	propionic acid	Greek: *propion*, first fat
$CH_3(CH_2)_2COOH$	butanoic acid	butyric acid	Latin: *butyrum*, butter
$CH_3(CH_2)_3COOH$	pentanoic acid	valeric acid	Latin: *valere*, to be strong

$CH_3(CH_2)_4COOH$	hexanoic acid	caproic acid	Latin: *caper*, goat
$CH_3(CH_2)_6COOH$	octanoic acid	caprylic acid	Latin: *caper*, goat
$CH_3(CH_2)_8COOH$	decanoic acid	capric acid	Latin: *caper*, goat
$CH_3(CH_2)_{10}COOH$	dodecanoic acid	lauric acid	Latin: *laurus*, laurel
$CH_3(CH_2)_{12}COOH$	tetradecanoic acid	myristic acid	Greek: *myristikos*, fragrant
$CH_3(CH_2)_{14}COOH$	hexadecanoic acid	palmitic acid	Latin: *palma*, palm tree
$CH_3(CH_2)_{16}COOH$	octadecanoic acid	stearic acid	Greek: *stear*, solid fat
$CH_3(CH_2)_{18}COOH$	eicosanoic acid	arachidic acid	Greek: *arachis*, peanut



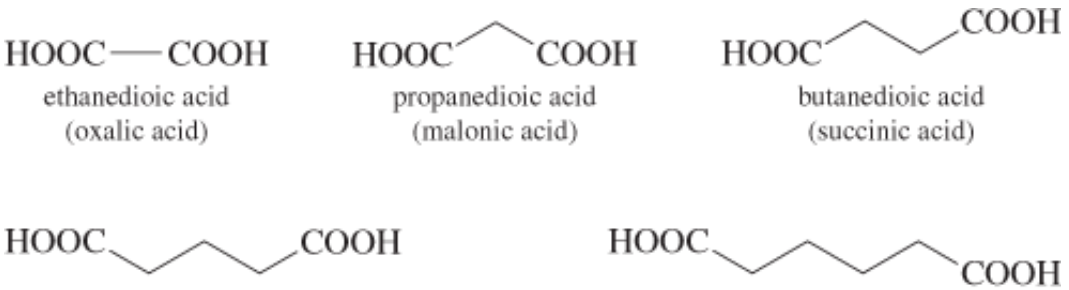
FIGURE 23.1 Formic acid was first obtained in 1670 from the destructive distillation of ants belonging to the genus *Formica*. It is one of the components of their venom.

In the IUPAC system, a carboxyl group takes precedence over most other functional groups (table 23.1, p. 937), including hydroxyl and amino groups, as well as the carbonyl groups of aldehydes and ketones. As illustrated in the following examples, an —OH group of an alcohol is indicated by the prefix *hydroxy*-, an $—NH_2$ group of an amine by *amino*-, and an $=O$ group of an aldehyde or ketone by *oxo*-.



5-hydroxyhexanoic acid | 4-aminobutanoic acid | 5-oxohexanoic acid

Dicarboxylic acids are named by adding the suffix *-dioic*, followed by the word *acid*, to the name of the carbon chain that contains both carboxyl groups. Because the two carboxyl groups can be only at the ends of the parent chain, there is no need to number them. The following are IUPAC names and common names for several important aliphatic dicarboxylic acids.



ethanedioic acid (oxalic acid) | propanedioic acid (malonic acid) | butanedioic acid (succinic acid)

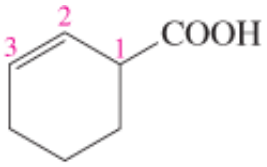
pentanedioic acid (glutaric acid) | hexanedioic acid (adipic acid)

The name *oxalic acid* is derived from one of its sources in the biological world, namely, plants of the genus *Oxalis*, one of which is the soursob (sourgrass) plant, *O. pes-caprae* (figure 23.2). Oxalic acid also occurs in human and animal urine, and calcium oxalate (the calcium salt of oxalic acid) is a major component of kidney stones. Adipic acid is one of the two monomers required for the synthesis of the polymer nylon 6,6.



FIGURE 23.2 The soursob plant is an introduced plant and is classified as a weed in many parts of Australia. It may cause oxalate poisoning if eaten by livestock.

A carboxylic acid containing a carboxyl group bonded to a cycloalkane ring is named by giving the name of the ring and adding the suffix *-carboxylic acid*. The atoms of the ring are numbered beginning with the carbon atom bearing the —COOH group.

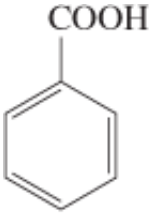


cyclohex-2-enecarboxylic acid

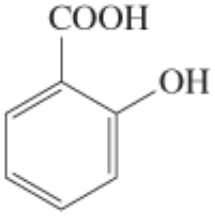


trans-cyclopentane-1,3-dicarboxylic acid

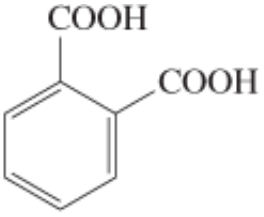
The simplest aromatic carboxylic acid is benzoic acid. Derivatives are named by using numbers and prefixes to show the presence and location of substituents relative to the carboxyl group. Certain aromatic carboxylic acids have common names by which they are more usually known. For example, 2-hydroxybenzoic acid is more often called salicylic acid, named because it was first obtained from the bark of the willow, a tree of the genus *Salix*. Aromatic dicarboxylic acids are named by adding the words *dicarboxylic acid* to *benzene*. Examples are benzene-1,2-dicarboxylic acid and benzene-1,4-dicarboxylic acid; these are more usually known by their common names, phthalic acid and terephthalic acid, respectively. Terephthalic acid is one of the two organic components required for the synthesis of PET (polyethylene terephthalate) plastic bottles.



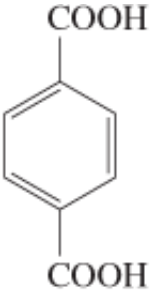
benzoic acid



2-hydroxybenzoic acid (salicylic acid)



benzene-1,2-dicarboxylic acid (phthalic acid)



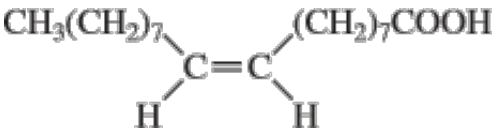
benzene-1,4-dicarboxylic acid (terephthalic acid)

WORKED EXAMPLE 23.1

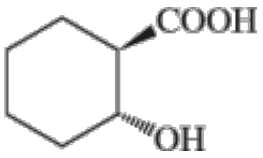
Naming Carboxylic Acids

Write the IUPAC name for each of the following carboxylic acids.

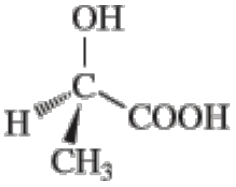
(a)



(b)



(c)



Analysis

(a) First determine the number of carbon atoms in the longest chain and then the position of any substituent or alkene (start numbering from the acid group). Where necessary, indicate the stereochemistry.

(b) This should be named as a cycloalkanecarboxylic acid.

(c) Determine the stereochemistry of the chiral centre (see section 17.3).

Solution

Common names are given in parentheses.

(a) *Z*-octadec-9-enoic acid (oleic acid, *cis*-octadec-9-enoic acid)

(b) (*R*, *R*)-2-hydroxycyclohexanecarboxylic acid

(c) (*R*-2-hydroxypropanoic acid ((*R*)-lactic acid or D-lactic acid)

Is our answer reasonable?

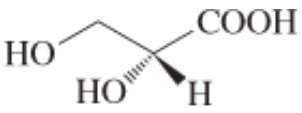
To check your answer, draw a structure from the name and see if it matches the structure given. Is this the only structure possible from your answer?

PRACTICE EXERCISE 23.1

Each of the following compounds has a well-recognised common name. A derivative of glyceric acid is an intermediate in glycolysis. Maleic acid is an intermediate in the tricarboxylic acid (TCA) cycle (also known as the citric acid or Krebs cycle). Mevalonic acid is an intermediate in the

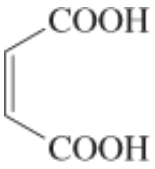
biosynthesis of steroids.

(a)



glyceric acid

(b)



maleic acid

(c)

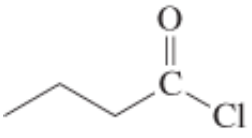


mevalonic acid

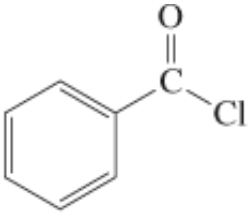
Write the IUPAC name for each of these compounds. Be certain to show the configuration of each.

Acid Halides

Acid halides are named by changing the suffix *-ic acid* in the name of the parent carboxylic acid to *-yl halide*.



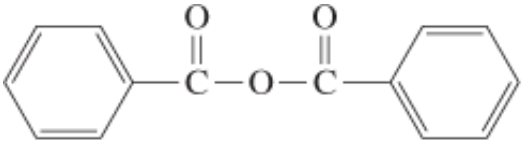
butanoyl chloride



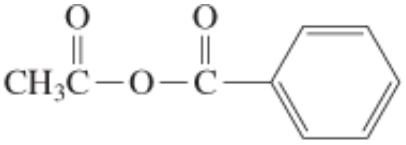
benzoyl chloride

Acid Anhydrides

Acid anhydrides are named by replacing the word *acid* with *anhydride*. When the anhydride is not symmetrical, both acid groups are named.



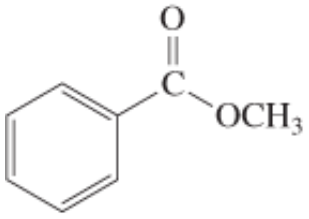
benzoic anhydride



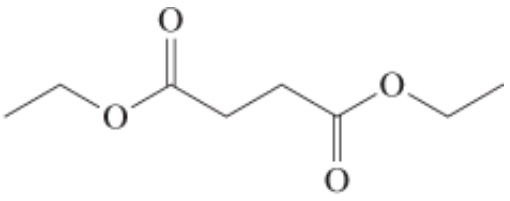
acetic benzoic anhydride
(a mixed anhydride)

Esters and Lactones

Both IUPAC and common names of esters are derived from the names of the parent carboxylic acids. The alkyl or aryl group bonded to the oxygen atom is named first. This is followed, as a separate word, by the name of the acid, in which the suffix *-ic acid* is replaced by the suffix *-ate*.



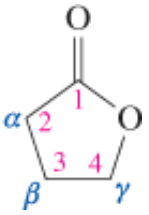
methyl benzoate



diethyl butanedioate
(diethyl succinate)

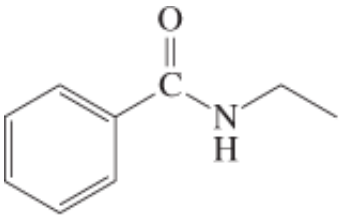
The IUPAC name of a lactone is formed by dropping the suffix *-oic acid* from the name of the parent carboxylic acid and adding the suffix *-olactone*. The common name is derived similarly. The location of the oxygen atom in the ring is indicated by a number if the IUPAC name of the acid is used and by a Greek letter (α, β, γ, δ, ε etc.) if the common name of the acid is used.

4-butanolactone
(a γ-lactone)

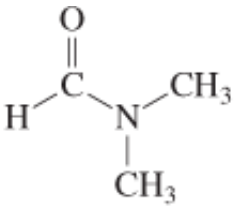


Amides and Lactams

Amides are named by dropping the suffix *-oic acid* from the IUPAC name of the parent acid, or *-ic acid* from its common name, and adding *-amide*. If the nitrogen atom of an amide is bonded to an alkyl or aryl group, the group is named and its location on the nitrogen atom is indicated by *N*-. Two alkyl or aryl groups on the nitrogen atom are indicated by *N, N*-di- if the groups are identical or by *-N*-alkyl-*N*-alkyl if they are different.

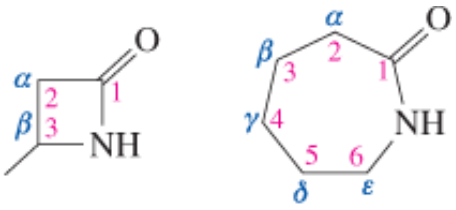


N-ethylbenzamide



N,N-dimethylformamide

Cyclic amides are given the special name lactam. Their common names are derived in the same way as lactones except that the suffix is *-olactam*.



3-butanolactam (a β-lactam) 6-hexanolactam (an ε-lactam)

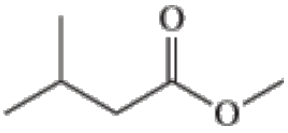
The compound 6-hexanolactam (caprolactam) is a key intermediate in the synthesis of nylon 6 (section 26.3, p. 1125). *Note:* The 'hex' in hexanolactam refers to the number of carbon atoms, rather than the ring size.

WORKED EXAMPLE 23.2

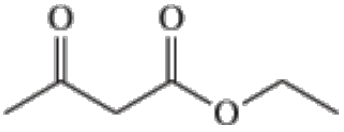
Nomenclature of Carboxylic Acid Derivatives

Write the IUPAC name for each of the following compounds.

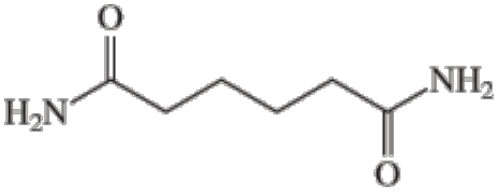
(a)



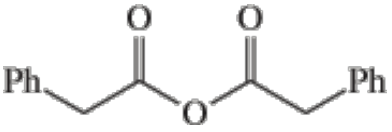
(b)



(c)



(d)



Analysis

First identify the functional group present and then the acid from which it is derived. The ketone group in (b) must be named with the prefix *oxo*. Compound (d) has been derived from a substituted acetic acid.

Solution

Common names and derivations are given in parentheses.

(a) methyl 3-methylbutanoate (methyl isovalerate, from isovaleric acid)

(b) ethyl 3-oxobutanoate (ethyl acetoacetate, from acetoacetic acid; ethyl β-ketobutyrate

from β-ketobutyric acid)

(c) hexanediamide (adipamide, from adipic acid)

(d) phenylethanoic anhydride (phenylacetic anhydride, from phenylacetic acid)

Is our answer reasonable?

To check your answer, draw a structure from the name and see if it matches the structure given.

PRACTICE EXERCISE 23.2

Draw a structural formula for each of the following compounds.

(a) *N*-cyclohexylacetamide

(b) butyl acetate

(c) cyclobutyl butanoate

(d) *N*-(2-octyl)benzamide

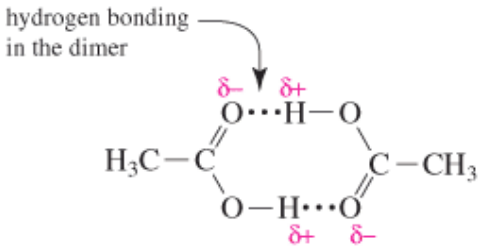
(e) diethyl adipate

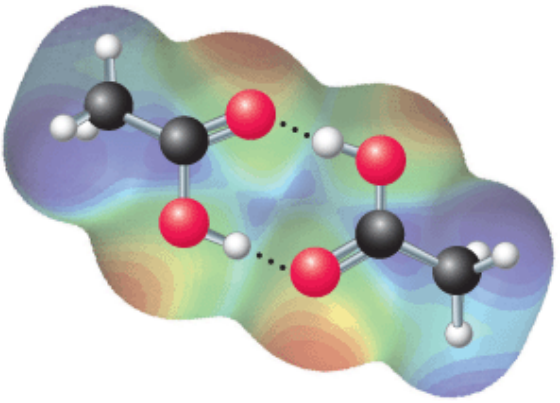
(f) propanoic anhydride

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23.3 Physical Properties

In the liquid and solid states, carboxylic acids are associated by intermolecular hydrogen bonding into dimers, as shown below for acetic acid.





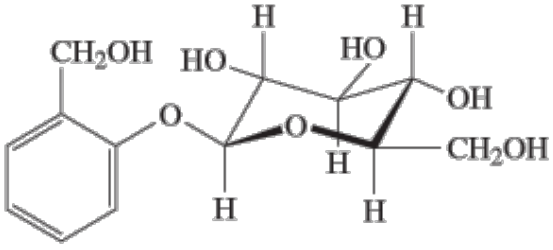
Chemical Connections

Carboxylic Acids and Derivatives in Medicine

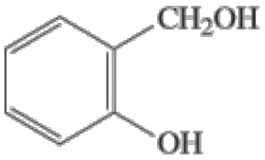
From tree bark to anti-inflammatory agents

The first drug developed for widespread use was aspirin, today's most common pain reliever. The story of the development of this modern pain reliever goes back more than 2000 years when the Greek physician Hippocrates recommended chewing the bark of the willow tree to alleviate the pain of childbirth and to treat eye infections.

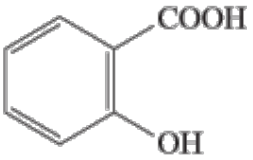
The active component of willow bark was found to be salicin, a compound composed of salicyl alcohol joined to a unit of β-D-glucose (chapter 22). Hydrolysis of salicin in aqueous acid gives salicyl alcohol, which can then be oxidised to salicylic acid, an even more effective reliever of pain, fever and inflammation than salicin, and without an extremely bitter taste.



salicin

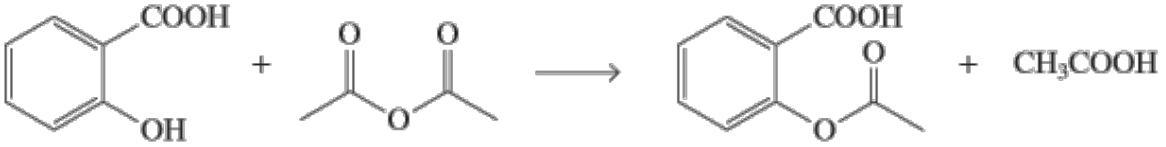


salicyl alcohol



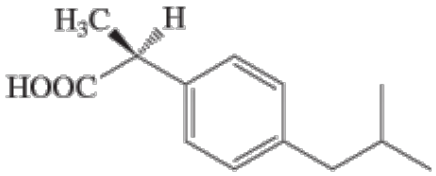
salicylic acid

In 1883, chemists at Bayer in Germany prepared acetylsalicylic acid (aspirin) and found it to be effective in relieving the pain and inflammation of rheumatoid arthritis. It also did not have salicylic acid's unpleasant side-effect of causing severe irritation of the mucous membrane lining the stomach. Bayer began large-scale production of aspirin in 1899.

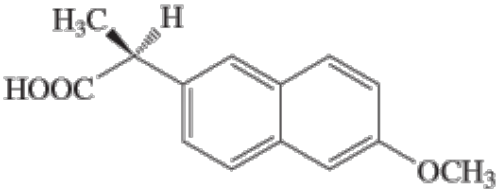


salicylic acid | acetic anhydride | acetyl salicylate (aspirin)

In the 1960s, in a search for more effective and less irritating analgesics and anti-inflammatory drugs, the Boots Pure Drug Company in England discovered an even more potent compound, ibuprofen, and soon thereafter Syntex Corporation in the United States developed naproxen.



(*S*)-ibuprofen



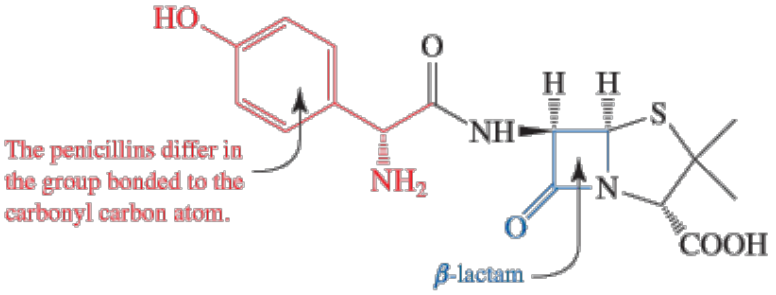
(*S*)-naproxen

In the early 1970s, scientists discovered that aspirin acts by inhibiting cyclooxygenase (COX), a key enzyme in the conversion of arachidonic acid to prostaglandins. Prostaglandins are biochemical regulators with many important functions including stimulating inflammation and inducing fever. Ibuprofen and naproxen are believed to act by inhibiting the COX enzyme.

The discovery that these drugs owe their effectiveness to the inhibition of COX opened an entirely new avenue for drug research. If we know more about the structure and function of this key enzyme, it might be possible to design and discover even more effective nonsteroidal anti-inflammatory drugs for the treatment of rheumatoid arthritis and other inflammatory diseases.

From mould to antibiotics

The penicillins were discovered in 1928 by the Scottish bacteriologist Sir Alexander Fleming. As a result of the brilliant experimental work of Sir Howard Florey, an Australian pathologist, and Ernst Chain, a German chemist who fled Nazi Germany, penicillin G was introduced into the practice of medicine in 1943. For their pioneering work in developing one of the most effective antibiotics of all time, Fleming, Florey and Chain were awarded the Nobel Prize in physiology or medicine in 1945. The penicillins owe their antibacterial activity to a common mechanism that inhibits the biosynthesis of a vital part of bacterial cell walls. The structural feature common to all penicillins is a lactam ring fused to a five-membered ring containing one sulfur atom and one nitrogen atom.



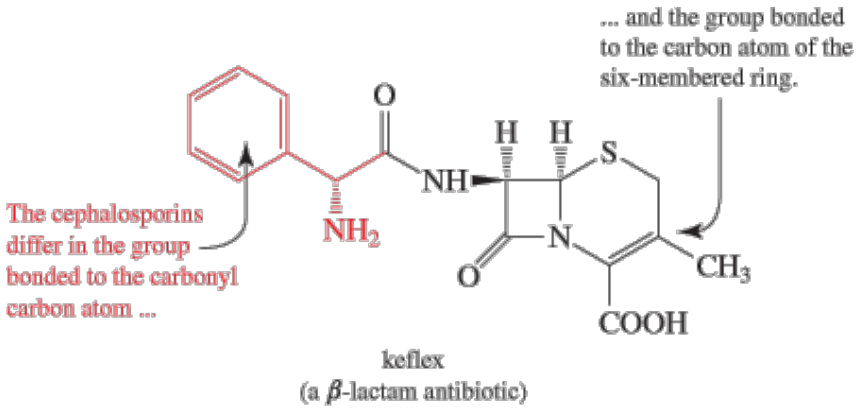
amoxicillin
(a *β*-lactam antibiotic)

Soon after the penicillins were introduced into medical practice, penicillin-resistant strains of bacteria began to appear and have since proliferated. One approach to combating resistant strains is to synthesise newer, more effective penicillins. Another approach is to search for newer, more effective β-lactam antibiotics. The most effective of these discovered so far are the cephalosporins, the first of which was isolated from the fungus *Cephalosporium acremonium*. This class of β-lactam antibiotics has an even broader spectrum of antibacterial activity than the penicillins and is effective against many penicillin-resistant bacterial strains.

From mouldy clover to anticoagulants

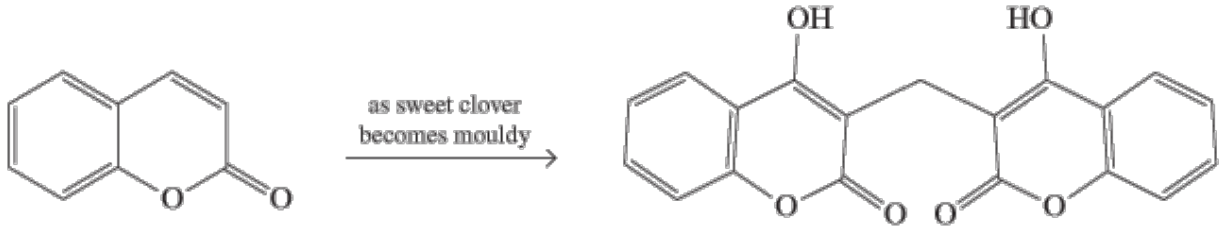
In 1933, a disgruntled farmer delivered a pail of unclotted blood to the laboratory of Dr Karl Link at the University of Wisconsin and told tales of cows bleeding to death from minor cuts. Over the next couple of years, Link and his collaborators discovered that, when cows are fed mouldy clover, their blood clotting is inhibited. From the mouldy clover, Link isolated the anticoagulant dicoumarol, a substance that delays or prevents blood from clotting by interfering with vitamin K activity. Within a few years after its discovery,

dicoumarol became widely used to treat victims of heart attack and others at risk of developing blood clots.



keflex
(a β-lactam antibiotic)

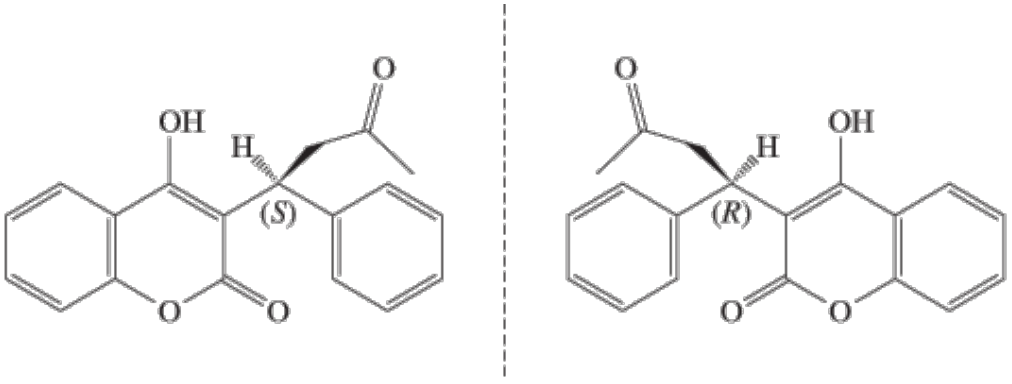
Coumarin is a lactone (cyclic ester) that gives clove its pleasant smell. It does not interfere with blood clotting and has been used as a flavouring agent in the food industry. Coumarin is converted to dicoumarol as sweet clover becomes mouldy.



coumarin
(from sweet clover)

dicoumarol
(an anticoagulant)

In a search for even more potent anticoagulants, Link developed warfarin, now used primarily as a rat poison: When rats consume warfarin, their blood fails to clot, and they bleed to death. Sold under the brand name Coumadin®, warfarin is also used as a blood thinner in humans. The commercial product is a racemic mixture, but the *S*-enantiomer is more active than the *R*-enantiomer.



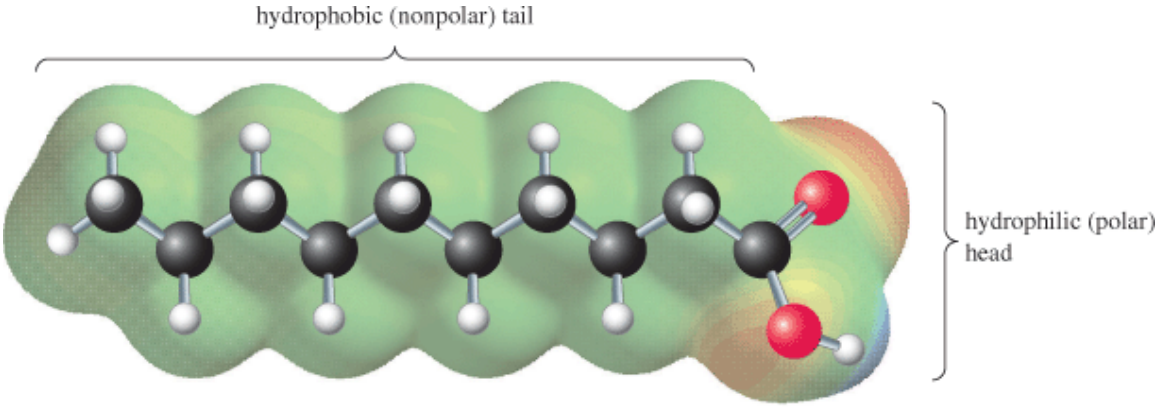
warfarin
(a synthetic anticoagulant)

Carboxylic acids have significantly higher boiling points than other types of organic compounds with similar numbers of electrons (and, therefore, comparable molar mass), such as alcohols, aldehydes and ketones. For example, butanoic acid (table 23.2) has a higher boiling point than either pentan-1-ol or pentanal. This is because carboxylic acids are polar and form very strong intermolecular hydrogen bonds.

TABLE 23.2 Boiling points and solubilities in water of selected carboxylic acids, alcohols and aldehydes of comparable molar mass.

Structure	Name	Molar mass	Number of electrons	Boiling point (°C)	Solubility (g/100 mL H_2O)
CH_3COOH	acetic acid	60.1	32	118	infinite
$CH_3CH_2CH_2OH$	propan-1-ol	60.1	34	97	infinite
CH_3CH_2CHO	propanal	58.1	32	48	16
$CH_3(CH_2)_2COOH$	butanoic acid	88.1	48	163	infinite
$CH_3(CH_2)_3CH_2OH$	pentan-1-ol	88.1	50	137	2.7
$CH_3(CH_2)_3CHO$	pentanal	86.1	48	103	slight
$CH_3(CH_2)_4COOH$	hexanoic acid	116.2	64	205	1.0
$CH_3(CH_2)_5CH_2OH$	heptan-1-ol	116.2	66	176	0.2
$CH_3(CH_2)_5CHO$	heptanal	114.1	64	153	0.1

Carboxylic acids also interact with water molecules by hydrogen bonding through both their carbonyl and hydroxyl groups. Because of these hydrogen bonds, carboxylic acids are more soluble in water than are alcohols, ethers, aldehydes and ketones of comparable molar mass. The solubility of a carboxylic acid in water generally decreases as its molar mass increases (table 23.2). We account for this trend in the following way. A carboxylic acid has two regions of different polarity — a polar hydrophilic carboxyl group and, except for formic acid, a nonpolar hydrophobic hydrocarbon chain. The **hydrophilic** (water-loving) carboxyl group increases water solubility; the **hydrophobic** (water-hating) hydrocarbon chain decreases water solubility.



decanoic acid
(solubility = 0.2 g/100 mL H_2O)

The first four aliphatic carboxylic acids (formic, acetic, propanoic and butanoic acids) are infinitely soluble in water because the hydrophilic character of the carboxyl group more than compensates for the hydrophobic character of the hydrocarbon chain. As the size of the hydro-carbon chain increases relative to the size of the carboxyl group, water solubility decreases. The solubility of hexanoic acid in water is 1.0 g/100 g water; that of decanoic acid is only 0.2 g/100 g water.

One other physical property of carboxylic acids must be mentioned. The liquid carboxylic acids, from propanoic acid to decanoic acid, have foul odours, although not as bad as those of thiols. Butanoic acid is found in rancid butter, stale parmesan cheese, stale perspiration and vomit. Pentanoic acid smells even worse — and goats, which secrete C_6, C_8 and C_{10} acids, are not famous for their pleasant odours.

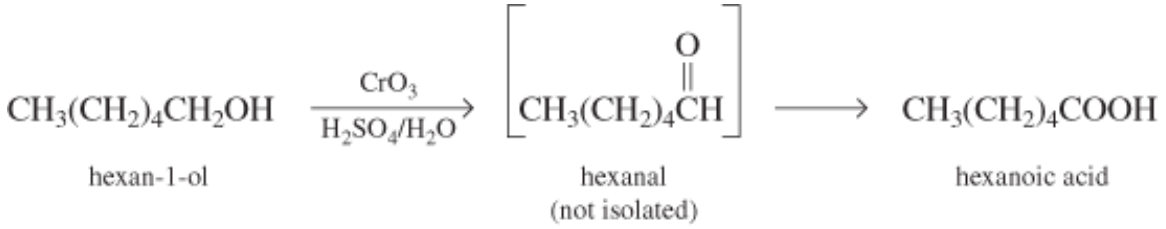
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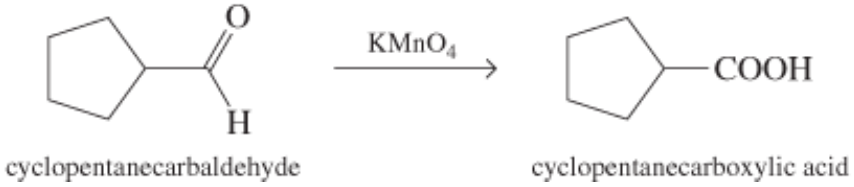
23.4 Preparation of Carboxylic Acids

There are many methods available for the preparation of carboxylic acids. Some of these will be discussed briefly here and in more detail elsewhere in this text.

Oxidation of Primary Alcohols and Aldehydes

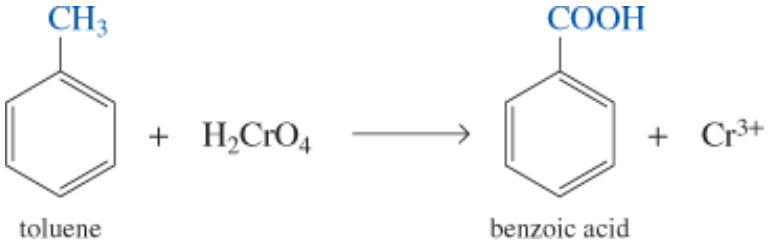
Primary alcohols and aldehydes are readily oxidised to carboxylic acids by a variety of common oxidising agents (discussed in greater detail in sections 19.2 and 21.5).





Oxidation of Alkylbenzenes

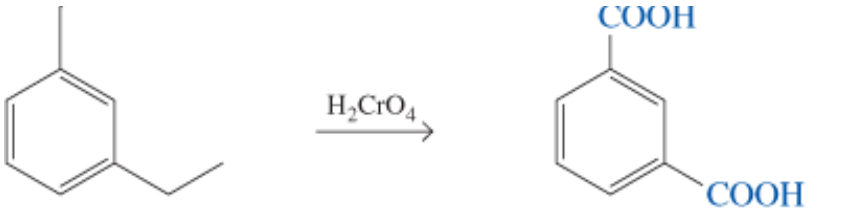
Although benzene is unaffected by strong oxidising agents, such as $KMnO_4$ and H_2CrO_4, alkylbenzenes are oxidised at the **benzylic carbon** (the carbon atom attached to the benzene ring) to give carboxylic acids. When we treat toluene with these oxidising agents under vigorous conditions, the side-chain methyl group is oxidised to a carboxyl group to give benzoic acid.



Ethylbenzene and isopropylbenzene are also oxidised to benzoic acid under these conditions. The side chain of *tert*-butylbenzene, which has no **benzylic hydrogen** (a hydrogen atom bonded to a benzylic carbon atom), is not affected by these oxidising conditions. From these observations, we can generalise that:

- if a benzylic hydrogen atom exists, the benzylic carbon atom is oxidised to a carboxyl group and all other carbon atoms of the side chain are removed
- if no benzylic hydrogen atom exists, as in *tert*-butylbenzene, the side chain is not oxidised
- if more than one alkyl side chain exists, each is oxidised to a carboxylic acid group.

Oxidation of 1,3-diethylbenzene gives benzene-1,3-dicarboxylic acid, more commonly named isophthalic acid.

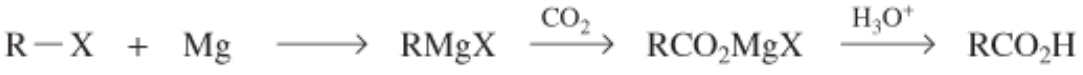


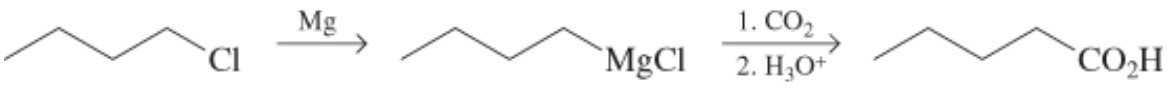
1,3-diethylbenzene

benzene-1,3-dicarboxylic acid
(isophthalic acid)

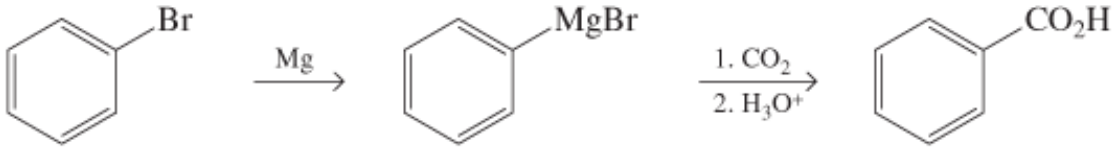
Carbonation of Grignard Reagents

Grignard reagents (section 21.5) react with carbon dioxide to give a magnesium carboxylate that is converted into the carboxylic acid by acidification. This reaction is applicable to alkyl and aryl halides and produces carboxylic acids with one carbon atom more than the original organohalide. A general reaction is given on the next page, followed by two specific examples.



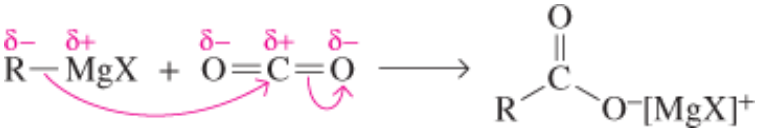


1-chlorobutane — butylmagnesium chloride — pentanoic acid (80% overall)



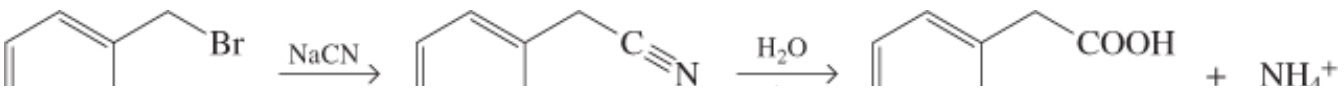
bromobenzene — phenylmagnesium bromide — benzoic acid (85% overall)

This reaction follows the same process as that in the reaction of Grignard reagents with aldehydes and ketones (section 21.5).



Formation and Hydrolysis of Nitriles

Another method of preparing carboxylic acids from haloalkanes is by the formation and subsequent hydrolysis of **nitriles** (compounds containing a cyano group, —C≡N). Like the carbonation reaction described above, this process produces carboxylic acids with one carbon atom more than the original haloalkane. The nitrile is formed by a nucleophilic substitution reaction (section 18.2) by cyanide ions on a haloalkane. The resulting nitrile can then be hydro-lysed by reaction with either hot aqueous acid or base.

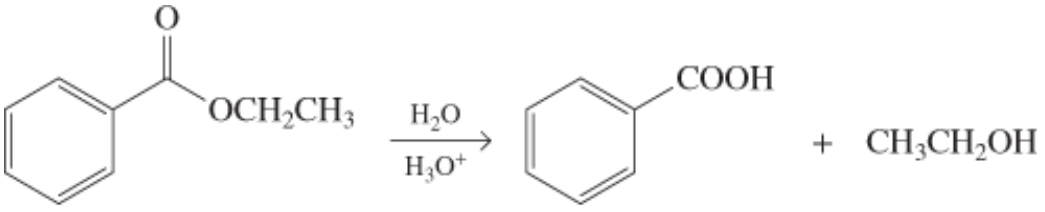




benzyl bromide phenylacetonitrile phenylacetic acid

Hydrolysis of Carboxylic Acid Derivatives

Carboxylic acids can also be obtained by the hydrolysis of carboxylic acid derivatives, particularly esters and amides — for example:



ethyl benzoate benzoic acid ethanol

The chemistry of this reaction will be discussed in detail in section 23.5.

WORKED EXAMPLE 23.3

Formation of Carboxylic Acids

Show how each of the following compounds can be converted into 3-methylbutanoic acid.

(a) 3-methylbutanal

(b) 1-bromo-2-methylpropane

Analysis

First, draw the structures of the product and the starting material. Now, compare the two compounds and determine what changes are required to go from the starting material to the product. The product has one more oxygen atom than (a), suggesting that oxidation is required. The product has one more carbon atom than (b), which means that we need to introduce another carbon atom; this might be done via a Grignard reaction or by the hydrolysis of a nitrile.

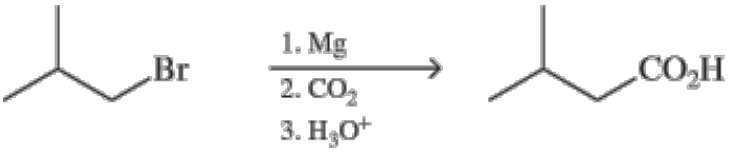
Solution

(a)



A range of oxidising agents can be used, including $KMnO_4$ solution or chromic acid, H_2CrO_4. PCC (pyridinium chlorochromate) is not suitable.

(b)



or



Is our answer reasonable?

In each case, check that the carbon skeleton is consistent with the number of carbon atoms. You should also check that the reagents chosen are appropriate for the proposed transformations.

PRACTICE EXERCISE 23.3

Show how each of the following compounds can be converted into benzoic acid.

(a) benzyl alcohol (phenylmethanol)

(b) iodobenzene

WORKED EXAMPLE 23.4

Oxidation at Benzylic Carbon Atoms

Draw the structural formula for the product of vigorous oxidation by H_2CrO_4 of each of the following compounds.

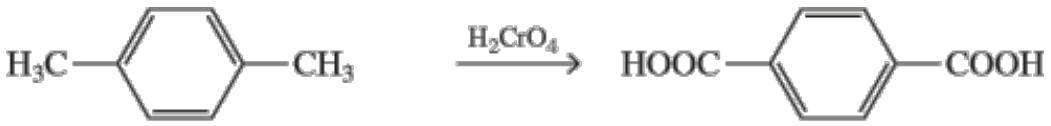
(a) 1,4-dimethylbenzene (*p*-xylene)

(b) 1-*tert*-butyl-4-ethylbenzene

Analysis Start by checking whether the alkyl groups have at least one benzylic hydrogen atom. If they do, then chromic acid oxidises them to carboxylic acid groups, —COOH. If not, then it is not oxidised.

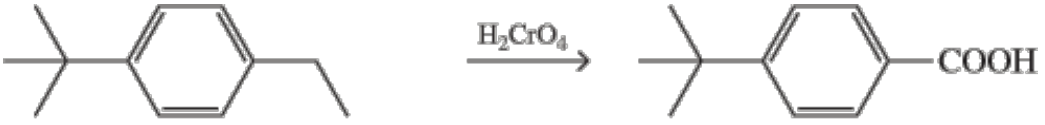
Solution

(a)



1,4-dimethylbenzene (*p*-xylene) → benzene-1,4-dicarboxylic acid (terephthalic acid)

(b)



1-*tert*-butyl-4-ethylbenzene → 4-*tert*-butylbenzoic acid

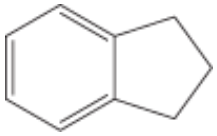
Is our answer reasonable?

Check that the carbon skeleton is consistent with the number of carbon atoms. Check also that the oxidation has occurred at the benzylic carbon atom.

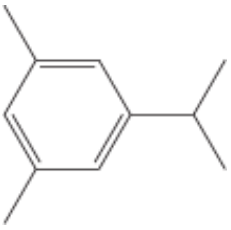
PRACTICE EXERCISE 23.4

Predict the products resulting from vigorous oxidation of each of the following compounds by H_2CrO_4.

(a)



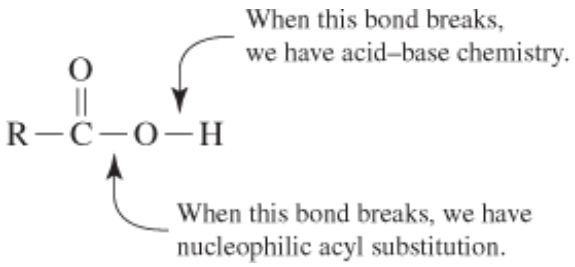
(b)



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23.5 Reactions of Carboxylic Acids and Derivatives

The reactions of carboxylic acids can be classified into two general types: (a) acid–base and (b) nucleophilic acyl substitution:



We will commence this section with the acid–base chemistry of carboxylic acids. We will then study the nucleophilic acyl substitution of the carboxylic acids and their derivatives.

Acidity

Although carboxylic acids are weak acids, relative to the mineral acids, they are significantly more acidic than alcohols and phenols (sections 19.2 and 19.3). At this point, it may be worthwhile to review chapter 11 and the discussion of the position of equilibrium in acid–base reactions.

Acid Ionisation Constants

Values of K_a for most unsubstituted aliphatic and aromatic carboxylic acids are between 10^{-4} and 10^{-5}. The value of K_a for acetic acid, for example, is 1.8×10^{-5}, so the pK_a of acetic acid is 4.74.

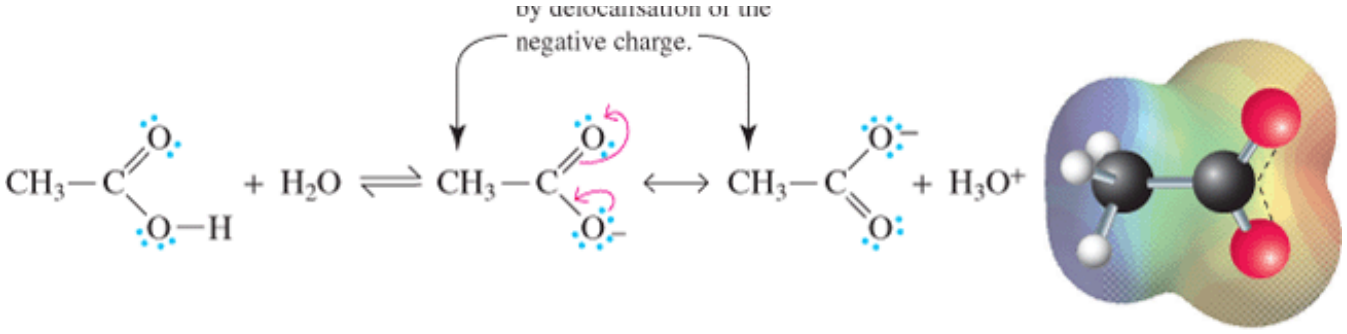
$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

$$pK_a = 4.74$$

Carboxylic acids (pK_a = 4-5) are stronger acids than alcohols (pK_a = 16-18) because resonance stabilises the carboxylate anion by delocalising its negative charge. No comparable resonance stabilisation exists in alkoxide ions.

These contributing structures are equivalent;
the carboxylate anion is stabilised
by delocalisation of the



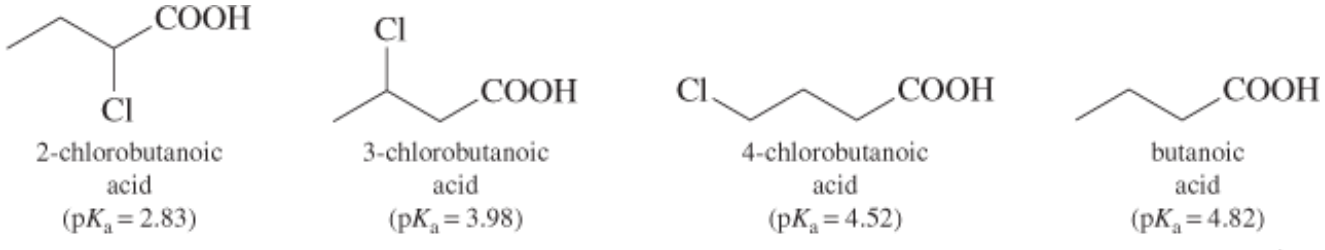
The electron density map shows the negative charge equally delocalised on the two carboxylate oxygen atoms.

Substitution at the α-carbon with an atom or a group of atoms of higher electronegativity than carbon increases the acidity of carboxylic acids, often by several orders of magnitude. Compare, for example, the acidities of acetic acid (pK_a = 4.74) and chloroacetic acid (pK_a = 2.85). A single chlorine substituent on the α-carbon atom increases the acidity constant by nearly 100 times! Both dichloroacetic acid and trichloroacetic acid are stronger acids than phosphoric acid (pK_a = 2.1).

Formula:	CH_3COOH	$ClCH_2COOH$	$Cl_2CHCOOH$	Cl_3CCOOH
Name:	acetic acid	chloroacetic acid	dichloroacetic acid	trichloroacetic acid
pK_a:	4.74	2.85	1.48	0.70

Increasing acid strength

The acid-strengthening effect of halogen substitution falls off rather rapidly with increasing distance from the carboxyl group. Although the acidity constant of 2-chlorobutanoic acid (pK_a = 2.83) is 100 times that of butanoic acid, the acidity constant of 4-chlorobutanoic acid (pK_a = 4.52) is only about twice that of butanoic acid.



2-chlorobutanoic acid (pK_a = 2.83)

3-chlorobutanoic acid (pK_a = 3.98)

4-chlorobutanoic acid (pK_a = 4.52)

butanoic acid (pK_a = 4.82)

Decreasing acid strength

Ring substituents have marked effects on the acidities of aromatic carboxylic acids through a combination of inductive and resonance effects (a similar effect was described for phenols in section 19.3). Electron-withdrawing groups, such as chloro, cyano and nitro, withdraw electron density from the aromatic ring, weaken the O—H bond and stabilise the carboxylate ion. Conversely, electron-donating groups, such as amino, alkoxy and alkyl, increase the electron density of the aromatic ring and destabilise the carboxylate ion. Table 23.3 lists the pK_a values of some aromatic acids.

TABLE 23.3 The pK_a values of some aromatic acids.

Name	pK_a
2,4,6-trinitrobenzoic acid	0.65

4-nitrobenzoic acid	3.43
4-chlorobenzoic acid	4.00
benzoic acid	4.20
4-methylbenzoic acid	4.37
4-methoxybenzoic acid	4.50

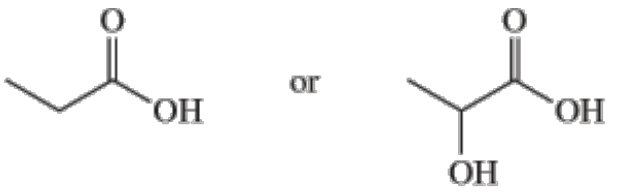
Increasing acid strength

WORKED EXAMPLE 23.5

Acidity

Which acid in each of the following sets is the stronger?

(a)



propanoic acid

2-hydroxypropanoic acid (lactic acid)

(b)



2-hydroxypropanoic acid (lactic acid)

2-oxopropanoic acid (pyruvic acid)

Analysis

First identify the difference between the two acids. In both cases it is the substituent on the α-carbon atom. The compound with the better electron-withdrawing group will be the stronger acid.

Solution

(a) The stronger acid is 2-hydroxypropanoic acid because of the electron-withdrawing inductive effect of the hydroxyl oxygen atom.

(b) The stronger acid is 2-oxopropanoic acid because the electron-withdrawing inductive effect of the carbonyl oxygen atom is greater than that of the hydroxyl oxygen atom.

Is our answer reasonable?

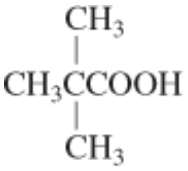
Check the pK_a values of the acids; a lower pK_a value means a stronger acid — propanoic acid

(pK_a = 4.89), 2-hydroxypropanoic acid (pK_a = 3.85) and 2-oxopropanoic acid (pK_a = 2.39).

PRACTICE EXERCISE 23.5

Match each of the following compounds with its appropriate pK_a value: 5.03, 3.85 or 0.22.

(a)



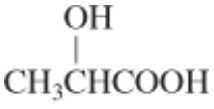
2,2-dimethyl-propanoic acid

(b)



trifluoro-acetic acid

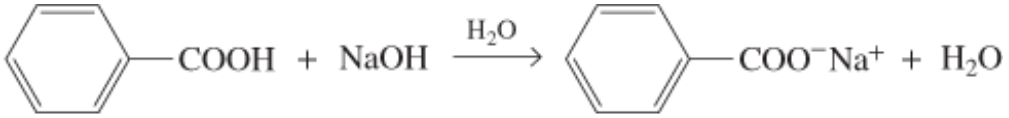
(c)



2-hydroxy-propanoic acid (lactic acid)

Reaction with Bases

All carboxylic acids, whether soluble or insoluble in water, react with NaOH, KOH and other strong bases to form water-soluble salts.

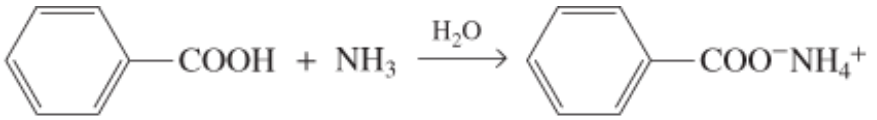


benzoic acid (slightly soluble in water)

sodium benzoate (solubility = 60 g/100 mL H_2O)

Sodium benzoate, a fungal growth inhibitor, is often added to baked goods ‘to retard spoilage’. Calcium propanoate is used for the same purpose.

Carboxylic acids also form water-soluble salts with ammonia and amines.



benzoic acid
(slightly soluble in water)

ammonium benzoate
(solubility = 20 g/100 mL H_2O)

Carboxylic acids react with sodium hydrogencarbonate and sodium carbonate to form water-soluble sodium salts and carbonic acid (a relatively weak acid). Carbonic acid, in turn, decomposes to give water and carbon dioxide, which evolves as a gas.

$$CH_3COOH + Na^+HCO_3^- \xrightarrow{H_2O} CH_3COO^-Na^+ + H_2CO_3$$

$$H_2CO_3 \longrightarrow CO_2 + H_2O$$

$$CH_3COOH + Na^+HCO_3^- \longrightarrow CH_3COO^-Na^+ + CO_2 + H_2O$$

Salts of carboxylic acids are named in the same way as salts of inorganic acids: Name the cation first and then the anion. Derive the name of the anion from the name of the carboxylic acid by dropping the suffix *-ic acid* and adding the suffix *-ate*. For example, the name of $CH_3CH_2COO^-Na^+$ is sodium propanoate, and that of $CH_3(CH_2)_{14}COO^-Na^+$ is sodium hexa decanoate (sodium palmitate).

Because carboxylic acid salts are water soluble, we can convert water-insoluble carboxylic acids to water-soluble alkali metal or ammonium salts and then extract them into aqueous solution. In turn, we can transform the salt into the free carboxylic acid by adding a strong acid, such as HCl or H_2SO_4. These reactions allow us to separate water-insoluble carboxylic acids from water-insoluble neutral compounds.

Figure 23.3 shows a flowchart for the separation of benzoic acid, a water-insoluble carboxylic acid, from benzyl alcohol, a water-insoluble nonacidic compound. First, we dissolve the mixture of benzoic acid and benzyl alcohol in diethyl ether. Next, we shake the ether solution with aqueous NaOH to convert benzoic acid to its water-soluble sodium salt. Then we separate the ether from the aqueous phase. Distillation of the ether solution yields first diethyl ether (bp = 35 °C) and then benzyl alcohol (bp = 205 °C). When we acidify the aqueous solution with HCl, benzoic acid precipitates as a water-insoluble solid (mp = 122 °C) and is recovered by filtration. Similar separation schemes were described previously for phenols (section 19.3) and amines (section 19.7).

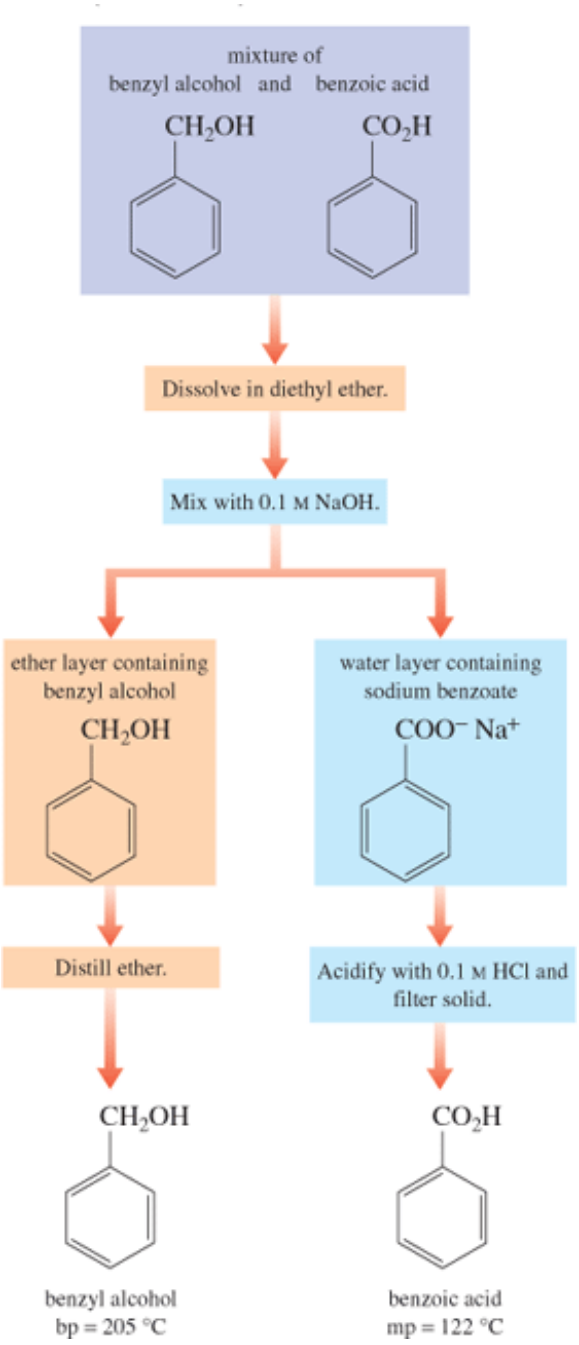
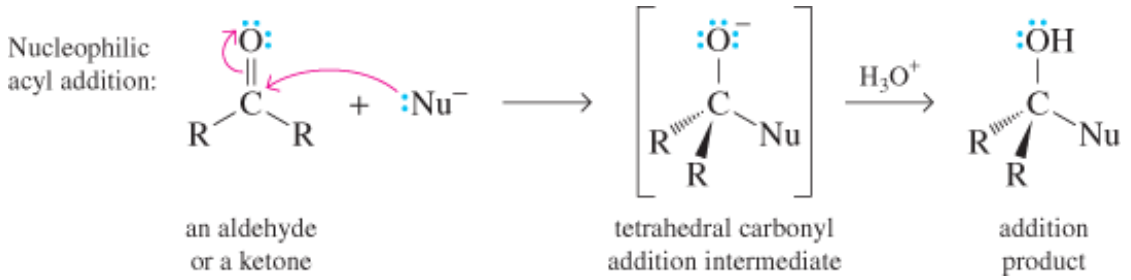


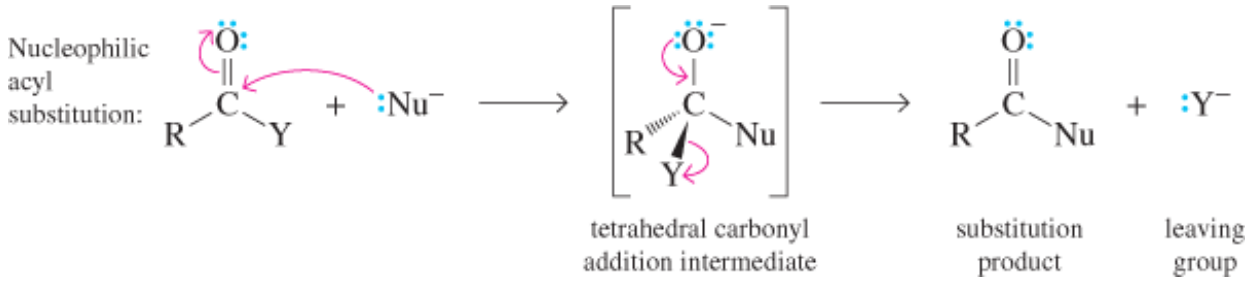
FIGURE 23.3 Flowchart for separating benzoic acid from benzyl alcohol.

Nucleophilic Acyl Substitution

The most common reaction of the carboxylic acid family (carboxylic acids, acid halides, anhydrides, esters and amides) is **nucleophilic acyl substitution**. The key step in this reaction is the addition of a nucleophile to the carbonyl carbon to form a tetrahedral carbonyl addition intermediate. In this respect, the reactions of these functional groups are similar to nucleophilic addition to the carbonyl groups in aldehydes and ketones (section 21.5). In the reactions of aldehydes and ketones, the tetrahedral carbonyl addition intermediate formed is then protonated. The result of this reaction is nucleophilic addition to a carbonyl group of an aldehyde or a ketone.

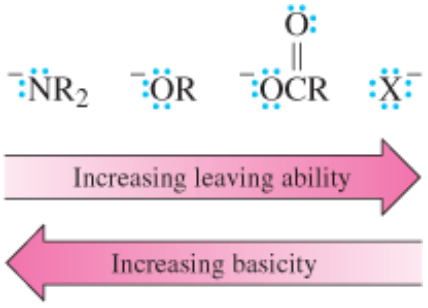


For functional derivatives of carboxylic acids, the fate of the tetrahedral carbonyl addition intermediate is quite different from that of aldehydes and ketones. This intermediate collapses to expel the leaving group and regenerate the carbonyl group. The result of this addition–elimination sequence is nucleophilic acyl substitution.

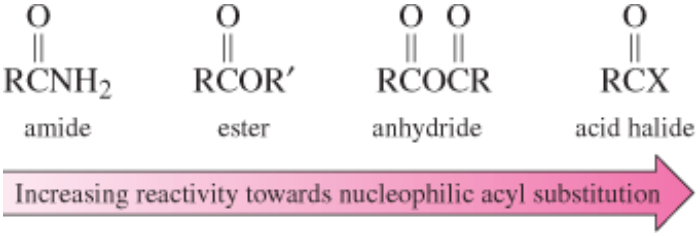


The major difference between these two types of carbonyl addition reactions is that aldehydes and ketones do not have a group, Y, that can leave as a stable anion. They undergo only nucleo philic acyl addition. The carboxylic acid derivatives we study in this chapter do have a group, Y, that can leave as a stable anion, so they can undergo nucleophilic acyl substitution.

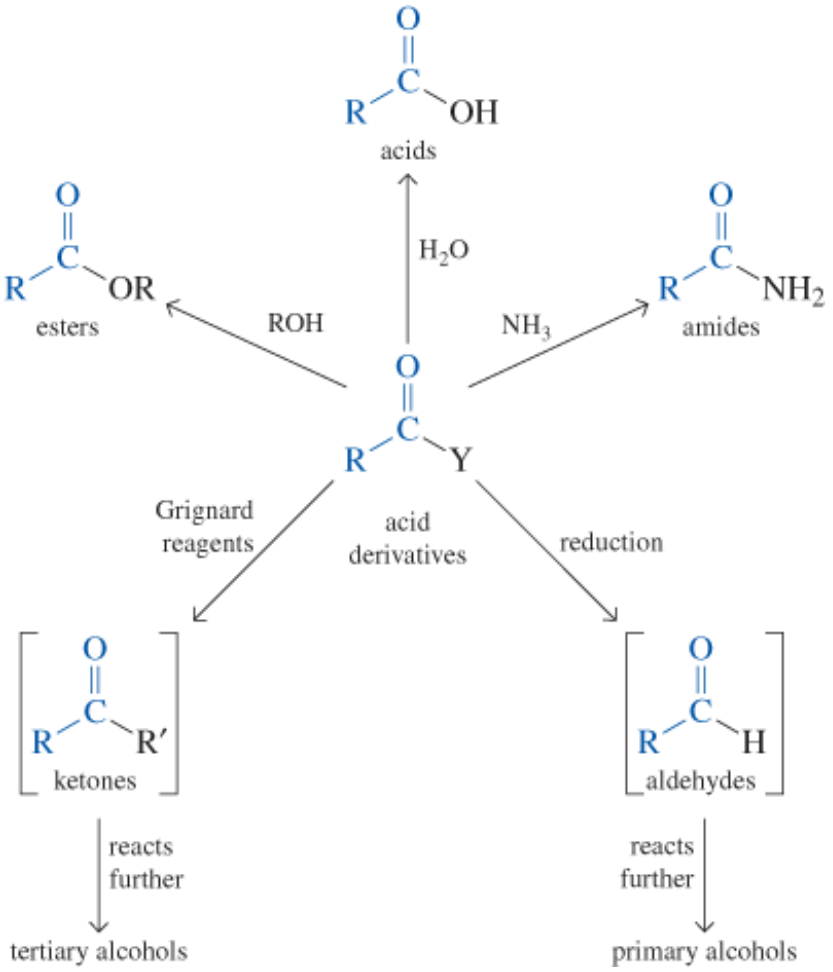
In the general reaction on the previous page, we show the nucleophile and the leaving group as anions. That need not be the case, however. Neutral molecules, such as water, alcohols, ammonia and amines, may also serve as nucleophiles in the acid-catalysed version of the reaction. On the right, we show the leaving groups as anions to illustrate an important point: the weaker the base, the better is the leaving group (section 18.2).



The weakest bases in the series on the right, and hence the best leaving groups, are the halide ions Cl^-, Br^- and I^-, and therefore acid halides are the most reactive towards nucleophilic acyl substitution. The strongest base, and hence the poorest leaving group, is the amide ion, and therefore amides are the least reactive towards nucleophilic acyl substitution. Acid halides and acid anhydrides are so reactive that they are not found in nature. Esters and amides, however, are extremely common.

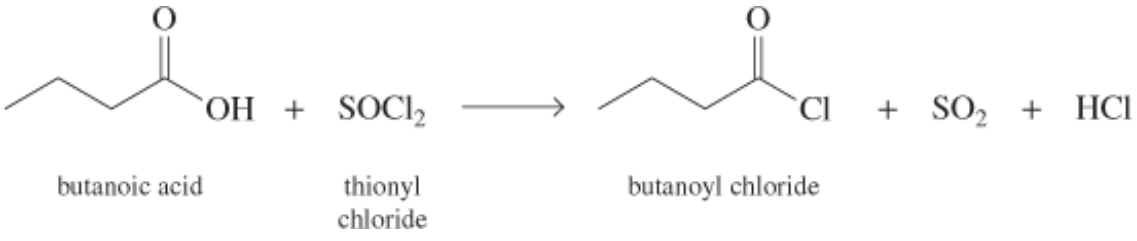


The figure below gives a summary of key examples of nucleophilic acyl substitution reactions that the carboxylic acid family can undergo. The amides (Y = NH_2), however, follow this general scheme only for the hydrolysis reaction (addition of water). All these will be discussed in more detail later in this chapter.



Acid Halide Formation

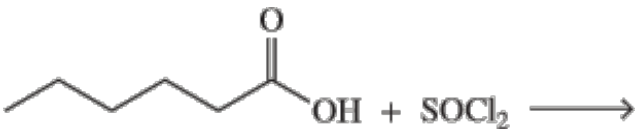
Among the acid halides, acid chlorides are the most frequently used in the laboratory and in industrial organic chemistry. Recall from section 19.2 that alcohols can be converted into chloroalkanes by treatment with thionyl chloride, $SOCl_2$, or with phosphorus chlorides, PCl_3 or PCl_5. These reagents also convert the —OH group of a carboxylic acid into a chloride, an example of a nucleophilic acyl substitution reaction. The most common way to prepare an acid chloride is to treat a carboxylic acid with thionyl chloride.



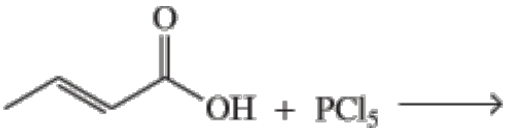
Formation of Acid Chlorides

Complete each of the following equations.

(a)



(b)

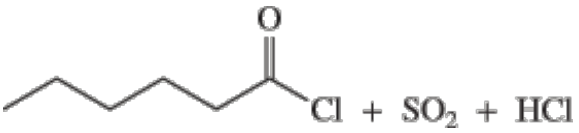


Analysis

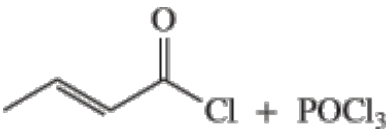
In this type of question, you should try to classify the reagent according to its purpose. In these examples, the reagents convert —OH groups to chlorides.

Solution

(a)



(b)



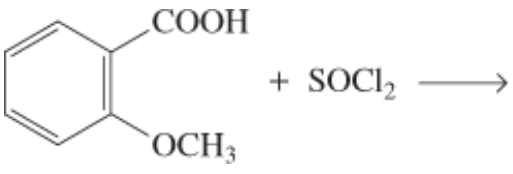
Is our answer reasonable?

The two principal reactions of carboxylic acids are breaking the O—H bond (acid dissociation) and breaking the C—OH bond (nucleophilic acyl substitution). In this case, it is the latter, so the products should show this; i.e. has the —OH group been replaced with Cl?

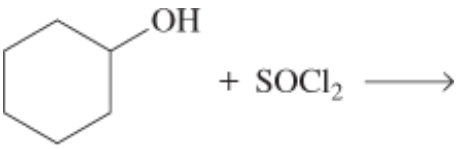
PRACTICE EXERCISE 23.6

Complete each of the following equations.

(a)



(b)



Reactions with Alcohols

The reaction of carboxylic acids and their derivatives with alcohols is important for the preparation of esters. In the following pages, we will discuss the esterification reaction starting with the reaction of carboxylic acids with alcohols. We will then investigate the reactions of acid chlorides, acid anhydrides, esters and amides with alcohols.

Carboxylic Acids — the Fischer Esterification

Treatment of a carboxylic acid with an alcohol in the presence of an acid catalyst (most commonly, concentrated sulfuric acid) gives an ester. This method of forming an ester is given the special name **Fischer esterification** after the German chemist Emil Fischer (1852–1919, Nobel Prize in chemistry, 1902). As an example of a Fischer esterification, treating acetic acid with ethanol in the presence of concentrated sulfuric acid gives ethyl acetate, a common solvent (figure 23.4), and water:

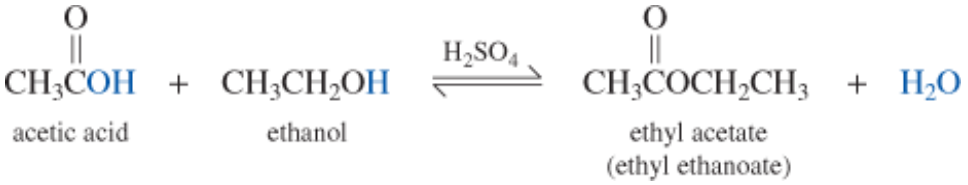




FIGURE 23.4 These products contain ethyl acetate as a solvent. Kari-Ann Tapp

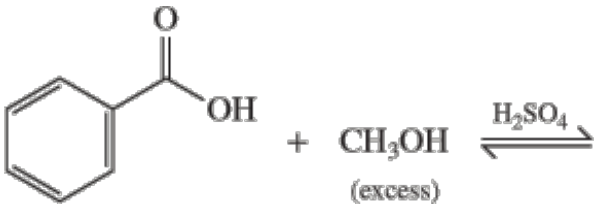
Acid-catalysed esterification is reversible, and generally, at equilibrium, significant quantities of carboxylic acid and alcohol remain. By controlling the experimental conditions, however, we can use Fischer esterification to prepare esters in high yields. If the alcohol is cheaper than the carboxylic acid, we can use a large excess of the alcohol to drive the reaction to the right and achieve a high conversion of carboxylic acid to its ester.

WORKED EXAMPLE 23.7

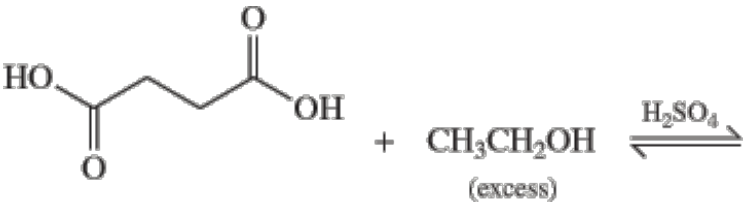
Fischer Esterification

Complete the following Fischer esterification reactions.

(a)



(b)

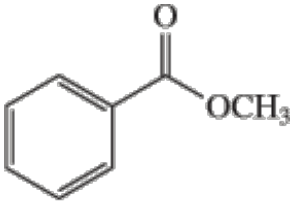


Analysis

Since these are examples of nucleophilic acyl substitution, we simply need to identify the nucleo phile and the group to be substituted. The nucleophile is the oxygen atom of the alcohol.

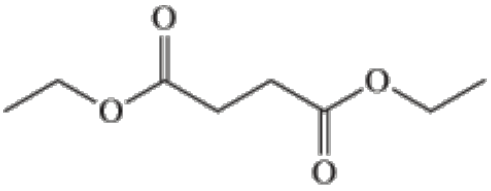
Solution

(a)



methyl benzoate

(b)



diethyl butanedioate
(diethyl succinate)

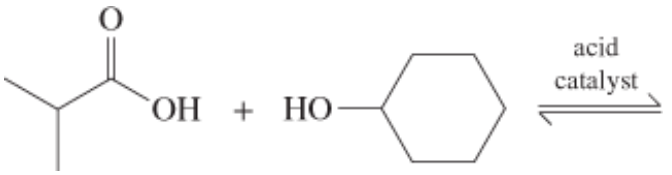
Is our answer reasonable?

Check that you have substituted all the —OH groups of the acids with —OR groups.

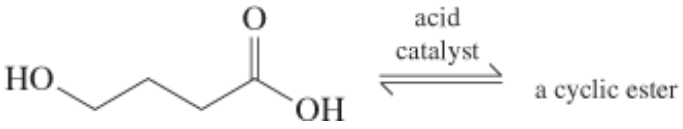
PRACTICE EXERCISE 23.7

Complete the following Fischer esterification reactions.

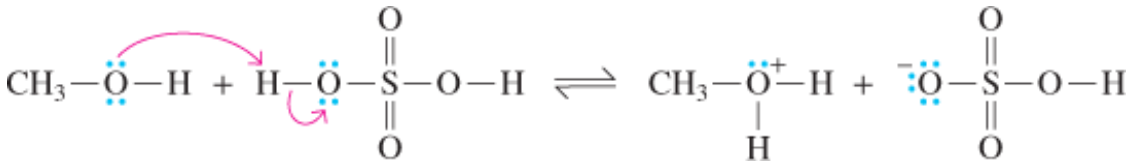
(a)



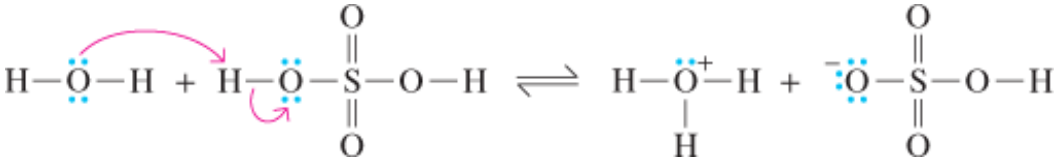
(b)



Note that, although we show the acid catalyst as H_2SO_4 when we write Fischer esterification reactions, the actual proton-transfer acid that initiates the reaction is the oxonium ion formed by the transfer of a proton from H_2SO_4 (the stronger acid) to the alcohol (the stronger base) used in the esterification reaction.



The reaction above is similar to the familiar reaction of water with sulfuric acid.



A mechanism for the Fischer esterification reaction is shown below and we urge you to study it carefully. Do not be overwhelmed by the number of steps; it is still basically only a nucleo philic acyl substitution.

Step 1: Proton transfer from the acid catalyst to the carbonyl oxygen atom increases the electrophilicity of the carbonyl carbon atom.

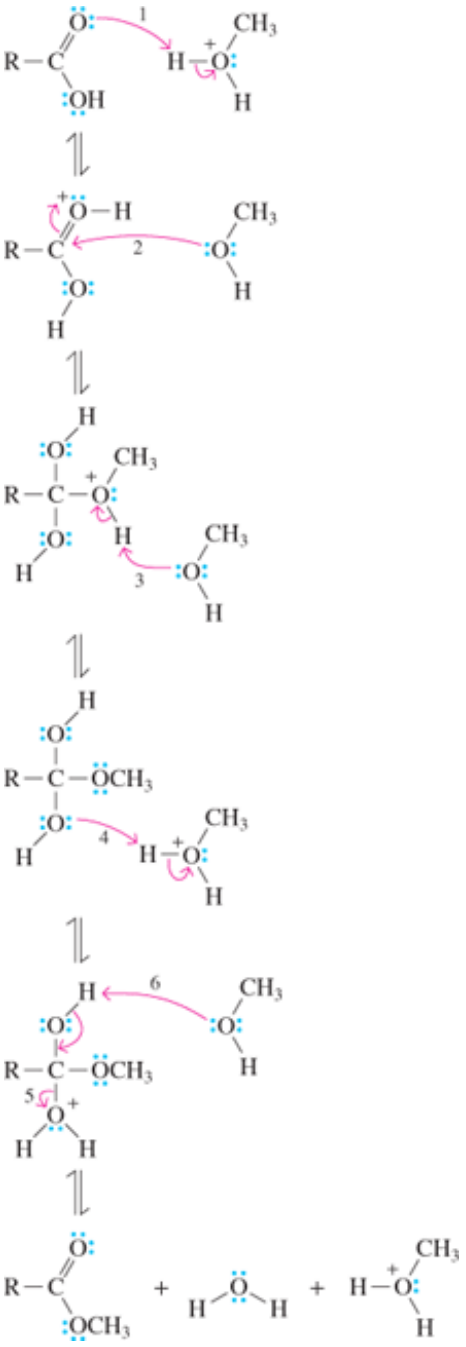
Step 2: The nucleophilic oxygen atom of an alcohol adds to the electrophilic carbonyl carbon atom to form an oxonium ion.

Step 3: Proton transfer from the oxonium ion to a second molecule of alcohol gives a tetrahedral carbonyl addition intermediate (TCAI).

Step 4: Proton transfer to one of the —OH groups of the TCAI gives a new oxonium ion.

Step 5: Water is lost from this oxonium ion.

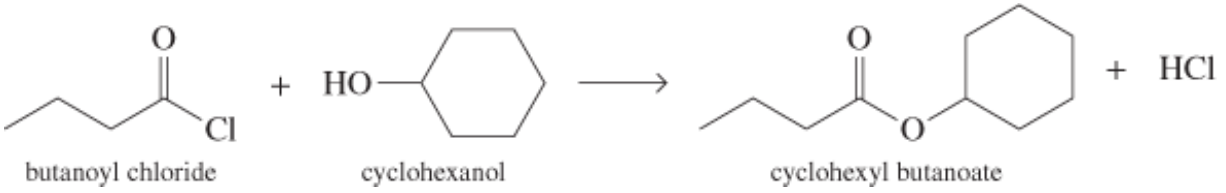
Step 6: Proton transfer to a molecule of alcohol gives the ester and water and regenerates the acid catalyst.



Note that, in the mechanism on the previous page, steps 1, 3, 4 and 6 are simply proton transfer processes. Step 2 is the formation of a C—O bond (the addition part of nucleophilic acyl substitution) and step 5 is the breaking of a C—O bond (the elimination part of nucleophilic acyl substitution). Note also that the oxygen atom of the alcohol is retained in the ester, while the —OH group of the carboxylic acid is lost (as water). This has been confirmed experimentally by using an alcohol labelled with a heavy isotope of oxygen (^{18}O). Upon separation of the components, it was found that the ester contained ^{18}O, while the water did not.

Acid Chlorides

Acid chlorides react with alcohols via a nucleophilic acyl substitution reaction to give an ester and HCl.



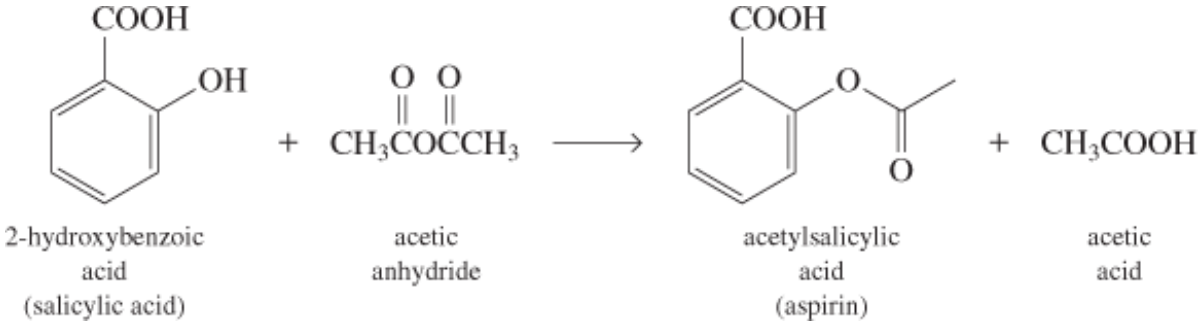
Because acid chlorides are so reactive towards even weak nucleophiles such as alcohols, no catalyst is necessary for these reactions. Phenol and substituted phenols also react with acid chlorides to give esters.

Acid Anhydrides

Acid anhydrides react with alcohols to give 1 mole equivalent of ester and 1 mole equivalent of a carboxylic acid:



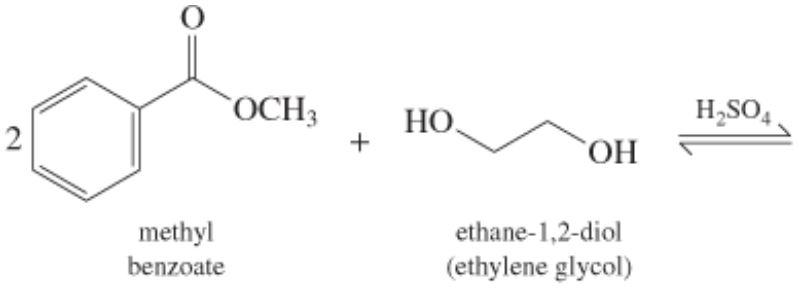
Aspirin is synthesised on an industrial scale by reacting acetic anhydride with salicylic acid:

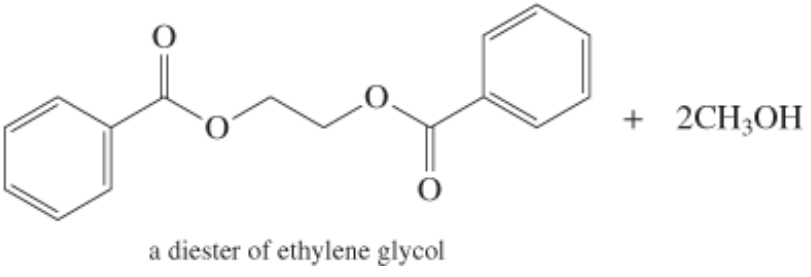


Note that, in the use of anhydrides for the preparation of esters (and amides), 1 mole of carboxylic acid is produced as a by-product. This is an inefficient use of the carboxylic acid and, consequently, anhydrides are used only when they are particularly cheap (e.g. acetic and phthalic anhydrides).

Esters

When treated with an alcohol in the presence of an acid or base catalyst, esters undergo an exchange reaction called **transesterification**. In this reaction, the original —OR group of the ester is exchanged for a new —OR group. In the following example, the transesterification can be driven to completion by heating the reaction at a temperature above the boiling point of methanol (65 °C) so that methanol distills from the reaction mixture:



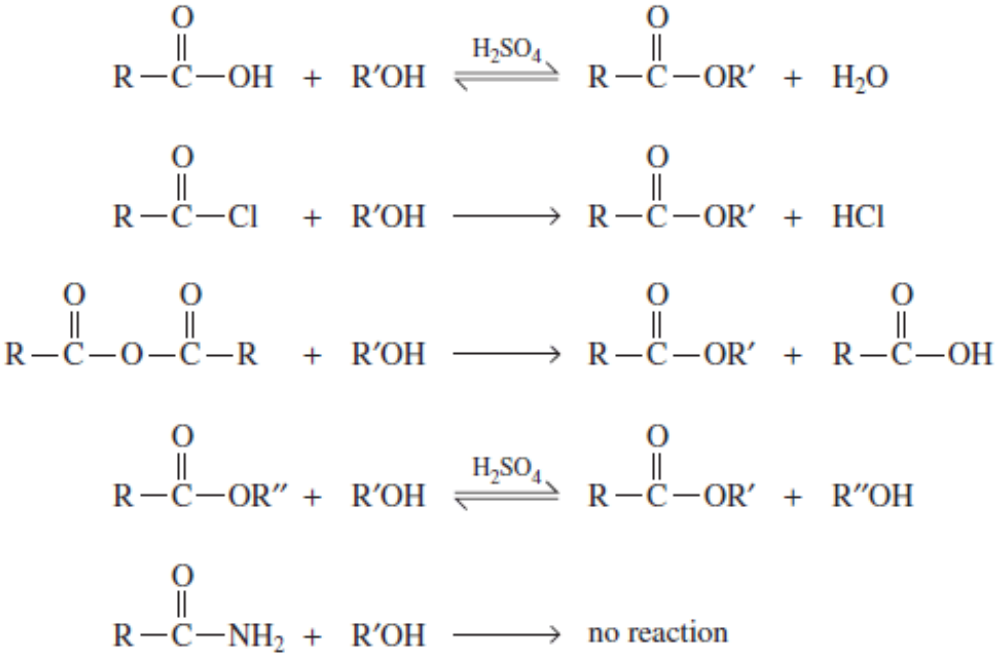


Amides

Amides do not react with alcohols under any experimental conditions. Alcohols are not strong enough nucleophiles to attack the carbonyl group of an amide.

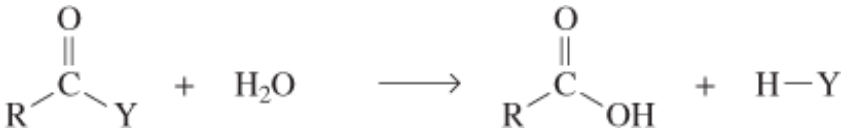
The reactions of carboxylic acids, acid chlorides, anhydrides, esters and amides with alcohols are summarised below. Note that there are large differences in the rates and experimental conditions under which these functional groups undergo reactions with alcohols. At one extreme are acid chlorides and anhydrides, which react rapidly; at the other extreme are amides, which do not react at all.

Summary of the reactions of carboxylic acids, acid chlorides, anhydrides, esters and amides with alcohols



Reaction with Water: Hydrolysis

The hydrolysis of carboxylic acid derivatives is yet another example of a nucleophilic acyl substitution reaction. Essentially, the carboxylic acid derivative reacts with water to give a carboxylic acid and H—Y.



Acid Chlorides

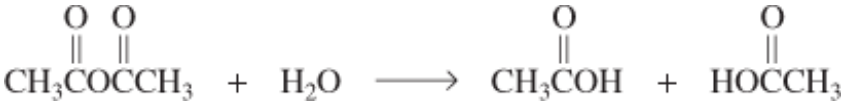
Low-molar-mass acid chlorides react very rapidly with water to form carboxylic acids and HCl.



High-molar-mass acid chlorides are less water soluble and so react less rapidly with water.

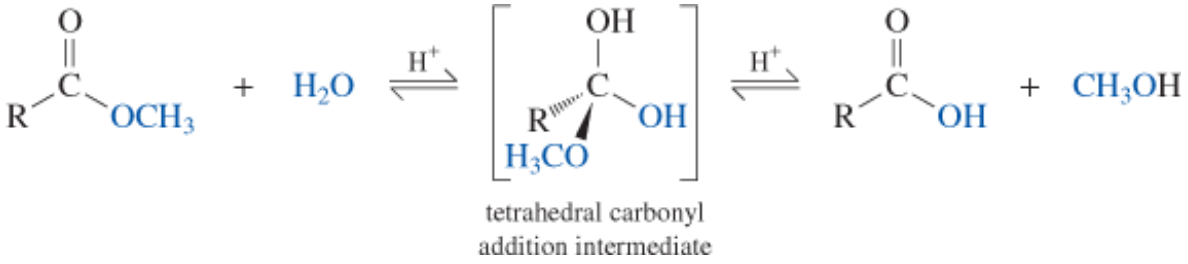
Acid Anhydrides

Acid anhydrides are generally less reactive than acid chlorides. Low-molar-mass anhydrides, however, react readily with water to form two mole equivalents of carboxylic acid.



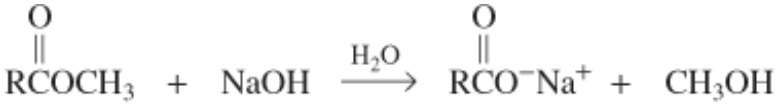
Esters

Esters are hydrolysed only very slowly, even in boiling water. Hydrolysis becomes considerably more rapid, however, when esters are heated in aqueous acid or base. When we discussed acid-catalysed (Fischer) esterification earlier (p. 1019), we pointed out that esterification is an equilibrium reaction. Hydrolysis of esters in aqueous acid is also an equilibrium reaction and proceeds by the same mechanism as esterification, except in reverse. The role of the acid catalyst is to protonate the carbonyl oxygen atom, thereby increasing the electrophilic character of the carbonyl carbon atom and so facilitating addition by water to form a tetrahedral carbonyl addition intermediate. Collapse of this intermediate gives the carboxylic acid and an alcohol.



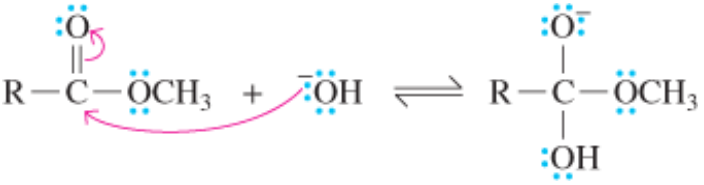
In this reaction, the acid is a catalyst as it is consumed in the first step and is regenerated at the end of the reaction.

Hydrolysis of esters can also be carried out with hot aqueous base, such as aqueous NaOH. Hydrolysis of esters in aqueous base is often called **saponification**, a reference to the use of this reaction in the manufacture of soaps (section 23.6). Each mole of ester hydrolysed requires 1 mole of base, as shown in the following balanced equation:

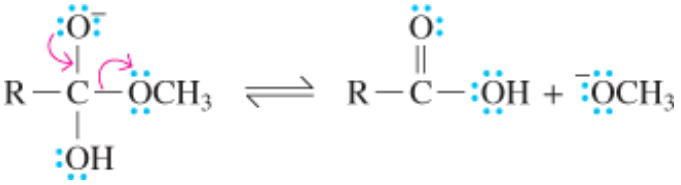


The following shows a mechanism for hydrolysis of an ester in aqueous base.

Step 1: Addition of a hydroxide ion to the carbonyl carbon atoms of the ester gives a tetrahedral carbonyl addition intermediate.



Step 2: Collapse of this intermediate gives a carboxylic acid and an alkoxide ion.



Step 3: Proton transfer from the carboxyl group (an acid) to the alkoxide ion (a base) gives the carboxylate anion. This step is irreversible because the alcohol is not a strong enough nucleophile to react with carboxylate anion.



Note that steps 1 and 2 describe a typical nucleophilic acyl substitution reaction; step 3 is simply an acid–base reaction.

There are two major differences between the hydrolysis of esters in aqueous acid and that in aqueous base.

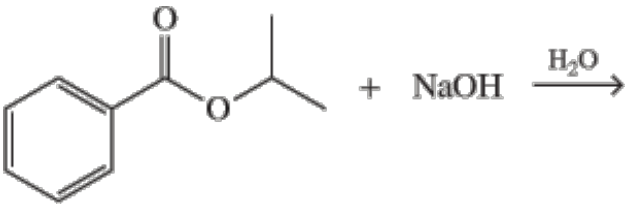
1. For hydrolysis in aqueous acid, acid is required in only catalytic amounts. For hydrolysis in aqueous base, base is required in equimolar amounts because it is a reactant, not just a catalyst.
2. Hydrolysis of an ester in aqueous acid is reversible. Hydrolysis in aqueous base is irreversible, because carboxylate anions do not react with alcohols.

WORKED EXAMPLE 23.8

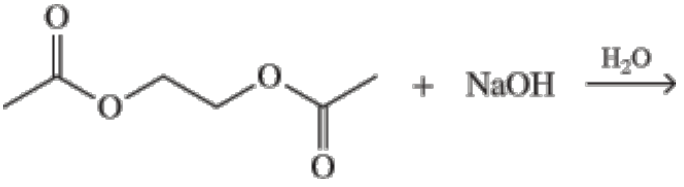
Hydrolysis of Esters

Complete and balance the following equations for the hydrolysis of each ester in aqueous sodium hydroxide, showing all products as they are ionised in aqueous NaOH.

(a)



(b)

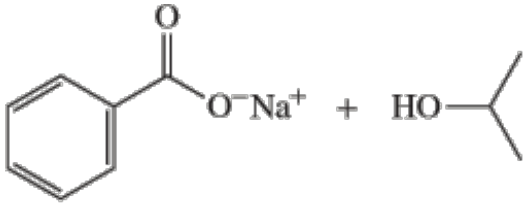


Analysis

First identify the carbonyl carbon atom(s) of the esters and the leaving groups. Substitution of the —OR group (the leaving group) by an —OH group occurs at these carbon atoms. Finally, the acid reacts with the strongly basic alkoxide ion (RO^-).

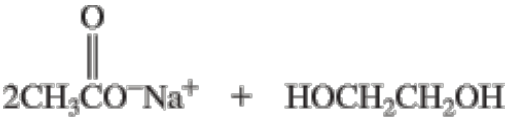
Solution

(a)



sodium benzoate — propan-2-ol (isopropyl alcohol)

(b)



sodium acetate — ethane-1,2-diol (ethylene glycol)

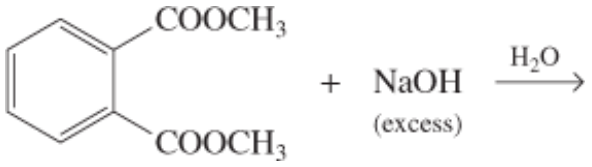
Is our answer reasonable?

The products of hydrolysis are a carboxylic acid and an alcohol. In aqueous NaOH, the carboxylic acid is converted to its sodium salt. Therefore, 1 mole of NaOH is required for the hydrolysis of 1 mole of ester. Compound (b) is a diester, so 2 moles of NaOH are required.

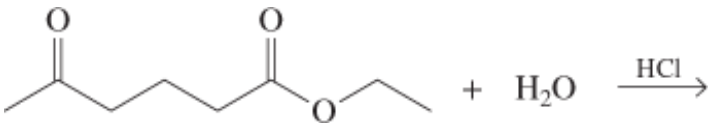
PRACTICE EXERCISE 23.8

Complete and balance the following equations for the hydrolysis of each ester in aqueous solution, showing each product as it is ionised under the given experimental conditions.

(a)

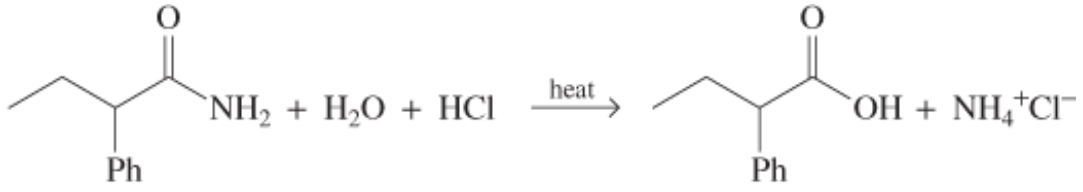


(b)



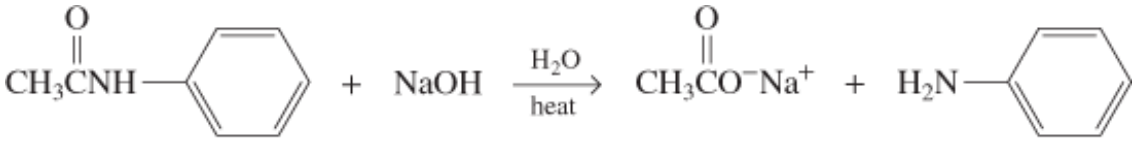
Amides

Amides require considerably more vigorous conditions for hydrolysis in both acid and base than do esters. Amides undergo hydrolysis in hot aqueous acid to give a carboxylic acid and ammonia (or amines). Hydrolysis is driven to completion by the acid–base reaction between ammonia or the amine and acid to form an ammonium salt. One mole of acid is required per mole of amide.



2-phenylbutanamide — 2-phenylbutanoic acid

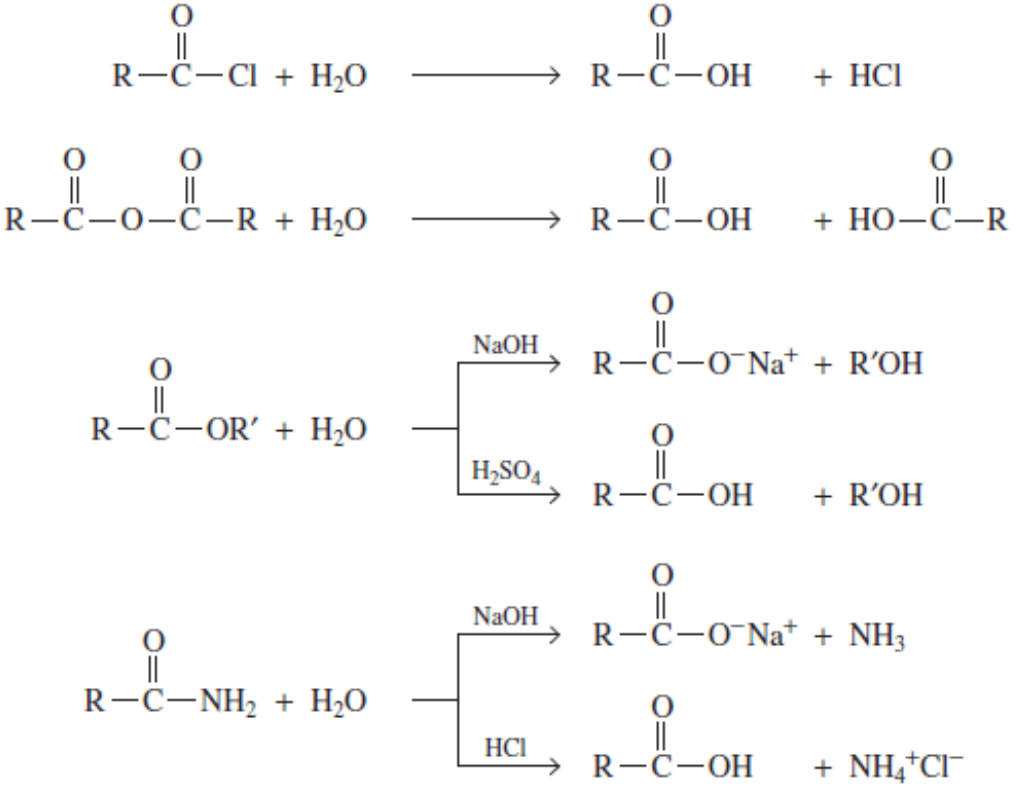
In aqueous base, the products of amide hydrolysis are a carboxylic acid and ammonia or an amine. Base-catalysed hydrolysis is driven to completion by the acid–base reaction between the carboxylic acid and base to form a salt. One mole of base is required per mole of amide.



N-phenylethanamide (acetanilide) — sodium acetate — aniline

The reactions of acid chlorides, anhydrides, esters and amides with water are summarised below. Remember that, although all four functional groups react with water, there are large differences in the rates and experimental conditions under which they are hydrolysed.

Summary of the reactions of acid chlorides, anhydrides, esters and amides with water



WORKED EXAMPLE 23.9

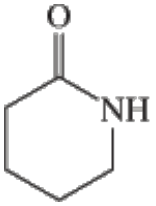
Hydrolysis of Amides

Write an equation for the hydrolysis of each of the following amides in concentrated aqueous HCl, showing all products as they exist in aqueous HCl and showing the amount of HCl required for the hydrolysis of each amide.

(a)



(b)

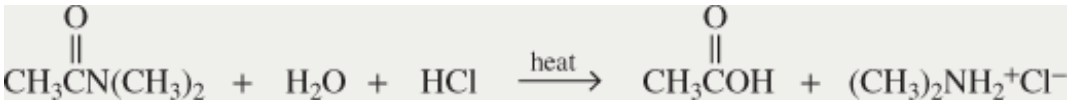


Analysis

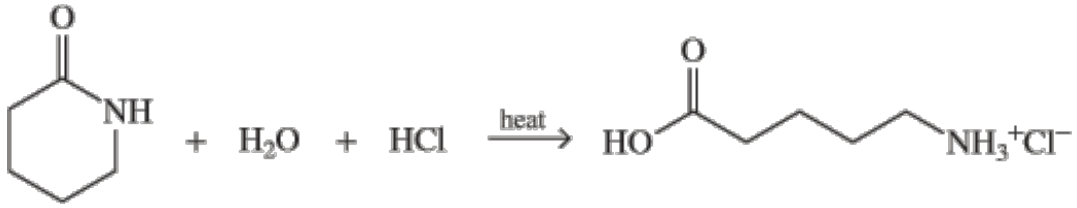
First identify the carbonyl carbon atom of the amide. Substitution of the —NR_2 or —NHR group by an —OH group will occur at this carbon atom. Remember that the hydrolysis of an amide gives a carboxylic acid and an amine (or ammonia). In (b), the carboxylic acid and the amine are part of the same molecule, so only one product will be formed. Finally consider the conditions of the reaction to determine the ionised form of the product(s).

Solution

(a) Hydrolysis of *N*,*N*-dimethylacetamide gives acetic acid and dimethylamine. Dimethylamine, a base, is protonated by HCl to form a dimethylammonium ion and is shown in the balanced equation as dimethylammonium chloride. Complete hydrolysis of this amide requires 1 mole of HCl for each mole of the amide.



(b) Hydrolysis of this δ-lactam gives the protonated form of 5-aminopentanoic acid. One mole of acid is required per mole of lactam.



Is our answer reasonable?

Check that the carbonyl carbon atom is now part of a carboxylic acid group and that the N part of the amide is now an amino group. Now check that the state of ionisation is correct for the reaction conditions used (acid conditions give ammonium ions; basic conditions give carboxylate ions). Since the reaction is carried out under acidic conditions, the amine product will react further to produce an ammonium ion.

PRACTICE EXERCISE 23.9

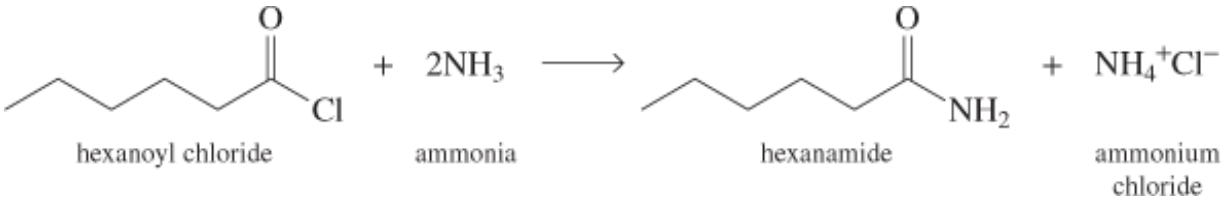
Complete equations for the hydrolysis of the amides in worked example 23.9 in concentrated aqueous NaOH. Show all products as they exist in aqueous NaOH, and show the amount of NaOH required for the hydrolysis of each amide.

Reactions with Ammonia and Amines

Carboxylic acids react with ammonia and amines in an acid–base neutralisation reaction to give ammonium carboxylates.

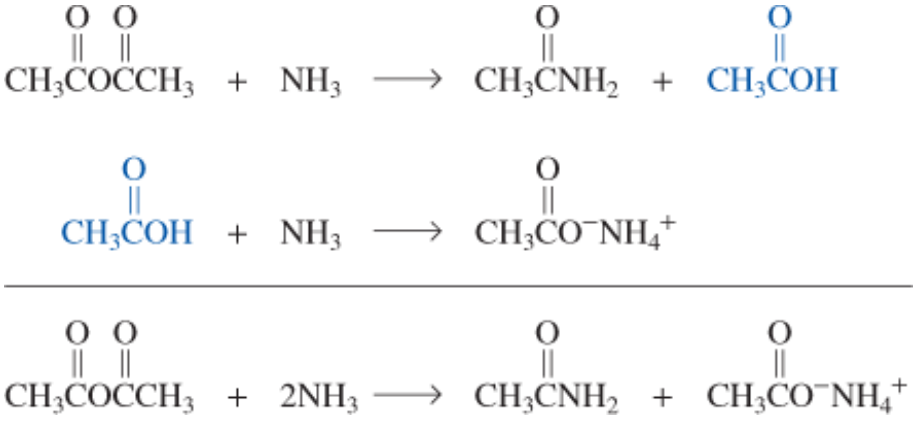
Acid Chlorides

Acid chlorides react readily with ammonia and with 1° and 2° amines to form amides. Complete conversion of an acid chloride to an amide requires 2 mole equivalents of ammonia or amine, 1 mole equivalent to form the amide and 1 mole equivalent to neutralise the hydrogen chloride formed.



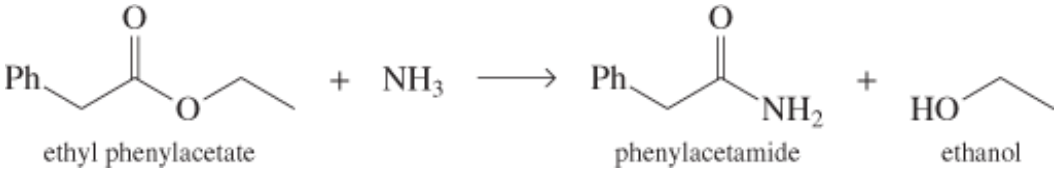
Acid Anhydrides

Acid anhydrides react with ammonia and with 1° and 2° amines to form amides. As with acid chlorides, 2 mole equivalents of ammonia or amine are required, 1 mole equivalent to form the amide and 1 mole equivalent to neutralise the carboxylic acid by-product. To help you see what happens, this reaction equation is broken into two steps, which, when added together, give the net reaction for the reaction of an anhydride with ammonia.



Esters

Esters react with ammonia and with 1° and 2° amines to form amides:



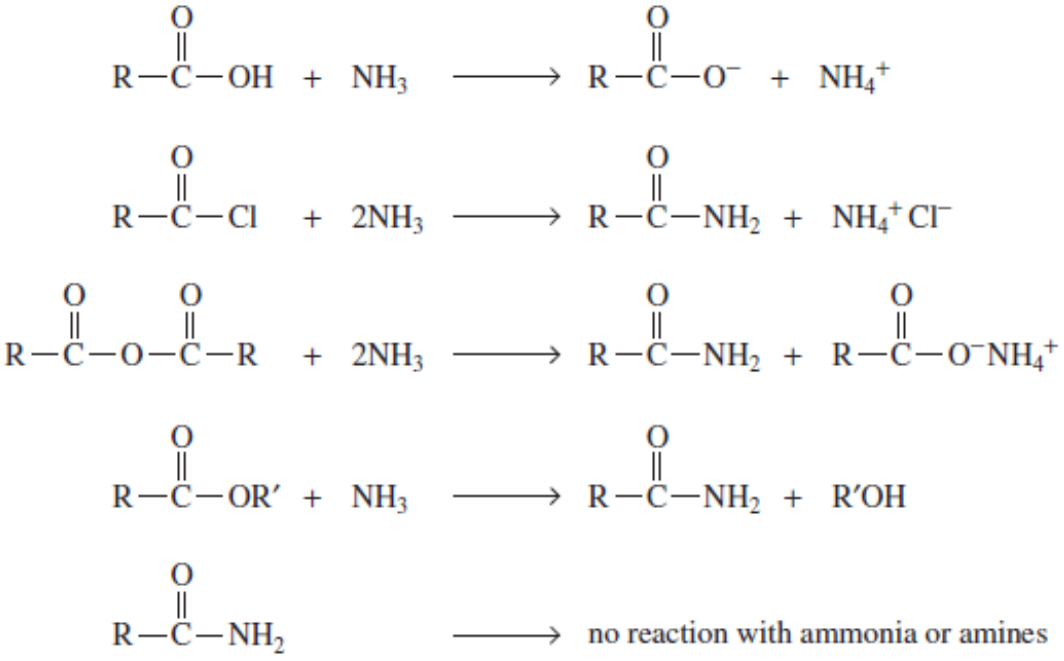
Because an alkoxide anion is a poorer leaving group than a halide or carboxylate ion, esters are less reactive towards ammonia, 1° amines and 2° amines than are acid chlorides or acid anhydrides.

Amides

Amides do not react with ammonia or amines.

The reactions of carboxylic acids, acid chlorides, anhydrides, esters and amides with ammonia and amines are summarised below.

Summary of the reactions of acid chlorides, anhydrides, esters and amides with ammonia and amines

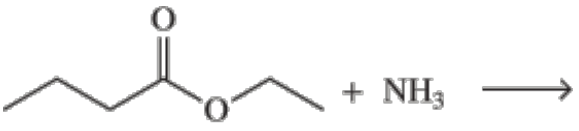


WORKED EXAMPLE 23.10

Formation of Amides from Esters

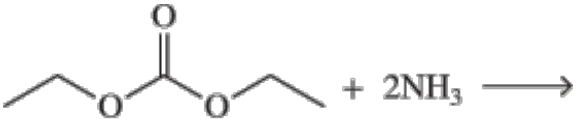
Complete the following equations (the stoichiometry of each is given in the equation).

(a)



ethyl butanoate

(b)



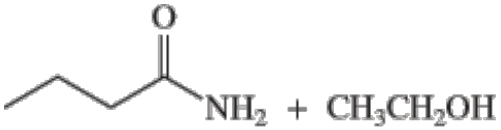
diethyl carbonate

Analysis

First identify the carbonyl carbon atom of the ester. Nucleophilic substitution occurs at this carbon atom. Substitute the —OR group with the nucleophile and then do the appropriate proton transfer reaction. In (b), the process occurs twice.

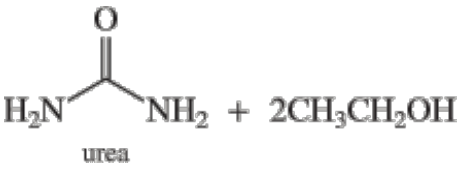
Solution

(a)



butanamide

(b)



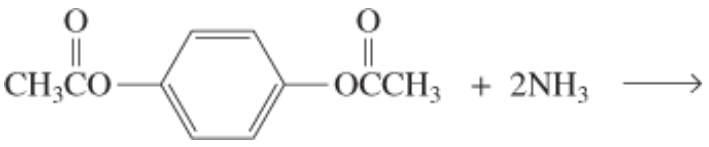
Is our answer reasonable?

Check that the substitution has occurred at the carbon atom of the carbonyl group. Check also that the alcohol formed corresponds to the —OR group of the starting esters.

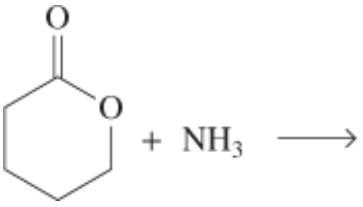
PRACTICE EXERCISE 23.10

Complete the following equations (the stoichiometry of each is given in the equation).

(a)



(b)



Reduction

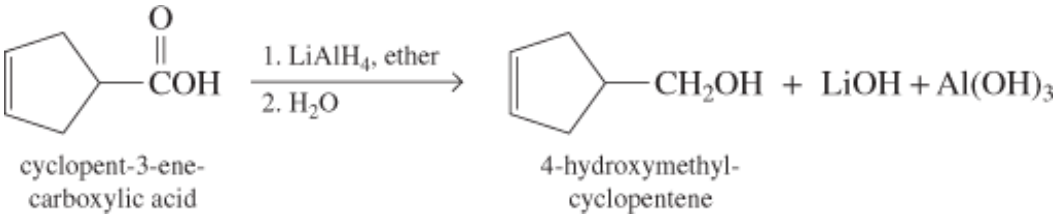
The carboxyl group is one of the organic functional groups that is most resistant to reduction. It is not affected by catalytic reduction under conditions that easily reduce aldehydes and ketones to alcohols, or alkenes to alkanes.

Most reductions of carbonyl compounds, including aldehydes and ketones, are now accomplished by transferring hydride ions from boron or aluminium hydrides. We have already seen the use of sodium borohydride and lithium aluminium hydride to reduce the carbonyl groups of aldehydes and ketones to hydroxyl groups (section 21.5). The most common reagent for the reduction of a carboxylic acid to a primary alcohol is the very powerful reducing agent lithium aluminium hydride; sodium borohydride is not a sufficiently powerful reducing agent to reduce the carboxylic acid derivatives.

Carboxylic Acids

Lithium aluminium hydride, $LiAlH_4$, reduces a carboxyl group to a primary alcohol in excellent yield. Reduction is most commonly carried out in diethyl ether or tetrahydrofuran (THF). An aluminium alkoxide is produced initially and is then treated with water to give the primary alcohol, and lithium and aluminium

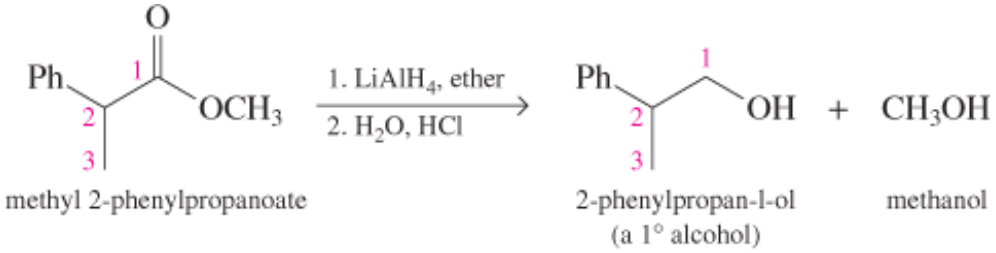
hydroxides. These hydroxides are insoluble in diethyl ether and THF so can be removed by filtration. Evap oration of the solvent yields the primary alcohol.



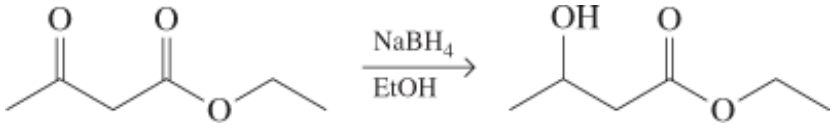
Alkenes are generally not affected by metal hydride reducing reagents. These reagents function as hydride ion donors (nucleophiles) and alkenes are not normally attacked by nucleophiles.

Esters

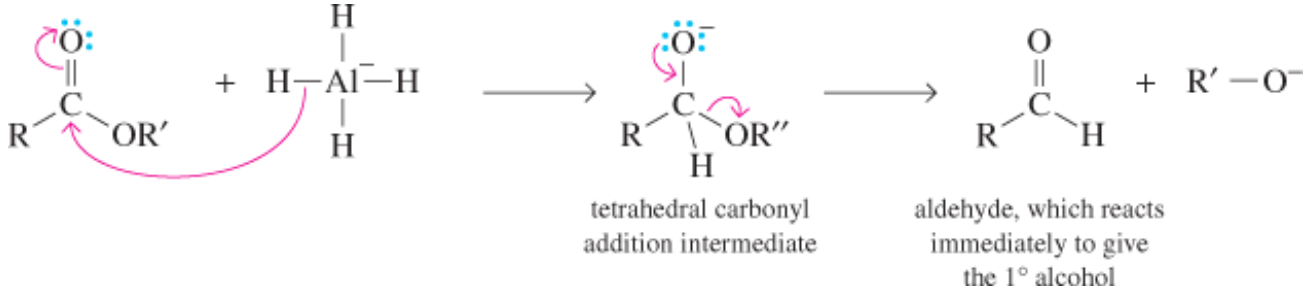
An ester is reduced by lithium aluminium hydride to two alcohols. The alcohol derived from the acyl group is primary.



Sodium borohydride is not normally used to reduce esters, because the reaction is very slow. Therefore, it is possible to use sodium borohydride to reduce the carbonyl group of an aldehyde or a ketone to a hydroxyl group without reducing an ester or carboxyl group in the same molecule.

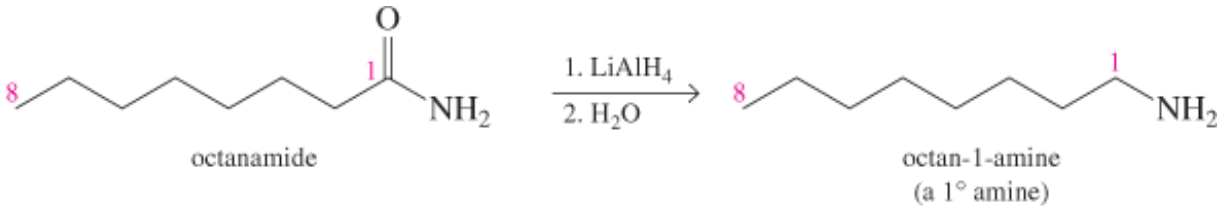


Although it may not be immediately obvious, the reduction of esters involves a nucleophilic acyl substitution mechanism followed by reduction of the resulting aldehyde to give, ultimately, the primary alcohol. The metal hydride reduction of aldehydes has been discussed in section 21.5.



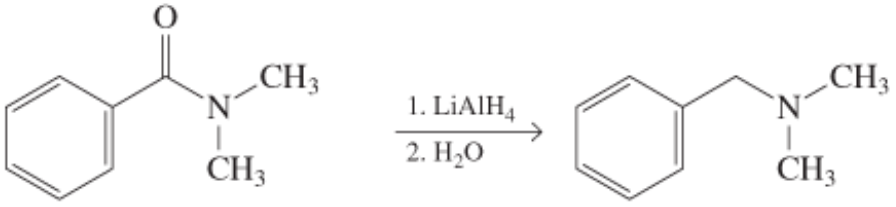
Amides

The reduction of amides by lithium aluminium hydride can be used to prepare 1°, 2° or 3° amines, depending on the degree of substitution of the amide.



octanamide

octan-1-amine
(a 1° amine)



N,N-dimethylbenzamide

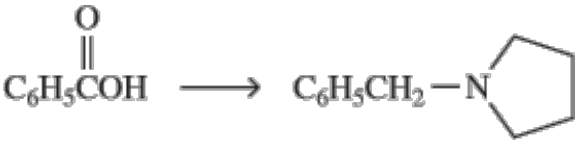
N,N-dimethylbenzylamine
(a 3° amine)

WORKED EXAMPLE 23.11

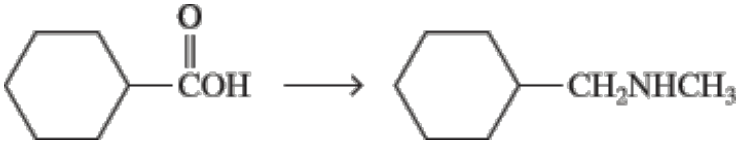
Synthesis of Amines from Carboxylic Acids

Show how to bring about each of the following conversions.

(a)



(b)



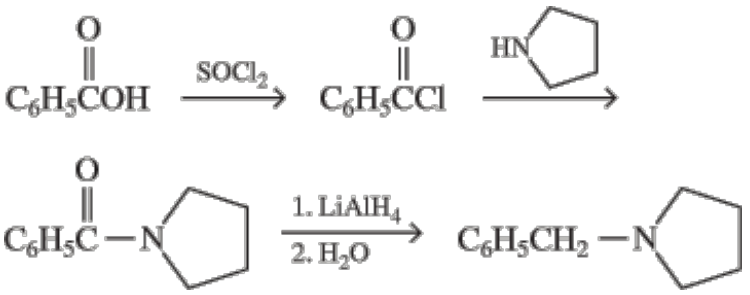
Analysis

The key step is to convert a carboxylic acid into an amide that can then be reduced with lithium aluminium hydride to give the required amine. We have discussed a couple of two-step methods of converting carboxylic acids to amides: via the acid chloride and via the ester.

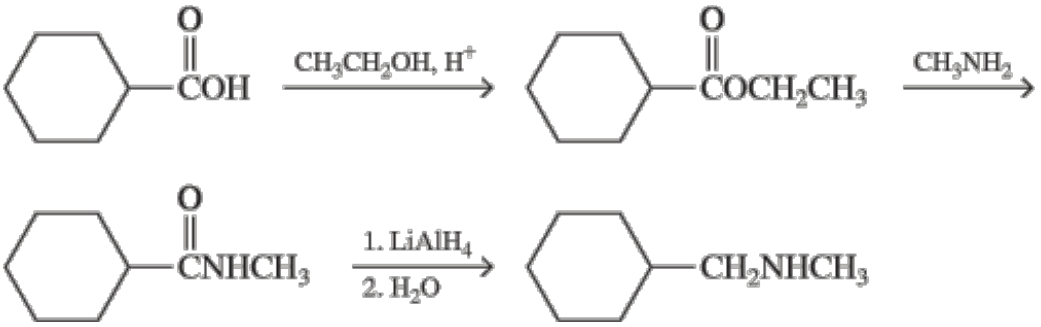
Solution

The amide can be prepared by treating the carboxylic acid with $SOCl_2$ to form the acid chloride and then treating the acid chloride with an amine. Alternatively, the carboxylic acid can be converted to an ester by Fischer esterification and the ester treated with an amine to give the amide. To illustrate both methods, we have shown the acid chloride route for conversion (a) and the ester route for conversion (b).

(a)



(b)



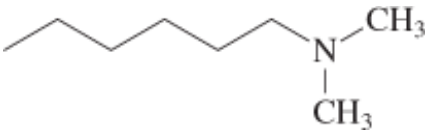
Is our answer reasonable?

Check that the products of each reaction step have the appropriate number of carbon and hydrogen atoms.

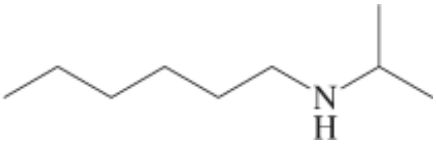
PRACTICE EXERCISE 23.11

Show how to convert hexanoic acid to each of the following amines in good yield.

(a)

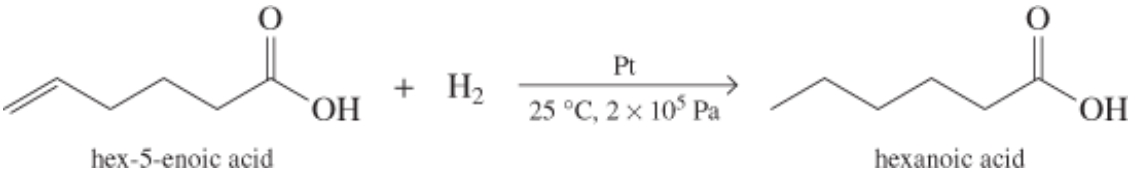


(b)



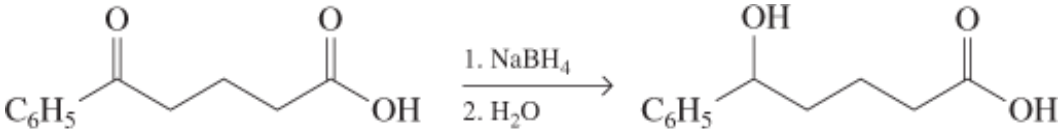
Selective Reduction of other Functional Groups

Catalytic hydrogenation does not reduce carboxyl groups, but does reduce alkenes to alkanes. Therefore, we can use H_2 and a metal catalyst to reduce this functional group selectively in the presence of a carboxyl group.



hex-5-enoic acid hexanoic acid

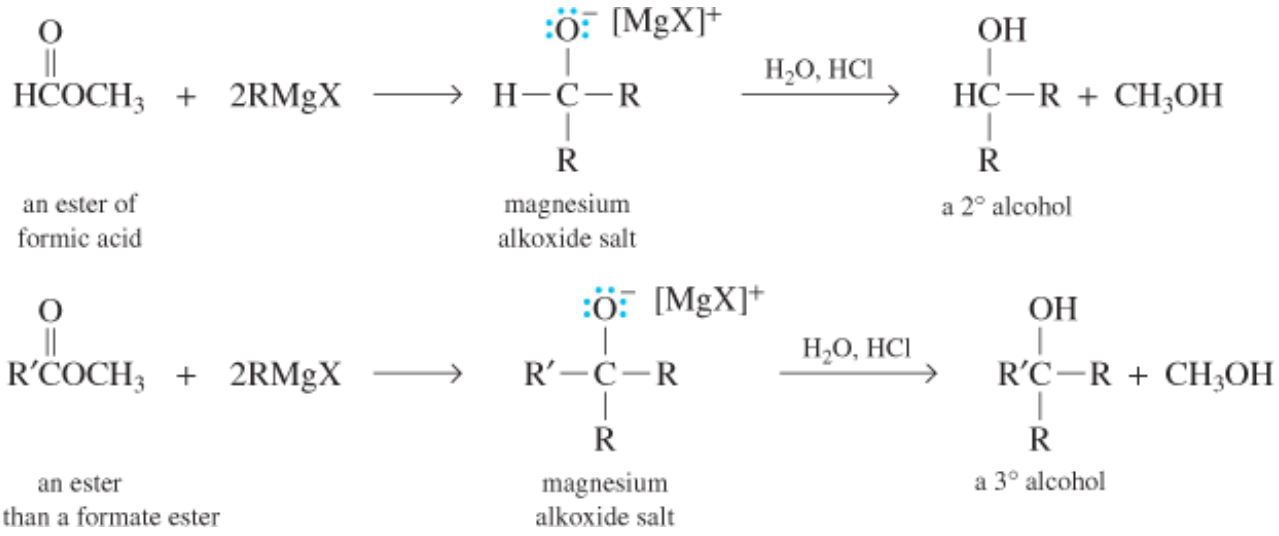
We saw in section 21.5 that aldehydes and ketones are reduced to alcohols by both $LiAlH_4$ and $NaBH_4$. Only $LiAlH_4$, however, reduces carboxyl groups. Thus, it is possible to reduce an aldehyde or a ketone carbonyl group selectively in the presence of a carboxyl group by using the less reactive $NaBH_4$ as the reducing agent.



5-oxo-5-phenylpentanoic acid — 5-hydroxy-5-phenylpentanoic acid

Esters with Grignard Reagents

Treating an ester of formic acid with 2 mole equivalents of a Grignard reagent, followed by hydrolysis of the magnesium alkoxide salt in aqueous acid, gives a 2° alcohol; treating an ester of any other carboxylic acid with a Grignard reagent gives a 3° alcohol in which two of the groups bonded to the carbon atom bearing the —OH group are the same.



Reaction of an ester with a Grignard reagent (shown above) involves the formation of two successive tetrahedral carbonyl addition intermediates. The first collapses to give a new carbonyl compound — an aldehyde from a formate ester, a ketone from all other esters. The second intermediate is stable and, when protonated, gives the final alcohol. It is important to realise that it is not possible to use RMgX and an ester to prepare an aldehyde or a ketone; the intermediate alde-hyde or ketone is more reactive than the ester and reacts immediately with the Grignard reagent to give an alcohol.

Steps 1 and 2: These two steps describe the nucleophilic acyl substitution reaction. The reaction begins in step 1 with the addition of 1 mole equivalent of Grignard reagent to the carbonyl carbon to form a tetrahedral carbonyl addition intermediate. This intermediate then collapses in step 2 to give a new carbonyl-containing compound and a magnesium alkoxide salt.



Steps 3 and 4: These two steps describe the typical carbonyl addition reaction of aldehydes and ketones (see section 21.5). The new carbonyl-containing compound reacts in step 3 with a second mole equivalent of Grignard reagent to form a second tetrahedral carbonyl addition compound, which, after hydrolysis in aqueous acid (step 4), gives a 3° alcohol (or a 2° alcohol if the starting ester was a formate).



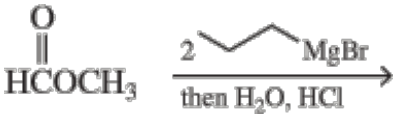
Although it may not be obvious from the products obtained in the reaction of esters with Grignard reagents or reducing agents, the reaction proceeds via a nucleophilic acyl substitution. However, in both cases, the products of this initial reaction react readily with the reagents present to ultimately produce alcohols.

WORKED EXAMPLE 23.12

Reaction of Esters with Grignard Reagents

Complete each of the following Grignard equations.

(a)



(b)

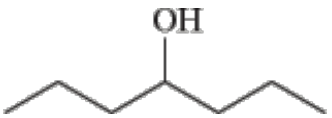


Analysis

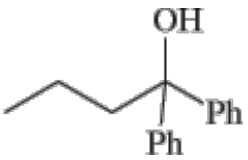
In both cases, identify the carbonyl carbon atom; this will be the carbon atom bearing the —OH group in the product. The first mole equivalent of Grignard reagent will substitute the alkoxy group (in these cases, the —OCH_3 group) to give an aldehyde or ketone. These then react further, in the usual fashion (see section 21.5), to produce alcohols.

Solution

(a)



(b)



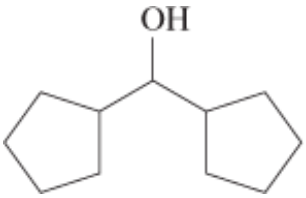
Is our answer reasonable?

Since (a) is an ester of formic acid, the final product should be a 2° alcohol. Ester (b) should produce a 3° alcohol. Both products should also have two equivalent —R groups.

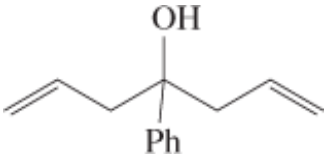
PRACTICE EXERCISE 23.12

Show how to prepare each of the following alcohols by treating an ester with a Grignard reagent.

(a)

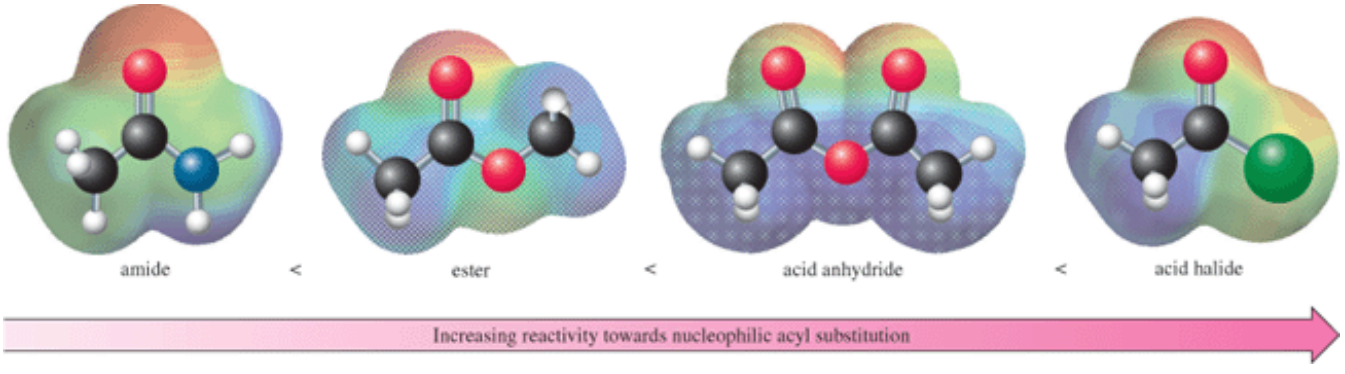


(b)



Interconversion of Functional Derivatives

On the last few pages, we have seen that acid chlorides are the most reactive carboxyl deriv atives towards nucleophilic acyl substitution and that amides are the least reactive.



Another useful way to think about the relative reactivities of these four functional derivatives of carboxylic acids is summarised in figure 23.5. Any functional group in this figure can be prepared from any functional group above it by treatment with an appropriate oxygen or nitrogen nucleophile. An acid chloride, for example, can be converted to an acid anhydride, an ester, an amide or a carboxylic acid. However, acid anhydrides, esters and amides do not react with chloride ions to give acid chlorides.

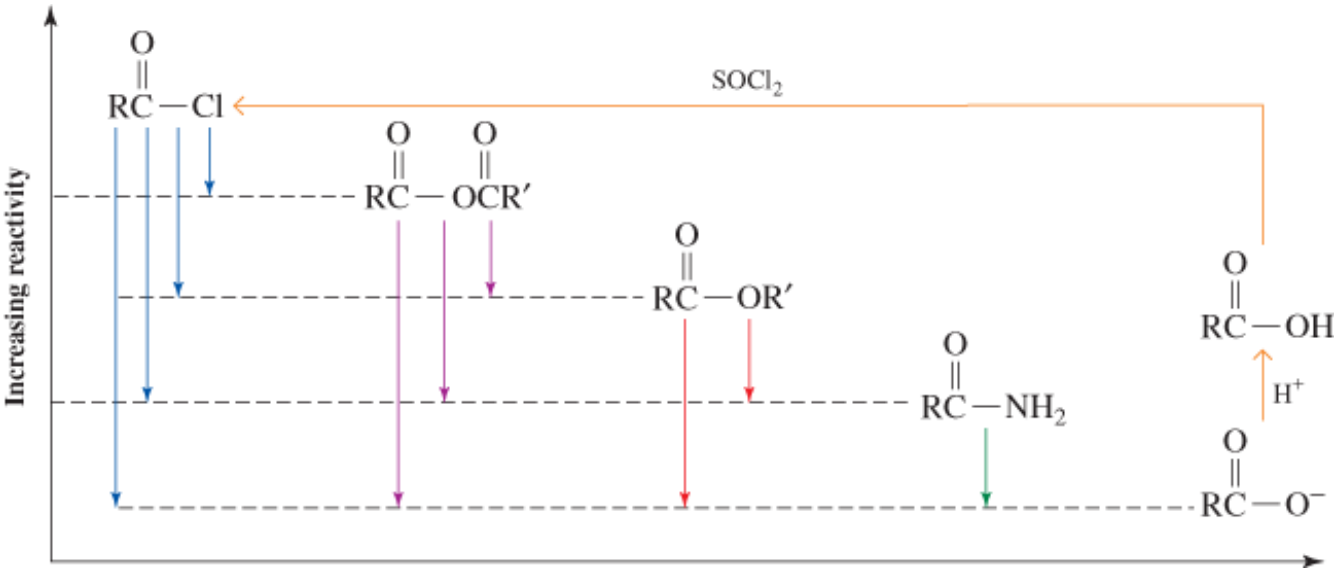


FIGURE 23.5 Relative reactivities of carboxylic acid derivatives towards nucleophilic acyl substitution. A more reactive derivative may be converted to a less reactive derivative by treatment with an appropriate reagent. Treatment of a carboxylic acid with thionyl chloride converts it to the more reactive acid chloride. Carboxylic acids are about as reactive as esters under acidic conditions but are converted to the unreactive carboxylate anions under basic conditions.

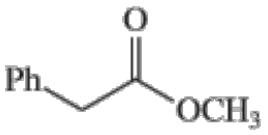
Notice that all carboxylic acid derivatives can be converted to carboxylic acids, which in turn can be converted to acid chlorides. Thus, any acid derivative can be used to synthesise another, either directly or via a carboxylic acid.

WORKED EXAMPLE 23.13

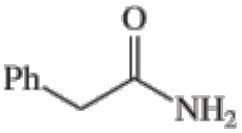
Interconversion of Functional Groups

Show how to convert phenylacetic acid into each of the following compounds.

(a)



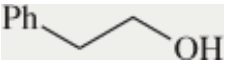
(b)



(c)



(d)

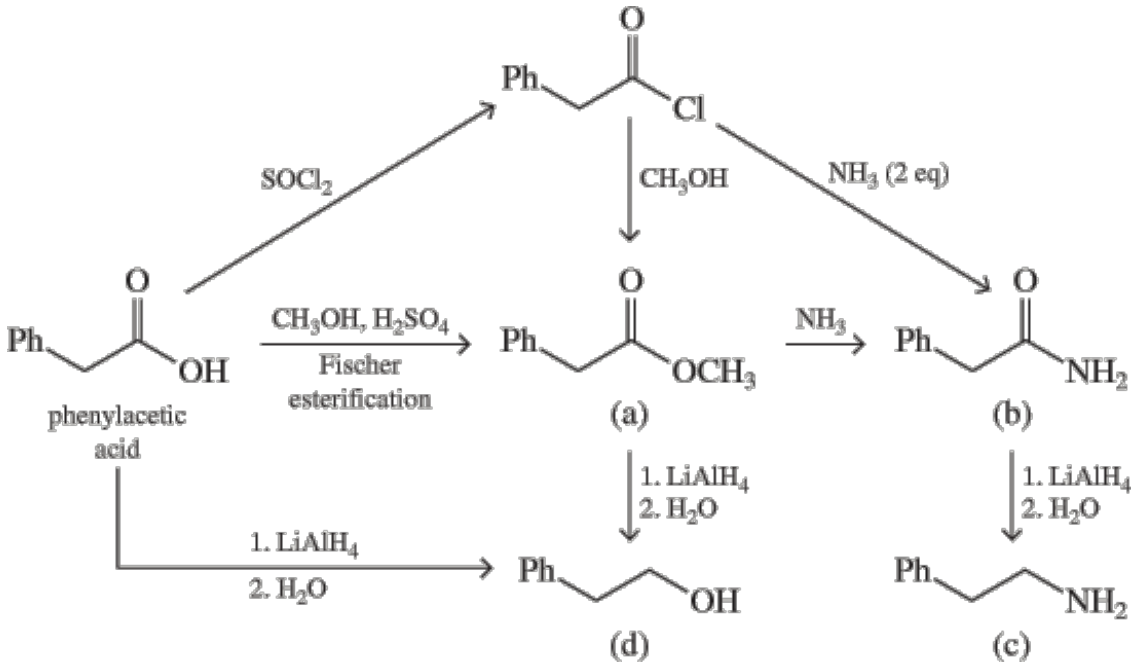


Analysis

First, draw the structure of phenylacetic acid and then compare this structure (the starting material) with those of the products. Compounds (a) and (b) are carboxylic acid derivatives, which can be obtained from phenylacetic acid by nucleophilic acyl substitution reactions (more than one step may be required). Compounds (c) and (d), however, are products obtained from the reduction of carboxylic acid derivatives.

Solution

Prepare the methyl ester (a) by Fischer esterification (pp. 1019–22) of phenylacetic acid with methanol. Then treat this ester with ammonia to prepare the amide (b). Alternatively, treat phenylacetic acid with thionyl chloride (table 23.5) to give an acid chloride, and then treat the acid chloride with two equivalents of ammonia to give amide (b). Reduction of amide (b) by $LiAlH_4$ gives the 1° amine (c). Similar reduction of either phenylacetic acid or ester (a) gives the 1° alcohol (d).



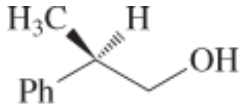
Is our answer reasonable?

Check that the carbon skeleton of phenylacetic acid is retained in each step; that is, the $PhCH_2$—C should be consistent throughout. In (a) and (b), the — C is part of a carbonyl group while in (c) and (d) it is a CH_2 group.

PRACTICE EXERCISE 23.13

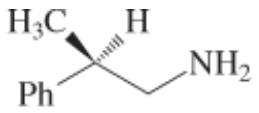
Show how to convert (*R*)-2-phenylpropanoic acid to each of the following compounds.

(a)



(*R*)-2-phenylpropan-1-ol

(b)



(*R*)-2-phenylpropan-1-amine

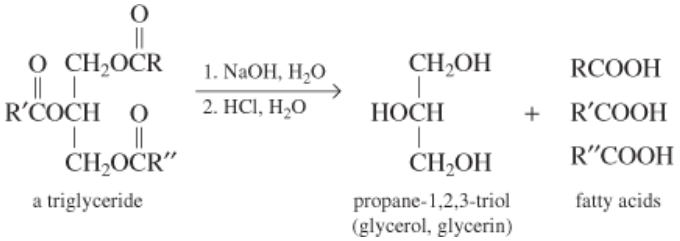
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23.6 Triglycerides

The triglycerides belong to a group of naturally occurring organic compounds called **lipids** that are classified together on the basis of their common solubility properties. Lipids are insoluble in water but soluble in relatively nonpolar, aprotic organic solvents, including diethyl ether and dichloromethane. (*Note:* This classification is based on a *physical property*, not a structural feature.)

Triglycerides or **triacylglycerols** are triesters of glycerol and long-chain carboxylic acids and they play a major role in human and animal biology. They are storage depots of chemical energy in the form of fats; humans store energy in the form of fat globules in adipose tissue.

Animal fats and vegetable oils, the most abundant naturally occurring lipids, are also called triglycerides or triacylglycerols. Hydrolysis of a triglyceride in aqueous base, followed by acidification, gives glycerol and three fatty acids (acids with long carbon chains).



Chemistry Research

Molecular Machines

Professor Chris Easton, Research School of Chemistry, Australian National University

Nanotechnology is a hot topic in chemistry research. It allows the control of matter and the fabrication of devices on the nanometre scale. This primarily involves molecules interacting with other molecules thereby giving rise to unique properties or functions different from those of the separate species. Chemists have named this special field of research ‘supramolecular chemistry’.

Professor Chris Easton's group at the Research School of Chemistry at the Australian National University (ANU) is very active in the area of supramolecular chemistry and has recently created an extraordinarily small nanotechnological device: a molecular machine. A machine is an apparatus consisting of interrelated parts with separate functions that can be used to do some form of work. Research chemists in Professor Easton's group have developed synthetic skills and techniques that allow them to assemble novel molecular structures that can essentially perform the actions of a machine, but on a nanoscale (represented conceptually in figure 23.6). Professor Easton's molecular machine (a molecular pump) uses an amide bond constrained at an odd angle through binding forces within a truncated cone-shaped molecule called a cyclodextrin (figure 23.7). Recall that amides are derivatives of carboxylic acids where the C—N bond has double bond character and so is not free to rotate.

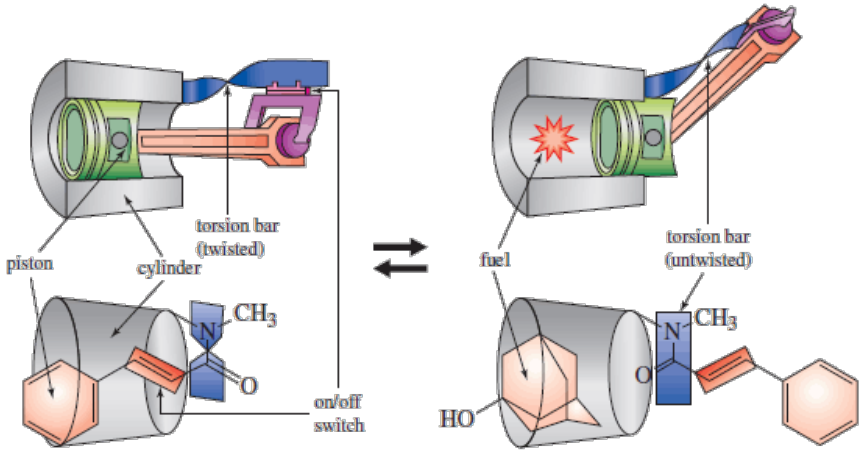


FIGURE 23.6 Conceptual representation of (top) a mechanical machine and (bottom) its molecular counterpart developed by researchers at ANU.

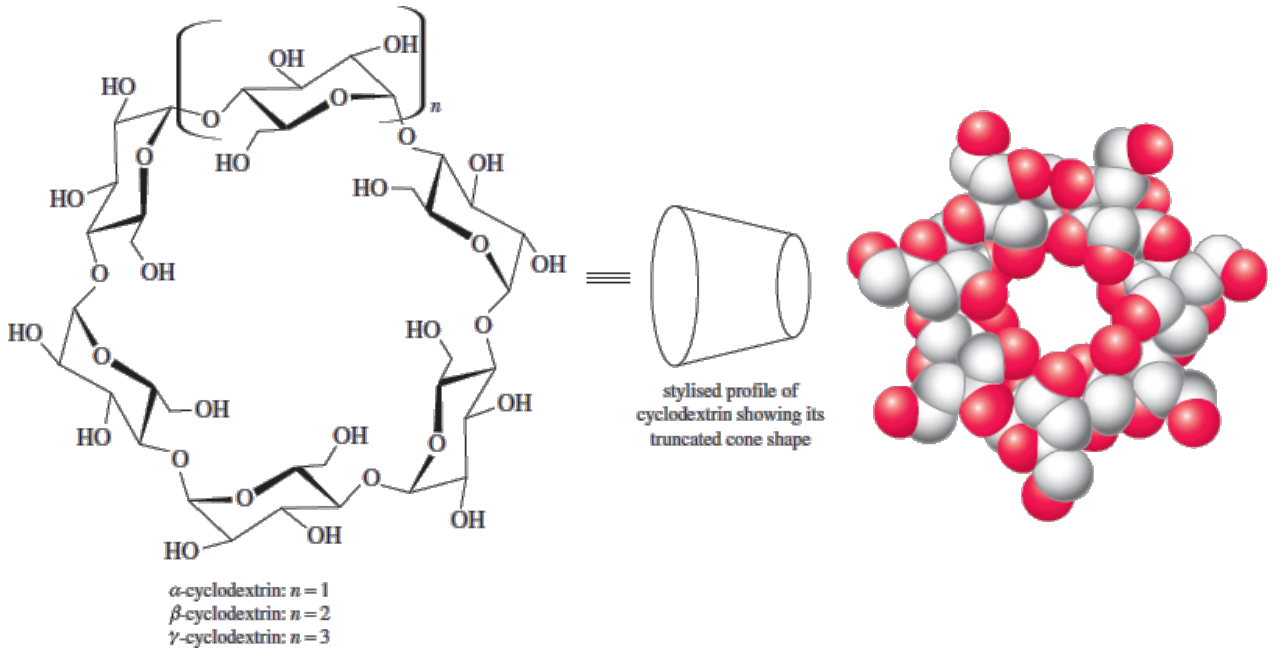


FIGURE 23.7 Cyclodextrins are formed from saccharide rings. The Easton group's work is based on β-cyclodextrin, in which $n = 2$.

With this molecular pump, the work done by the system controls molecular motions and occurs in response to external stimuli that may be chemical, thermal or photochemical. The basis for the machine's function is that an external stimulus is used to push the system out of equilibrium and work is done when the system responds to restore equilibrium, Professor Easton's group has measured the work output resulting from this molecular interaction to be of the order of 5.9 kJ mol^{-1}.

The simplest form of the machine (figure 23.8) comprises an aromatic substituent attached to a cyclodextrin. Cyclodextrins are unusual truncated cone-shaped molecules generated when a polysaccharide chain is joined to form a large cyclic structure. The cyclodextrin and its side chain behave as the cylinder and piston, respectively, of a molecular pump. The pump is fuelled by 1-adamantanol.

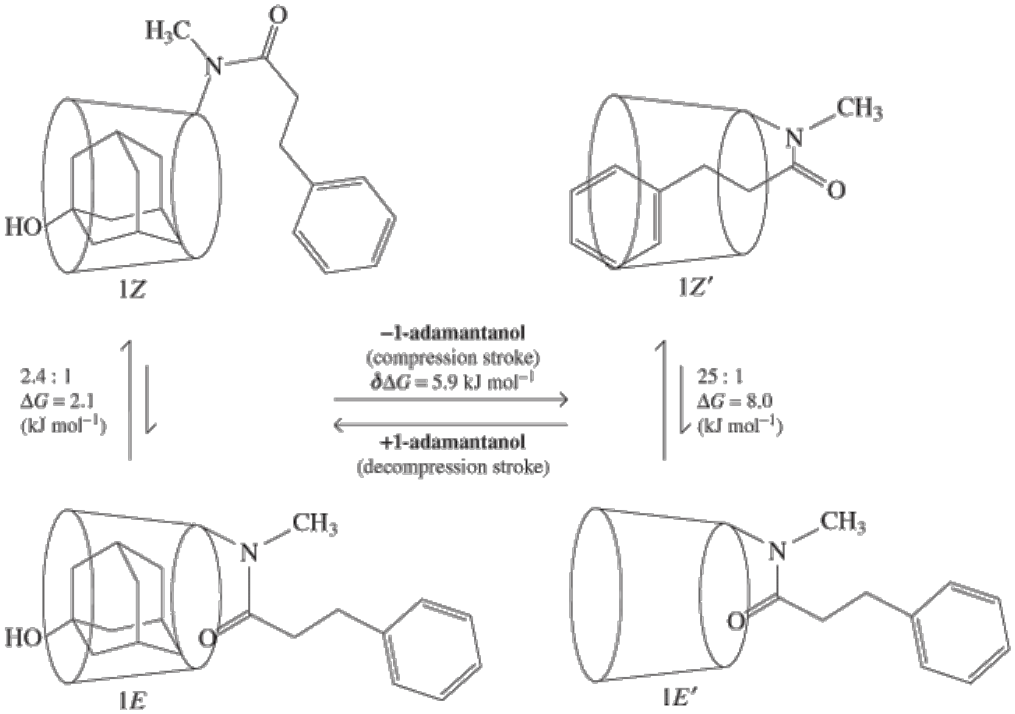


FIGURE 23.8 Graphical representation of the simplest form of the molecular machine (structure 1) comprising cyclodextrin ('cylinder') and its aromatic side chain ('piston'). *E* and *Z* refer to the (*E*)- and (*Z*)-type isomers.

During the compression stroke of the piston, the aromatic side-chain substituent is inserted within the cyclodextrin cavity and 1-adamantanol is removed by an external stimulus. This insertion process takes energy but is driven by the nonpolar binding between the inner surface of the cyclodextrin and the hydrocarbons of the side chain. This intramolecular insertion distorts the side chain from the preferred (*E*)-type isomer for the partial double bond character of the amide group linking the cyclodextrin to the phenyl substituent. As the group is drawn into the cyclodextrin cavity, the distortion creates strain energy in the amide bond so this functional group then serves as a torsion bar holding energy in the system ready for release.

During the decompression stroke of the piston, 1-adamantanol is added again. The 1-adamantanol is more preferentially bound within the cyclodextrin than is the side chain and so, as it re-enters the system, the side chain is released, thus releasing energy.

As this molecular machine is far too small to be seen by any microscopy technique, the conformations of the device were determined by ^{1}H-NMR spectroscopy. The equilibrium levels of the various isomers were used to calculate the energy differences between the isomers present.

The group has also produced a more advanced form of the machine, which uses two isomers that can be interconverted photochemically. Only one of the isomers can be forced to fit into the cyclodextrin and perform the work, so the photoisomerisation turns the machine on and off. In this more advanced version of the machine (figure 23.9), the —CH_2—CH_2— linking the phenyl ring to the cyclodextrin was converted to an alkene, and this serves as a photochemical on/off switch. Irradiation at 300 nm converts the *trans* cinnamide side chain of structure 2 to the *cis* isomer of structure 3, while the reverse process occurs at 254 nm. The work output of the 'switchED-on' machine is of the order of 8.8 kJ mol^{-1}.

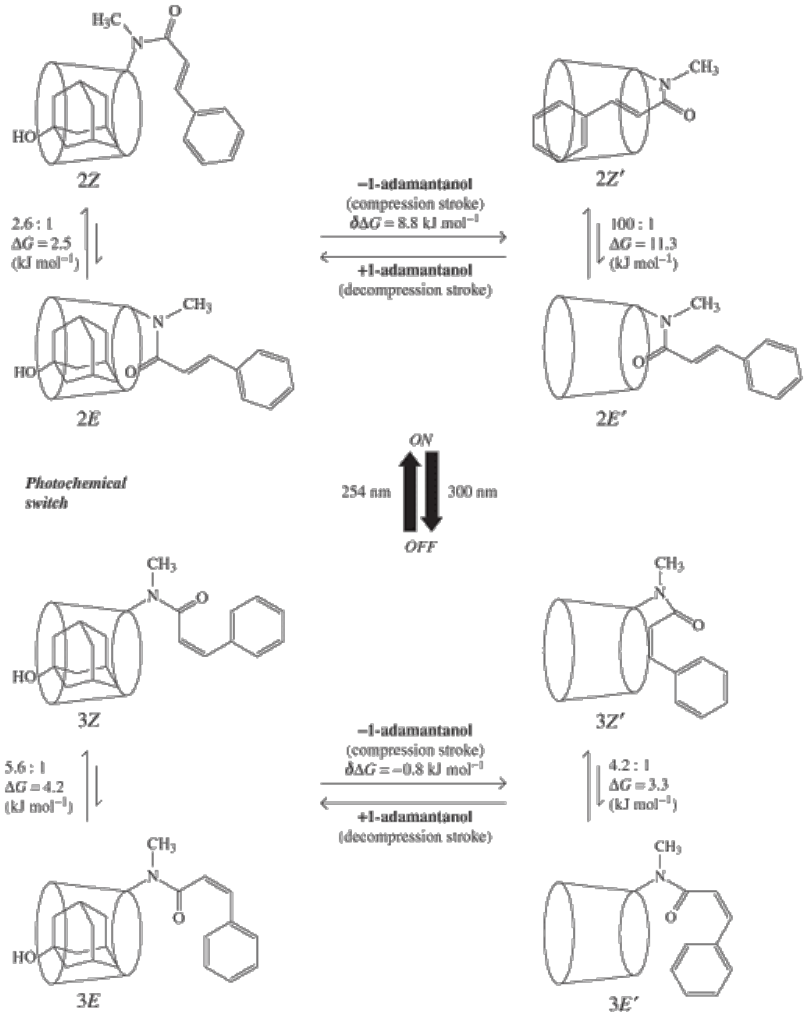


FIGURE 23.9 Graphical representation of a more advanced form of the molecular machine (structures 2 and 3) using two isomers that can be interconverted photochemically to create an on/off switch. *E* and *Z* refer to the (*E*)- and (*Z*)-type isomers.

The ratios of the amide isomers of structures 2 and 3 (in figure 23.9) were determined as for structure 1 (in figure 23.8). In this case, however, the orientation of the *cis* double bond prevents the side chain inserting into the cavity and so in that mode the machine is turned off. By contrast, the *trans* alkene moiety does allow insertion, and so in this mode the machine is turned on.

The apparatus developed by the Easton research group constitutes arguably the smallest machine ever built. This nanotechnological device is a machine where the output energy of molecular binding is harnessed to do work and constrain the geometry of an amide bond. The photoisomerisation of the *trans* cinnamide side chain of structure 2 and the *cis* isomer of structure 3 provides the machine with an on/off switch. The apparent work performed on the amide bond has a maximum of 8.8 kJ mol^{-1}. This demonstration by the Easton group that work output can be harnessed and quantified in such molecular machines takes researchers one step closer to the practical application of nanotechnology.

Fatty Acids

More than 500 different **fatty acids** have been isolated from various cells and tissues. Table 23.4 gives common names and structural formulae

for the most abundant fatty acids. The number of carbons in a fatty acid and the number of carbon–carbon double bonds in its hydrocarbon chain are shown by two numbers separated by a colon. In this notation, linoleic acid, for example, is designated as an 18:2 fatty acid; its 18-carbon chain contains two carbon–carbon double bonds. The three most abundant fatty acids in nature are palmitic acid (16:0), stearic acid (18:0) and oleic acid (18:1).

TABLE 23.4 The Most Abundant Fatty Acids in Animal Fats, Vegetable Oils (figure 23.10) and Biological Membranes

Carbon atoms: double bonds	Structure	Common name	Melting point (°C)
Saturated fatty acids			
12:0[(a)]	$CH_3(CH_2)_{10}COOH$	lauric acid	44
14:0	$CH_3(CH_2)_{12}COOH$	myristic acid	58
16:0	$CH_3(CH_2)_{14}COOH$	palmitic acid	63
18:0	$CH_3(CH_2)_{16}COOH$	stearic acid	70
20:0	$CH_3(CH_2)_{18}COOH$	arachidic acid	77
Unsaturated fatty acids			
16:1	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	palmitoleic acid	1
18:1	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	oleic acid	16
18:2	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$	linoleic acid	-5
18:3	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	linolenic acid	-11
20:4	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	arachidonic acid	-49

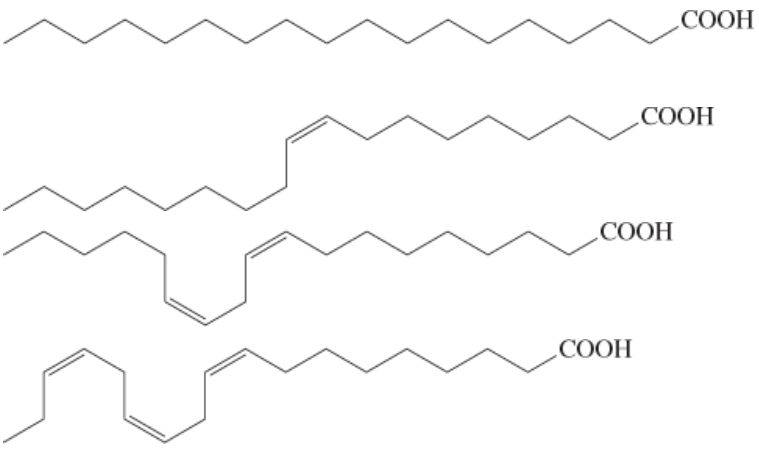
(a) The first number is the number of carbon atoms in the fatty acid; the second is the number of carbon–carbon double bonds in its hydrocarbon chain.



FIGURE 23.10 Some vegetable oils used in cooking. Kari-Ann Tapp

The most abundant fatty acids found in higher plants and animals have several important characteristics:

1. Nearly all fatty acids have an even number of carbon atoms, most between 12 and 20, in an unbranched chain.
2. In most unsaturated fatty acids, the *cis* isomer predominates; the *trans* isomer is rare.
3. Unsaturated fatty acids have lower melting points than their saturated counterparts. The greater the degree of unsaturation, the lower the melting point. Compare, for example, the melting points of these four 18-carbon fatty acids.



stearic acid (18:0)

(mp = 70 °C)

oleic acid (18:1)

(mp = 16 °C)

linoleic acid (18:2)

(mp = -5 °C)

linolenic acid (18:3)

(mp = -11 °C)

WORKED EXAMPLE 23.14

Triglyceride Structure

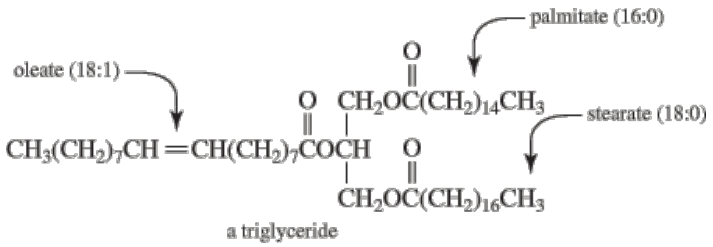
Draw the structural formula of a triglyceride derived from one molecule each of palmitic acid, oleic acid and stearic acid, the three most abundant fatty acids in the biological world.

Analysis

The triglyceride is a triester of glycerol (a triol) so each of the three carboxylic acids will form an ester with an —OH group of glycerol. There is more than one possible triglyceride using three different fatty acids.

Solution

In this structure, palmitic acid is esterified at C(1) of glycerol, oleic acid at C(2), and stearic acid at C(3).



Is our answer reasonable?

Check that the ester group is drawn the correct way around. That is, is the alkoxy group (—OR) derived from glycerol? Check also that the number of carbon atoms is correct.

PRACTICE EXERCISE 23.14

(a) How many constitutional isomers are possible for a triglyceride containing one molecule each of palmitic acid, oleic acid and stearic acid?

(b) Which of the constitutional isomers that you found in (a) are chiral?

Physical Properties

The physical properties of a triglyceride depend on its fatty acid components. In general, the melting point of a triglyceride increases as the number of carbon atoms in its hydrocarbon chains increases and as the number of carbon–carbon double bonds decreases. Triglycerides rich in oleic acid, linoleic acid and other unsaturated fatty acids are generally liquids at room temperature and are called **oils** (e.g. corn oil and olive oil). Triglycerides rich in palmitic, stearic and other saturated fatty acids are generally semisolids or solids at room temperature and are called **fats** (e.g. human fat and butter fat). Fats of land animals typically contain approximately 40% to 50% saturated fatty acids by weight (table 23.5). Most plant oils, on the other hand, contain 20% or less saturated fatty acids and 80% or more unsaturated fatty acids. The notable exception to this generalisation about plant oils are the **tropical oils** (e.g. coconut and palm oils), which are considerably richer in low-molar-mass saturated fatty acids.

TABLE 23.5 Grams of Fatty Acid Per 100 g of Triglyceride of Several Fats and Oils

	Saturated fatty acids			Unsaturated fatty acids	
Fat or oil	Lauric (12:0)	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)
human fat	-	24.0	8.4	46.9	10.2
beef fat	-	27.4	14.1	49.6	2.5
butter fat	2.5	29.0	9.2	26.7	3.6
canola oil	-	3.9	1.9	64.1	18.7
coconut oil	45.4	10.5	2.3	7.5	trace
corn oil	-	10.2	3.0	49.6	34.3
olive oil	-	6.9	2.3	84.4	4.6
palm oil	-	40.1	5.5	42.7	10.3

peanut oil	-	8.3	3.1	56.0	26.0
soybean oil	0.2	9.8	2.4	28.9	50.7
sunflower oil	0.5	6.8	4.7	18.6	68.7

Note: Only the most abundant fatty acids are given; other fatty acids are present in lesser amounts.

The lower melting points of triglycerides that are rich in unsaturated fatty acids are related to differences in three-dimensional shape between the hydrocarbon chains of their unsaturated and saturated fatty acid components. In a saturated triglyceride, the hydrocarbon chains lie parallel to each other, giving the molecule an ordered, compact shape. Because of this compact three-dimensional shape and the resulting strength of the dispersion forces (section 6.8) between hydrocarbon chains of adjacent molecules, triglycerides that are rich in saturated fatty acids have melting points above room temperature.

The three-dimensional shape of an unsaturated fatty acid, particularly those containing *cis*-(*Z*)- alkenes, is quite different from that of a saturated fatty acid. Recall that unsaturated fatty acids of higher organisms are predominantly of the *cis*-(*Z*)- configuration; *trans*-(*E*)- configurations are rare.

Polyunsaturated triglycerides (triglycerides with several carbon–carbon double bonds) have a less ordered structure and do not pack together as closely or as compactly as saturated triglycerides. Therefore, intramolecular and intermolecular dispersion forces are weaker, so polyunsaturated triglycerides have lower melting points than their saturated counterparts.

Reduction of Fatty-acid Chains

For a variety of reasons, in part convenience and in part dietary preference, the conversion of oils to fats has become a major industry. The process is called **hardening** of oils and involves the catalytic reduction of some or all of an oil's carbon–carbon double bonds. In practice, the degree of hardening is carefully controlled to produce fats of a desired consistency. The resulting fats are sold for kitchen use. Margarine and other butter substitutes are produced by partial hydrogen ation of polyunsaturated oils derived from canola, sunflower, olive and soybean oils (see figure 23.11). To the hardened oil are added β-carotene (to give it a yellow colour and make it look like butter), salt and about 15% milk by volume to form the final emulsion. Vitamins A and D may be added as well. Finally, because the product at this stage is tasteless, acetoin and diacetyl, two compounds that mimic the characteristic flavour of butter, are often added:

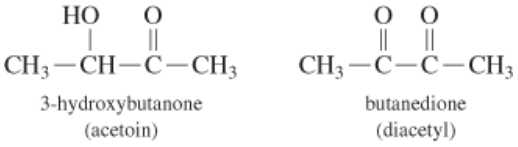


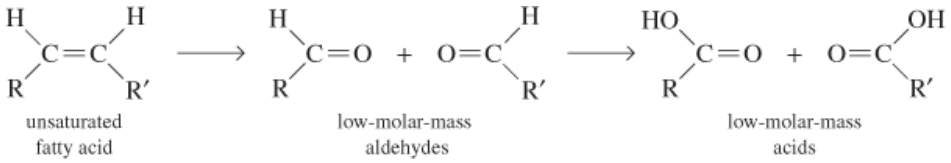


FIGURE 23.11 Some common products containing hydrogenated vegetable oils. Kari-Ann Tapp

An unintended consequence of partial hydrogenation of the alkene groups in polyunsaturated oils is the isomerisation of a small proportion of the *cis* alkenes to *trans* alkenes. These are known as *trans*-fats and are of concern as they are believed to increase the risk of coronary heart disease. These *trans*-fats do occur naturally, although only to a small extent. Canola oil naturally has a relatively high level of *trans*-fats, but most other natural oils have very little *trans*-fat. Lamb and mutton also naturally contain moderate levels of *trans*-fats.

Rancidification of Fats and Oils

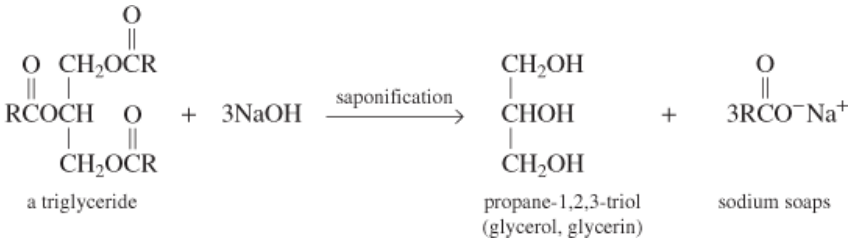
Unsaturated fats and oils, when exposed to air, can undergo a process of rancidification. In this process the alkene units are oxidatively cleaved to give low-molar-mass aldehydes and carboxylic acids. These compounds have unpleasant odours and flavours, thus making the food unpalatable.



Often antioxidants are added to unsaturated fats and oils to retard this oxidation process.

Soaps and Detergents

Natural **soaps** are prepared most commonly from a blend of tallow and coconut oil. In the preparation of tallow, the solid fats of cattle are melted with steam, and the tallow layer that forms on the top is removed. The preparation of soaps begins by boiling these triglycerides with sodium hydroxide. The reaction that takes place is called *saponification* (from the Latin *saponem* meaning 'soap').



At the molecular level, saponification corresponds to base-promoted hydrolysis of the ester groups in triglycerides (section 23.5). The resulting soaps contain mainly the sodium salts of palmitic, stearic and oleic acids from tallow and the sodium salts of lauric and myristic acids from coconut oil.

After hydrolysis is complete, sodium chloride is added to precipitate the soap as thick curds. The water layer is then drawn off, and glycerol is recovered by vacuum distillation. The crude soap contains sodium chloride, sodium hydroxide and other impurities that are removed by boiling the curd in water and precipitating again with more sodium chloride. After several purifications, the soap can be used as an inexpensive industrial soap without further processing. Other treatments transform the crude soap into pH-controlled cosmetic soaps, medicated soaps and the like.

How Soap Cleans

Soap owes its remarkable cleaning properties to its ability to act as an emulsifying agent. Because the long hydrocarbon chains of natural soaps are insoluble in water, they tend to cluster to minimise their contact with surrounding water molecules. The polar carboxylate groups, by contrast, tend to remain in contact with the surrounding water molecules. Thus, in water, soap molecules spontaneously cluster into **micelles** (figure 23.12). A micelle is a spherical arrangement of organic molecules in water solution clustered so that their hydrophobic parts are buried inside the sphere and their hydrophilic parts are on the surface of the sphere and in contact with water.

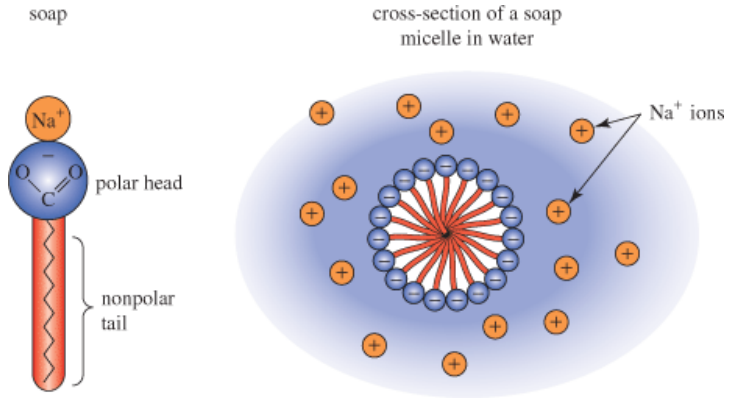


FIGURE 23.12 Soap micelles. Nonpolar (hydrophobic) hydrocarbon chains are clustered in the interior of the micelle, and polar (hydrophilic) carboxylate groups are on the surface of the micelle. Soap micelles repel each other because of their negative surface charges.

Most of the things we commonly think of as dirt (such as grease, oil and fat stains) are non-polar and insoluble in water. When soap and this type of dirt are mixed together, as in a washing machine, the nonpolar hydrocarbon inner parts of the soap micelles 'dissolve' the nonpolar dirt molecules. In effect, new soap micelles are formed, this time with nonpolar dirt molecules in the centre (figure 23.13). In this way, nonpolar organic grease, oil and fat are 'dissolved' and washed away in the polar wash water.

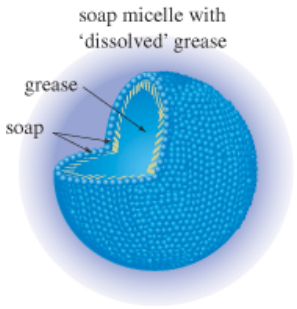


FIGURE 23.13 A soap micelle with a 'dissolved' oil or grease droplet.

Soaps, however, have their disadvantages, the main one being that they form water-insoluble salts when used in 'hard' water, which contains Ca(II), Mg(II) or Fe(III) ions.

$$\underset{\text{a sodium soap}}{2CH_3(CH_2)_{14}COO^-Na^+} + Ca^{2+} \rightarrow \underset{\text{calcium salt of a fatty acid}}{[CH_3(CH_2)_{14}COO^-]_2Ca^{2+}} + 2Na^+$$

(soluble in water as micelles) (insoluble in water)

These calcium, magnesium and iron salts of fatty acids create problems, including rings around the bathtub, films that spoil the lustre of hair, and greyness and roughness that build up on textiles after repeated washings.

Synthetic Detergents

After the cleaning action of soaps was understood, chemists were in a position to design a synthetic detergent. Molecules of a good detergent, they reasoned, must have a long hydrocarbon chain — preferably 12 to 20 carbon atoms long — and a polar group at one end of the molecule that does not form insoluble salts with the Ca(II), Mg(II) or Fe(III) ions in hard water. These essential characteristics of a soap, they recognised, could be produced in a molecule containing a sulfonate ($—SO_3^-$) group instead of a carboxylate ($—COO^-$) group. Calcium, magnesium and iron salts of monoalkylsulfuric and sulfonic acids are much more soluble in water than comparable salts of fatty acids.

The most widely used synthetic detergents today are the linear alkylbenzenesulfonates (LAS). One of the most common of these is sodium 4-dodecylbenzenesulfonate. To prepare this type of detergent, a linear alkylbenzene is treated with sulfuric acid to form an alkylbenzenesulfonic acid, followed by neutralisation of sulfonic acid with NaOH:

$$\underset{\text{dodecylbenzene}}{CH_3(CH_2)_{10}CH_2-C_6H_4} \xrightarrow[2.\ NaOH]{1.\ H_2SO_4} \underset{\text{sodium 4-dodecylbenzenesulfonate (an anionic detergent)}}{CH_3(CH_2)_{10}CH_2-C_6H_4-SO_3^-Na^+}$$

The product is mixed with building agents and spray dried to give a smooth, flowing powder. The most common builder is sodium silicate. Alkylbenzenesulfonate detergents were introduced in the late 1950s, and today they command close to 90% of the market once held by natural soaps.

Among the most common additives to detergent preparations are foam stabilisers (to encourage longer lasting bubbles), bleaches and optical brighteners. The amide prepared from dodecanoic acid (lauric acid) and 2-aminoethanol (ethanolamine) is a common foam stabiliser added to liquid soaps, but not laundry detergents for obvious reasons — imagine a top-loading washing machine with foam spewing out of the lid! The most common bleach used in washing powders is sodium perborate, which decomposes at temperatures above 50 °C to give hydrogen peroxide, the actual bleaching agent.

$$\underset{\text{}}{CH_3(CH_2)_{10}\overset{\overset{O}{\|}}{C}NHCH_2CH_2OH} \qquad \underset{\text{}}{O=B-O-O^-Na^+\cdot 4H_2O}$$

N-(2-hydroxyethyl)dodecanamide (a foam stabiliser)

sodium perborate tetrahydrate (a bleach)

Also added to laundry detergents are optical brighteners (optical bleaches). These substances are absorbed into fabrics and, after absorbing ambient light, fluoresce with a blue colour, offsetting the yellow colour acquired by fabric as it ages. Optical brighteners produce a 'whiter-than-white' appearance (see figure 23.14). You most certainly have observed their effects if you have seen the glow of white T-shirts or blouses when they are exposed to black light (UV radiation).



FIGURE 23.14 Optical brighteners convert UV light to brighter fluorescent colours. Stone/Jayme Thornton

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SUMMARY

Structure and Bonding

The carboxylic acid functional group is the carboxyl group, — COOH. The acid halide functional group is an acyl group bonded to a halogen atom. The most common and widely used of the acid halides are the acid chlorides. The carboxylic anhydride functional group is two acyl groups bonded to an oxygen atom. The ester functional group is an acyl group bonded to an —OR or —OAr group. A cyclic ester is given the name lactone. The amide functional group is an acyl group bonded to a trivalent nitrogen atom. A cyclic amide is given the name lactam.

Nomenclature

IUPAC names of carboxylic acids are derived from the parent alkane by dropping the suffix *-e* and adding *-oic acid*. Dicarb oxylic acids are named as *-dioic acids*. Acid halides are named by changing the suffix *-ic acid* in the name of the parent carboxylic acid to *-yl halide*. Acid anhydrides are named by replacing the word *acid* with *anhydride*. When the anhydride is not symmetrical, both acid groups are named. In esters, the alkyl or aryl group bonded to oxygen is named first, followed as a separate word by the name of the acid in which the suffix *-ic acid* is replaced by the suffix *-ate*. Amides are named by dropping the suffix *-oic acid* from the IUPAC name of the parent acid, or *-ic acid* from its common name, and adding *-amide*.

Physical Properties

Carboxylic acids are polar compounds that associate by hydrogen bonding into dimers in the liquid and solid states. Carboxylic acids have higher boiling points and are more soluble in water than alcohols, aldehydes, ketones and ethers of comparable molar mass. A carboxylic acid consists of two regions of different polarity: a polar, hydrophilic carboxyl group, which increases solubility in water, and a nonpolar, hydrophobic hydrocarbon chain, which decreases solubility in water. The first four aliphatic carboxylic acids are infinitely soluble in water, because the hydrophilic carboxyl group more than offsets the hydrophobic hydrocarbon chain. As the size of the carbon chain increases, however, the hydrophobic group becomes dominant and solubility in water decreases.

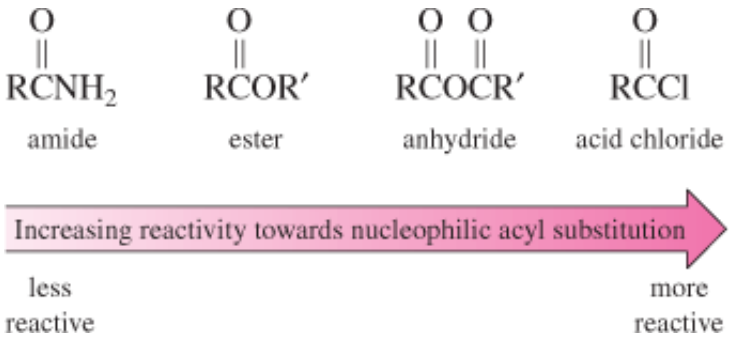
Preparation of Carboxylic Acids

Carboxylic acids can be prepared by the oxidation of primary alcohols, aldehydes and alkylbenzene derivatives. They can be prepared by the reaction of Grignard reagents with carbon dioxide and by the hydrolysis of nitriles and carboxylic acid derivatives.

Reactions of Carboxylic Acids and Derivatives

Values of pK_a for aliphatic carboxylic acids range from 4.0 to 5.0. Electron-withdrawing substituents near the carboxyl group increase acidity in both aliphatic and aromatic carboxylic acids.

A common reaction theme of functional derivatives of carboxylic acids is nucleophilic acyl addition to the carbonyl carbon atom to form a tetrahedral carbonyl addition intermediate, which then collapses to regenerate the carbonyl group. The result is nucleophilic acyl substitution. Listed in order of increasing reactivity towards nucleo philic acyl substitution, these functional derivatives are:



Any more reactive functional derivative can be directly converted to any less reactive functional derivative by reaction with an appropriate oxygen or nitrogen nucleophile.

Triglycerides

Lipids are a heterogeneous class of compounds grouped together on the basis of their solubility properties; they are insoluble in water but soluble in diethyl ether and dichloromethane. Carbohydrates, amino acids and proteins are largely insoluble in these organic solvents.

Triglycerides (triacylglycerols), the most abundant lipids, are triesters of glycerol and fatty acids. Fatty acids are long-chain carboxylic acids derived from the hydrolysis of fats, oils and the phospholipids of biological membranes. The melting point of a triglyceride increases as (1) the length of its hydrocarbon chains increases and (2) its degree of saturation increases. Triglycerides rich in saturated fatty acids are generally solids at room temperature; those rich in unsaturated fatty acids are generally oils at room temperature.

Soaps are sodium or potassium salts of fatty acids. In water, soaps form micelles, which ‘dissolve’ nonpolar organic grease and oil. Natural soaps precipitate as water-insoluble salts with Mg^{2+}, Ca^{2+} and Fe^{3+} ions in hard water. The most common and most widely used synthetic detergents are linear alkylbenzenesulfonates.

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Preparation of carboxylic acids by oxidation of primary alcohols and aldehydes *(section 23.4)*

Primary alcohols and aldehydes are readily oxidised to carboxylic acids with a variety of oxidising agents.



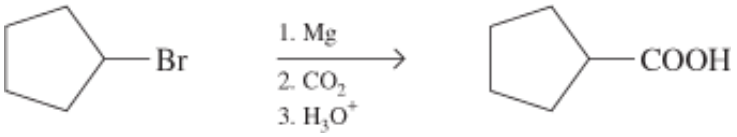
Preparation of carboxylic acids by oxidation of alkylbenzenes *(section 23.4)*

Alkylbenzenes are oxidised to benzoic acids under vigorous oxidising conditions.



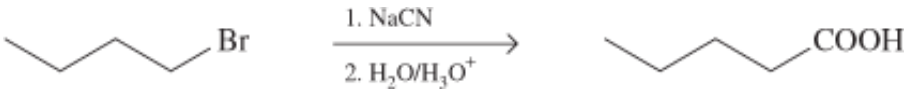
Preparation of carboxylic acids by carbonation of Grignard reagents *(section 23.4)*

Carboxylic acids can be prepared by treatment of Grignard reagents with CO_2.



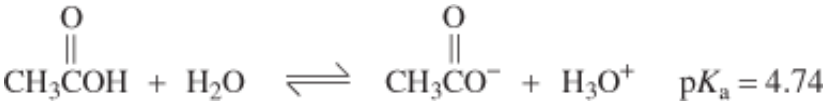
Preparation of carboxylic acids by formation and hydrolysis of nitriles *(section 23.4)*

Carboxylic acids can be prepared from alkyl halides by formation and subsequent hydrolysis of nitriles.



Acidity of carboxylic acids *(section 23.5)*

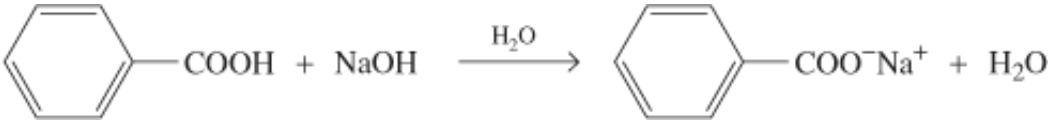
Values of pK_a for most unsubstituted aliphatic and aromatic carboxylic acids range from 4 to 5.



Substitution by electron-withdrawing groups decreases the pK_a value (increases acidity).

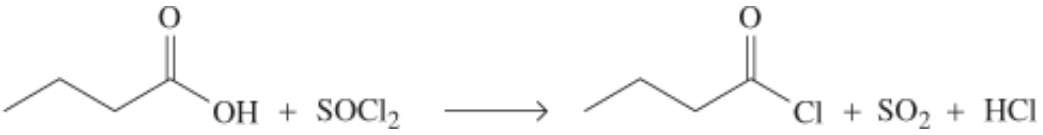
Reaction of carboxylic acids with bases *(section 23.5)*

Carboxylic acids form water-soluble salts with alkali metal hydroxides, carbonates and bicarbonates, as well as with ammonia and amines.



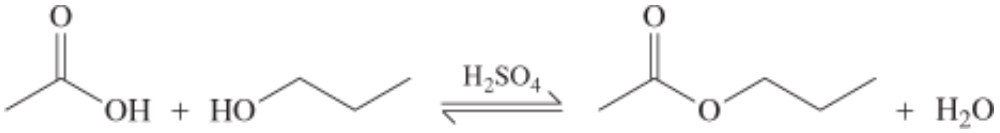
Conversion to acid halides *(section 23.5)*

Acid chlorides, the most common and widely used of the acid halides, are prepared by treating carboxylic acids with thionyl chloride.



Fischer esterification *(section 23.5)*

Fischer esterification is reversible.



To force the reaction to the right, use excess alcohol.

Reaction of an acid chloride with an alcohol *(section 23.5)*

Treatment of an acid chloride with an alcohol gives an ester and HCl.



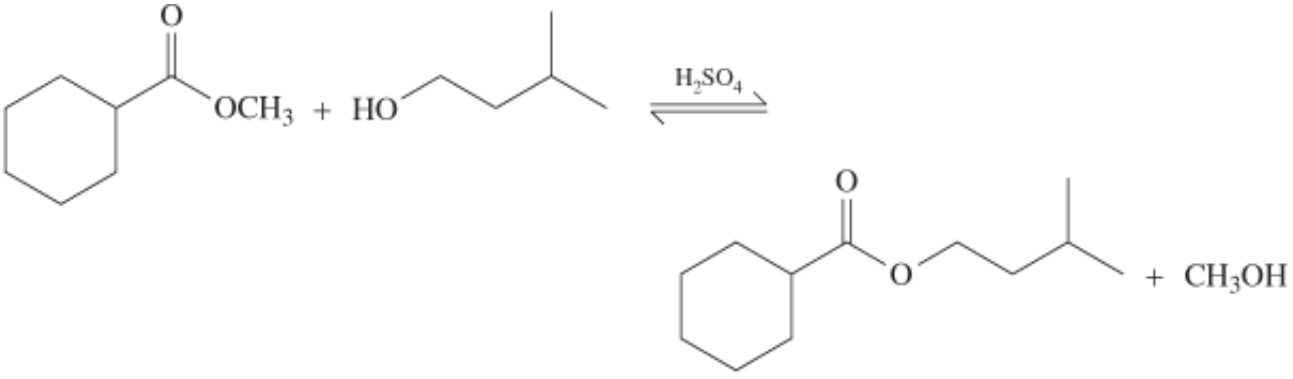
Reaction of an acid anhydride with an alcohol *(section 23.5)*

Treatment of an acid anhydride with an alcohol gives an ester and a carboxylic acid.



Reaction of an ester with an alcohol *(section 23.5)*

Treatment of an ester with an alcohol in the presence of an acid catalyst results in transesterification: that is, the replacement of one —OR group by a different —OR group.



Hydrolysis of an acid chloride *(section 23.5)*

Low-molar-mass acid chlorides react vigorously with water; high-molar-mass acid chlorides react less rapidly.



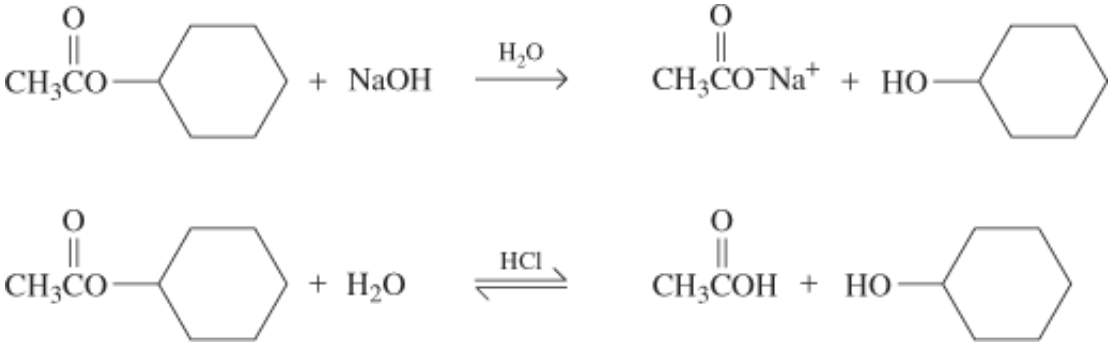
Hydrolysis of an acid anhydride *(section 23.5)*

Low-molar-mass acid anhydrides react readily with water; high-molar-mass acid anhydrides react less rapidly.



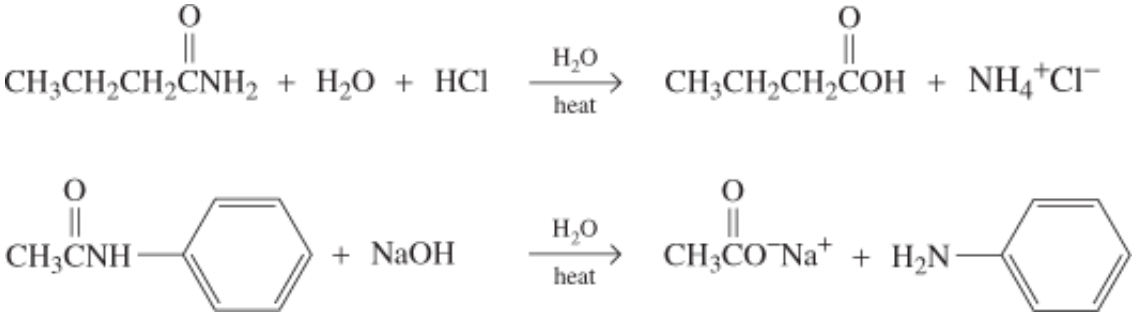
Hydrolysis of an ester *(section 23.5)*

Esters are hydrolysed only in the presence of base or acid; base is required in an equimolar amount; acid is a catalyst.



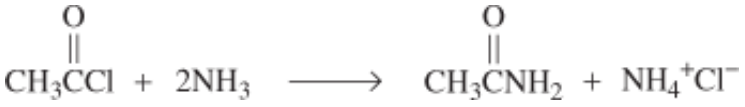
Hydrolysis of an amide *(section 23.5)*

Either acid or base is required in an amount equivalent to that of the amide.



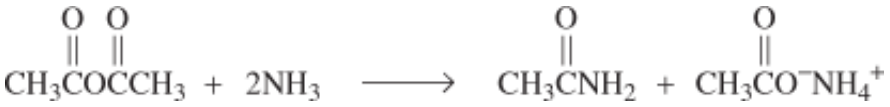
Reaction of an acid chloride with ammonia or an amine *(section 23.5)*

This reaction requires 2 mole equivalents of ammonia or amine — 1 mole equivalent to form the amide and 1 mole equivalent to neutralise the HCl by-product.



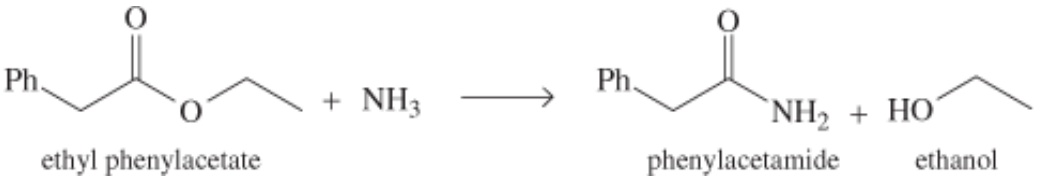
Reaction of an acid anhydride with ammonia or an amine *(section 23.5)*

This reaction requires 2 mole equivalents of ammonia or amine — 1 mole equivalent to form the amide and 1 mole equivalent to neutralise the carboxylic acid by-product.



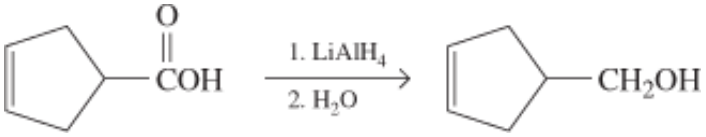
Reaction of an ester with ammonia or an amine *(section 23.5)*

Treatment of an ester with ammonia, a 1° amine or a 2° amine gives an amide.



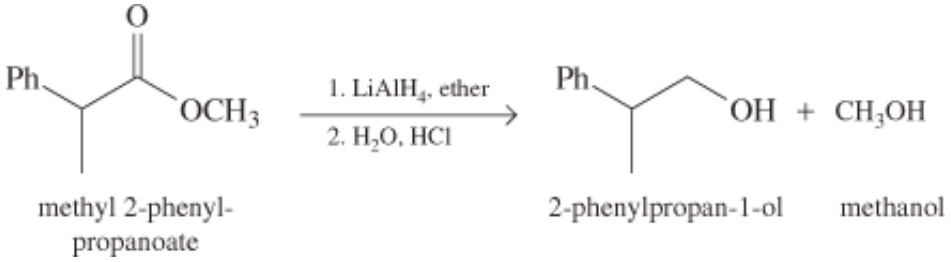
Reduction by lithium aluminium hydride *(section 23.5)*

Lithium aluminium hydride reduces a carboxyl group to a primary alcohol.



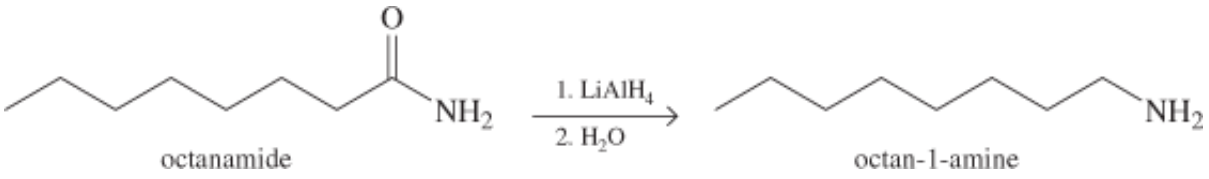
Reduction of an ester *(section 23.5)*

Reduction of esters by lithium aluminium hydride gives two alcohols.



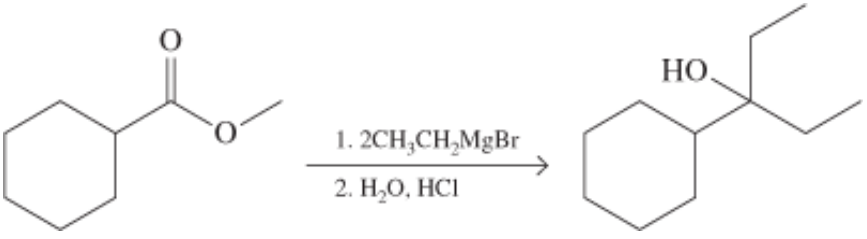
Reduction of an amide *(section 23.5)*

Reduction of an amide by lithium aluminium hydride gives an amine.



Reaction of an ester with a Grignard reagent *(section 23.5)*

Treating a formate ester with a Grignard reagent, followed by hydrolysis, gives a 2° alcohol, whereas treating any other ester with a Grignard reagent gives a 3° alcohol.



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REVIEW QUESTIONS

Structure and Bonding

23.1 Draw structural formulae for the four carboxylic acids with the molecular formula $C_5H_{10}O_2$. Which of these carboxylic acids is chiral?

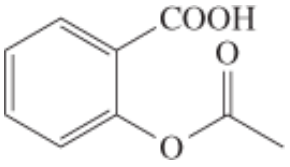
23.2 Draw the structural formulae for the seven carboxylic acids with the molecular formula $C_6H_{12}O_2$. Which of these is chiral?.

23.3 Draw structural formulae for (a) an ester, (b) an acid chloride, (c) an anhydride and (d) an amide.

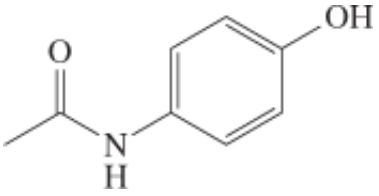
23.4 On the structures you have drawn in question 23.3, show the polarity of the atoms in the functional groups using the δ+/δ– notation.

23.5 Identify the functional groups in each of the following compounds.

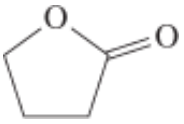
(a)



(b)

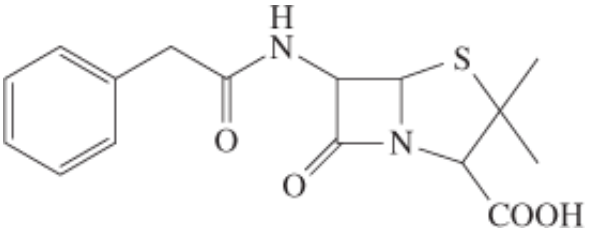


(c)

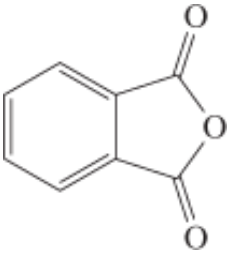


23.6 Identify the functional groups in each of the following compounds.

(a)



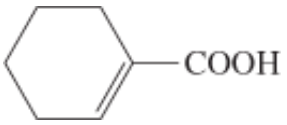
(b)



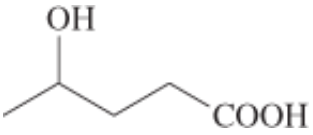
Nomenclature

23.7 Write the IUPAC name for each of the following compounds.

(a)



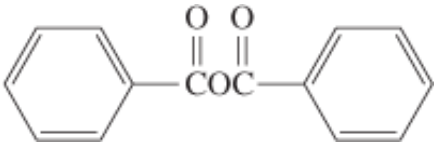
(b)



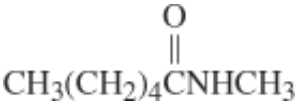
(c)



(d)



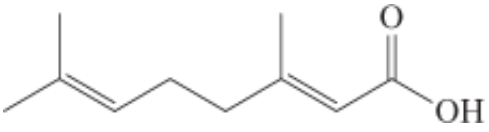
(e)



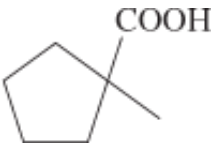
(f) $CH_2(COOCH_2CH_3)_2$

23.8 Write the IUPAC name for each of the following compounds.

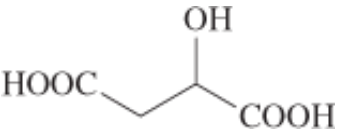
(a)



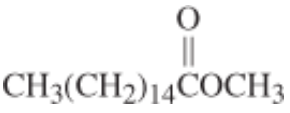
(b)



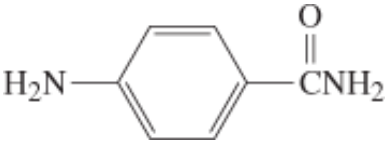
(c)



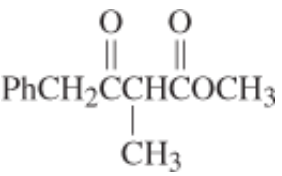
(d)



(e)



(f)



23.9 Draw the structural formula for each of the following carboxylic acids.

(a) 4-nitrophenylacetic acid

(b) 4-aminopentanoic acid

(c) 3-chloro-4-phenylbutanoic acid

(d) *cis*-hex-3-enedioic acid

23.10 Draw the structural formula for each of the following carboxylic acids.

(a) 2,3-dihydroxypropanoic acid

(b) 3-oxohexanoic acid

(c) 2-oxocyclohexanecarboxylic acid

(d) 2,2-dimethylpropanoic acid

23.11 Draw the structural formula for each of the following compounds.

(a) dimethyl carbonate

(b) *p*-nitrobenzamide

(c) octanoyl chloride

(d) diethyl oxalate (diethyl ethanedioate)

23.12 Draw the structural formula for each of the following compounds.

(a) ethyl *cis*-pent-2-enoate

(b) butanoic anhydride

(c) dodecanamide

(d) ethyl 3-hydroxybutanoate

23.13 Draw the structural formula for methyl linoleate. Be certain to show the correct configuration of groups around each carbon– carbon double bond.

23.14 Draw structural formulae for each of the following salts.

(a) sodium benzoate

(b) lithium acetate

(c) ammonium acetate

(d) disodium adipate (disodium hexanedioate)

(e) sodium salicylate (sodium 2-hydroxybenzoate)

(f) calcium butanoate

Physical Properties

23.15 Acetic acid and methyl formate are constitutional isomers. Both are liquids at room temperature, one with a boiling point of 32 °C, the other with a boiling point of 118 °C. Which of the two has the higher boiling point?

23.16 Acetic acid has a boiling point of 118 °C, whereas its methyl ester has a boiling point of 57 °C. Account for the fact that the boiling point of acetic acid is higher than that of its methyl ester, even though acetic acid has a lower molar mass.

23.17 Arrange the compounds in each of the following sets in order of increasing boiling point.

(a) $CH_3(CH_2)_5COOH$, $CH_3(CH_2)_6CHO$, $CH_3(CH_2)_6CH_2OH$

(b) CH_3CH_2COOH, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2OCH_2CH_3$

23.18 Arrange the compounds in each of the following sets in order of increasing solubility in water.

(a) $CH_3(CH_2)_5COOH$, $CH_3(CH_2)_6CHO$, $CH_3(CH_2)_6CH_2OH$

(b) CH_3CH_2COOH, $CH_3CH_2CH_2CH_2OH$, $CH_3CH_2OCH_2CH_3$

23.19 Decanoic acid is not very soluble in water. Would it be more soluble under acidic or basic conditions? Explain your answer.

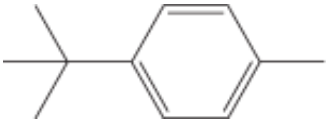
23.20 Characterise the structural features necessary to make a good synthetic detergent.

Preparation of Carboxylic Acids

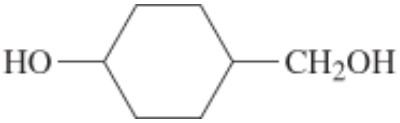
23.21 Draw a structural formula for the product formed by treating each of the following compounds with warm chromic acid, H_2CrO_4.

(a) $CH_3(CH_2)_4CH_2OH$

(b)

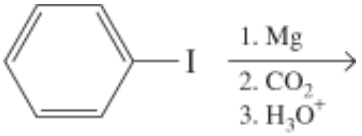


(c)

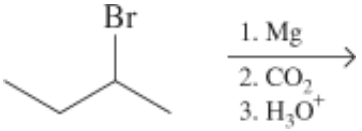


23.22 Give the structure of the carboxylic acids formed in each of the following reactions.

(a)



(b)



Reactions of Carboxylic Acids and Derivatives

23.23 Which is the stronger acid in each of the following pairs?

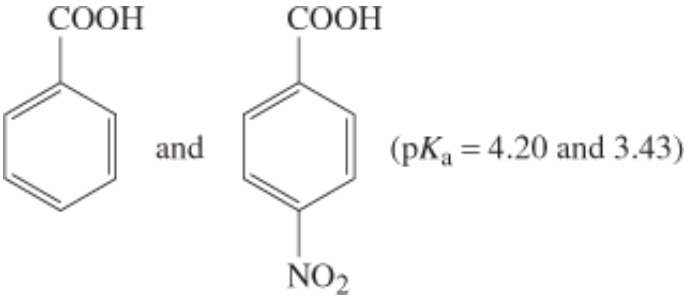
(a) phenol ($pK_a = 9.89$) or benzoic acid ($pK_a = 4.20$)

(b) lactic acid ($K_a = 1.4 \times 10^{-4}$) or ascorbic acid ($K_a = 7.9 \times 10^{-5}$)

23.24 Arrange these compounds in order of increasing acidity: benzoic acid, benzyl alcohol, phenol.

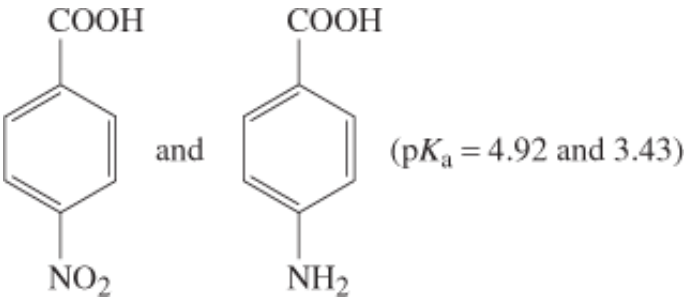
23.25 Assign the appropriate pK_a to each of the acids in the following sets.

(a)



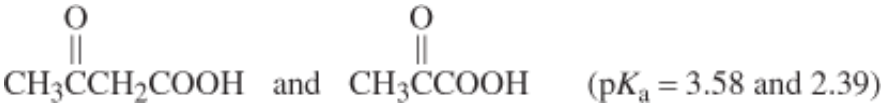
($pK_a = 4.20$ and 3.43)

(b)

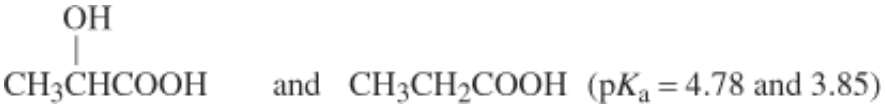


23.26 Assign the appropriate pK_a to each of the acids in the following sets.

(a)



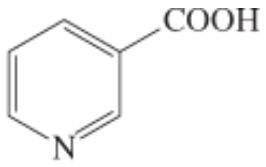
(b)



23.27 Rank the following in order of increasing acidity: butanoic acid, 2-chlorobutanoic acid, 3-chlorobutanoic acid, 4-chlorobutanoic acid.

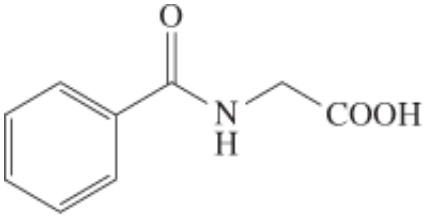
23.28 Rank the following in order of increasing acidity: 2-bromobutanoic acid, 2-chlorobutanoic acid, 2-fluorobutanoic acid, 2-iodobutanoic acid.

23.29 At room temperature, nicotinic acid has a moderate solubility in water of approximately 1 gram per 60 mL. How would its solubility change if the pH of the water was (a) decreased to pH = 2 and (b) increased to pH = 10? Use equations to explain your answer.



nicotinic acid
(niacin)

23.30 Hippuric acid is only slightly soluble (4 g/L) in water at room temperature. How would its solubility change if the pH of the water was (a) decreased to pH = 2 and (b) increased to pH = 10? Use equations to explain your answer.



hippuric acid

23.31 Give the expected organic products formed (if any) when phenylacetic acid, $PhCH_2COOH$, is treated with each of the following reagents.

(a) $SOCl_2$

(b) $NaHCO_3$, H_2O

(c) NH_3, H_2O

(d) $LiAlH_4$ then H_2O

(e) CH_3OH, H_2SO_4 (catalyst)

(f) H_2/Ni at 25 °C and 300 kPa pressure

23.32 Give the expected organic products formed (if any) when 4-chlorobenzoic acid is treated with each of the following reagents.

(a) PCl_5

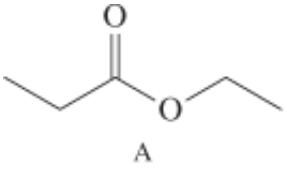
(b) NaOH, H_2O

(c) $CH_3CH_2NH_2$

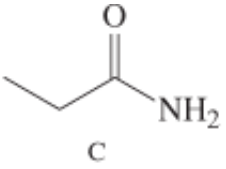
(d) $NaBH_4$ then H_2O

(e) $(CH_3)_2CHOH$, H_2SO_4 (catalyst)

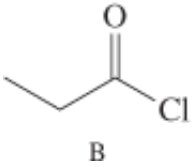
23.33 Arrange the following compounds in order of increasing reactivity towards nucleophilic acyl substitution.



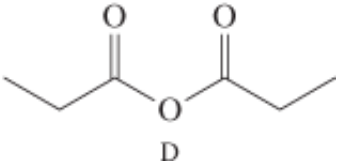
A



C



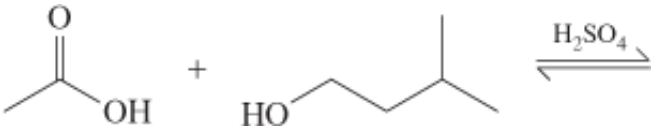
B



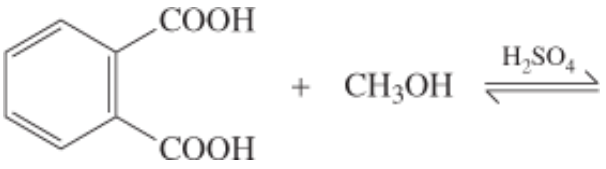
D

23.34 Complete the following Fischer esterification equations. (Assume excess alcohol.)

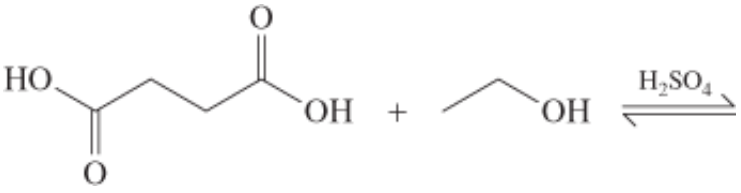
(a)



(b)

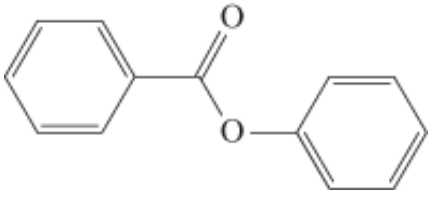


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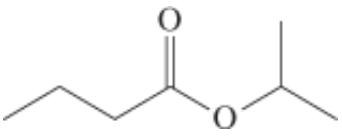


23.35 Identify the carboxylic acid and the alcohol that are necessary in order to make each of the following compounds via a Fischer esterification.

(a)



(b)



(c) $CH_3CH_2CO_2C(CH_3)_3$

23.36 Write the product(s) of the treatment of propanoyl chloride with each of the following reagents.

(a) ethanol (1 equivalent)

(b) ammonia (2 equivalents)

23.37 Write the product(s) of the treatment of benzoic anhydride with each of the following reagents.

(a) ethanol (1 equivalent)

(b) ammonia (2 equivalents)

23.38 What product(s) is(are) formed when ethyl benzoate is treated with the following reagents?

(a) H_2O, NaOH, heat

(b) $LiAlH_4$ then H_2O

(c) H_2O, H_2SO_4, heat

(d) $CH_3CH_2CH_2CH_2NH_2$

(e) C_6H_5MgBr (2 moles) then H_2O, HCl

23.39 What product(s) is(are) formed when benzamide is treated with the following reagents?

(a) H_2O, HCl, heat

(b) NaOH, H_2O, heat

(c) $LiAlH_4$ then H_2O

23.40 Show how to convert butanoic acid into each of the following compounds (more than one step may be required).

(a) methyl butanoate

(b) *N*-methylbutanamide

(c) butanoyl chloride

(d) 2-methylpentan-2-ol

(e) ammonium butanoate

23.41 Show how to convert ethyl benzoate into each of the following compounds (more than one step may be required).

(a) benzyl alcohol

(b) benzoic acid

(c) benzoyl chloride

(d) benzamide

(e) 3-phenylpentan-3-ol

Triglycerides

23.42 Define the term ‘hydrophobic’.

23.43 What is meant by the term ‘hardening’ as applied to vegetable oils?

23.44 Explain why the melting points of unsaturated fatty acids are lower than those of saturated fatty acids.

23.45 Which would you expect to have the higher melting point, glyceryl trioleate or glyceryl trilinoleate?

23.46 What amount of H_2 is used in the catalytic hydrogenation of 1 mole of a triglyceride derived from glycerol, stearic acid, linoleic acid and oleic acid?

23.47 What amount of hydrogen is used in the catalytic hydrogenation of 1 mole of a triglyceride derived from glycerol, stearic acid, linoleic acid and arachidonic acid?

23.48 Draw the structure of a triglyceride derived from glycerol, palmitic acid, and two equivalents of oleic acid that is not chiral. On this structure identify the hydrophobic and hydrophilic regions.

23.49 Draw the structure of a triglyceride derived from glycerol, stearic acid, and two equivalents of oleic acid that is chiral. If this was hydrogenated, would the product be chiral? Explain.

23.50 Show how to convert palmitic acid (hexadecanoic acid) into each of the following.

(a) ethyl palmitate

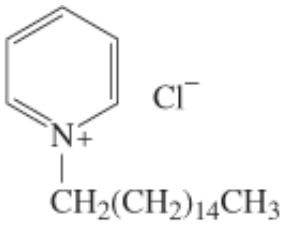
(b) palmitoyl chloride

(c) hexadecan-1-ol (cetyl alcohol)

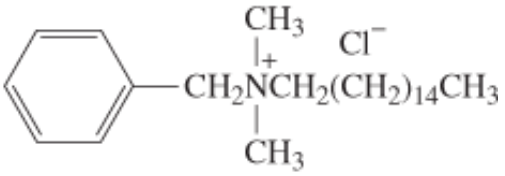
(d) hexadecan-1-amine

(e) *N*,*N*-dimethylhexadecanamide

23.51 Palmitic acid (hexadecanoic acid, 16:0) is the source of the hexadecyl (cetyl) group in the following compounds.



cetylpyridinium chloride



benzylcetyldimethylammonium chloride

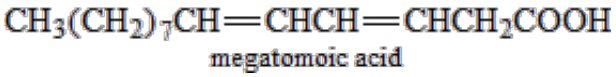
Each compound is a mild, surface-acting germicide and fungicide and is used as a topical antiseptic and disinfectant.

(a) Cetylpyridinium chloride is prepared by treating pyridine with 1-chlorohexadecane (cetyl chloride). Show how to convert palmitic acid to cetyl chloride.

(b) Benzylcetyldimethylammonium chloride is prepared by treating benzyl chloride with *N*, *N*-dimethylhexadecan-1-amine. Show how this tertiary amine can be prepared from palmitic acid.

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23.52 Megatomoic acid, the sex attractant of the female black carpet beetle, has the structure:



megatomoic acid

(a) What is the IUPAC name for megatomoic acid?

(b) How many stereoisomers are possible for this compound?

23.53 The IUPAC name for ibuprofen is 2-[4-(2-methylpropyl)phenyl]propanoic acid. Draw the structural formula for ibuprofen. On the structure, identify the 2-methylpropyl and the propanoic acid components.

23.54 The monopotassium salt of oxalic acid is present in certain leafy vegetables, including rhubarb. Both oxalic acid and its salts are poisonous in high concentrations. Draw the structural formula for monopotassium oxalate.

23.55 Potassium sorbate is added as a preservative to certain foods to prevent spoilage by bacteria and moulds and to extend the shelf life. The IUPAC name for potassium sorbate is potassium (2*E*,4*E*)-hexa-2,4-dienoate. Draw the structural formula for potassium sorbate.

23.56 Draw the structural formula of a compound with each of the following molecular formulae that, on oxidation by chromic acid, gives the carboxylic acid or dicarboxylic acid shown.

(a)



(b)



(c)



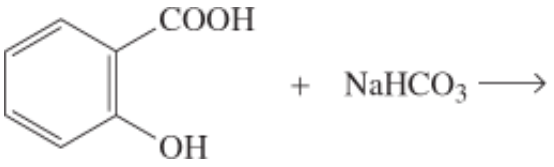
23.57 Complete the following acid–base reactions.

(a)



(b) $CH_3CH{=}CHCH_2COOH + NaHCO_3 \rightarrow$

(c)



(d)



(e) $CH_3CH{=}CHCH_2COO^-Na^+ + HCl \rightarrow$

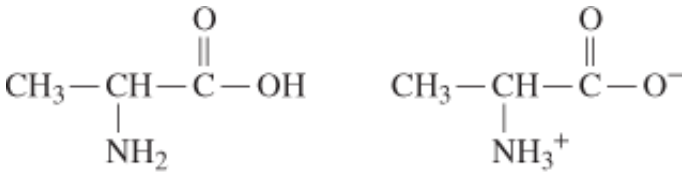
23.58 The normal pH range for blood plasma is 7.35–7.45. Under these conditions, would you expect the carboxyl group of lactic acid ($pK_a = 3.85$) to exist primarily as a carboxyl group or as a carboxylate anion? Explain.

23.59 The pK_a of ascorbic acid is 4.10. Would you expect ascorbic acid dissolved in blood plasma (pH = 7.35-7.45) to exist primarily as ascorbic acid or as ascorbate anions? Explain.

23.60 Excess ascorbic acid (pK_a = 4.10) is excreted in the urine, the pH of which is normally 4.8-8.4. What form of ascorbic acid — ascorbic acid itself or ascorbate anions — would you expect to be present in urine with pH = 8.4?

23.61 The pH of human gastric juice is normally 1.0 –3.0. What form of lactic acid (pK_a = 3.85) — lactic acid itself or its anion — would you expect to be present in the stomach?

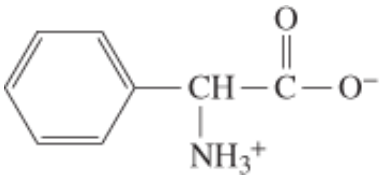
23.62 In chapter 24, we discuss a class of compounds called amino acids, so named because they contain both an amino group and a carboxyl group. The following are two structural formulae for the amino acid alanine.



A B

Is alanine better represented by structural formula A or B? Explain.

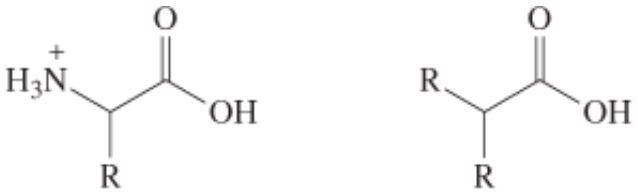
23.63 The following is the structural formula for the amino acid phenyalanine in the form of a zwitterion.



phenylalanine

What would you expect to be the major form of phenylalanine present in aqueous solution at (a) pH = 2.0, (b) pH = 5– 6 and (c) pH = 11.0? Explain.

23.64 Explain why α-amino acids, the building blocks of proteins (chapter 24), have pK_a values nearly a thousand times higher than aliphatic carboxylic acids.



a protonated α-amino acid
pK_a = 2

an aliphatic acid
pK_a = 5

23.65 Formic acid is one of the components responsible for the sting of biting ants and is injected under the skin by bees and wasps. A way to relieve the pain is to rub the area of the sting with a paste of baking soda and water, which neutralises the acid. Write an equation for this reaction.

23.66 Show how to convert *trans*-3-phenylpropenoic acid (cinnamic acid) to each of the following compounds.

(a)



(b)

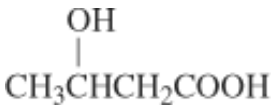


(c)

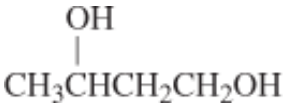


23.67 Show how to convert 3-oxobutanoic acid (acetoacetic acid) to each of the following compounds.

(a)



(b)



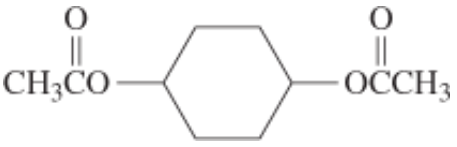
(c) $CH_3CH{=}CHCOOH$

23.68 Methyl 2-hydroxybenzoate (methyl salicylate) has the odour of oil of wintergreen (Dencorub®). This ester is prepared by Fischer esterification of 2-hydroxybenzoic acid (salicylic acid) with methanol. Draw the structural formula for methyl 2-hydroxybenzoate.

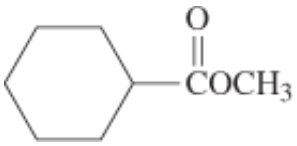
23.69 Benzocaine, a topical anaesthetic, is prepared by treating 4-aminobenzoic acid with ethanol in the presence of an acid catalyst, followed by neutralisation. Draw the structural formula for benzocaine.

23.70 From which carboxylic acid and alcohol is each of the following esters derived?

(a)

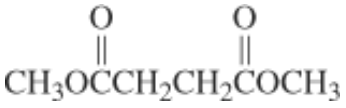


(b)

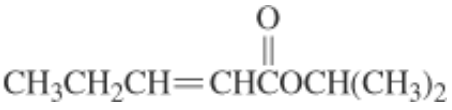


23.71 From which carboxylic acid and alcohol is each of the following esters derived?

(a)



(b)



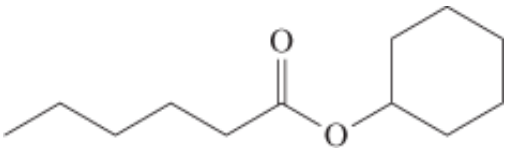
23.72 When treated with an acid catalyst, 4-hydroxybutanoic acid forms a cyclic ester (a lactone). Draw the structural formula of this lactone.

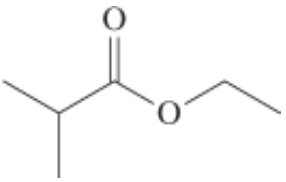
23.73 The analgesic phenacetin is synthesised by treating 4-ethoxyaniline with acetic anhydride. Write an equation for the formation of phenacetin.

23.74 A carboxylic acid can be converted to an ester by Fischer esterification. Show how to synthesise each of the following esters from a carboxylic acid and an alcohol by Fischer esterification.

(a)

(b)



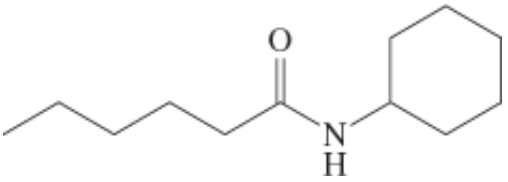


23.75 A carboxylic acid can be converted to an ester in two reactions by first converting the carboxylic acid to its acid chloride and then treating the acid chloride with an alcohol. Show how to prepare each ester in question 23.74 from a carboxylic acid and an alcohol by this two-step scheme.

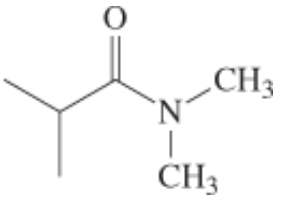
23.76 Write a mechanism for the reaction of butanoyl chloride and ammonia to give butanamide and ammonium chloride.

23.77 Show how to prepare each of the following amides by reaction of an acid chloride with ammonia or an amine.

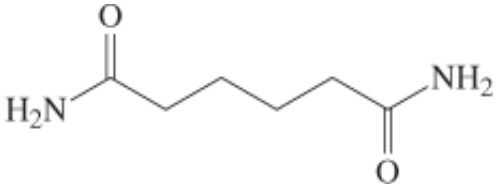
(a)



(b)



(c)



23.78 What product is formed when benzoyl chloride is treated with each of the following reagents?

(a) C_6H_6, $AlCl_3$

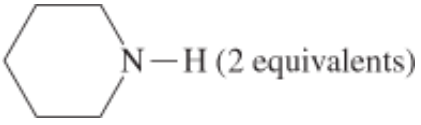
(b) $CH_3CH_2CH_2CH_2OH$

(c) $CH_3CH_2CH_2CH_2SH$

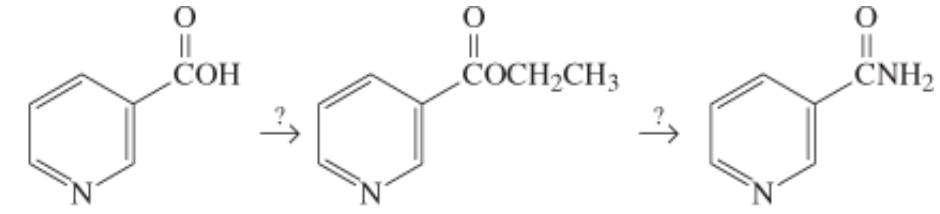
(d) $CH_3CH_2CH_2CH_2NH_2$ (2 equivalents)

(e) H_2O

(f)



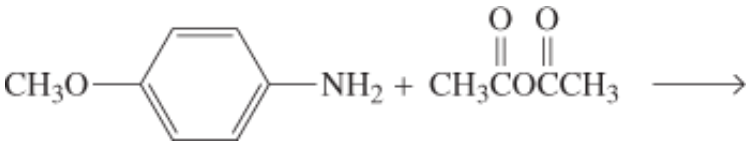
23.79 Nicotinic acid, more commonly named niacin, is one of the B vitamins. Show how nicotinic acid can be converted to ethyl nicotinate and then to nicotinamide.



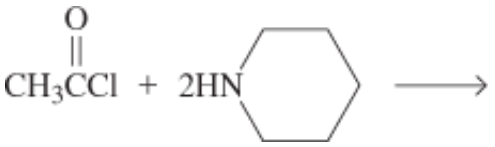
nicotinic acid (niacin) — ethyl nicotinate — nicotinamide

23.80 Complete the following reactions.

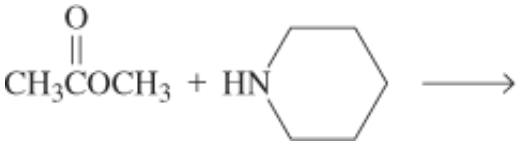
(a)



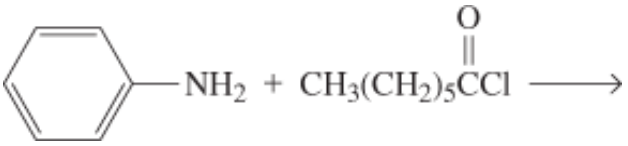
(b)



(c)

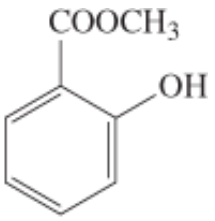


(d)



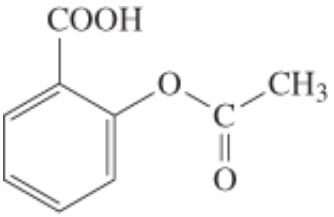
23.81 Show how to convert 2-hydroxybenzoic acid (salicylic acid) to each of the following compounds.

(a)



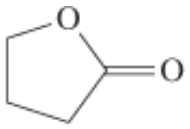
methyl salicylate (oil of wintergreen)

(b)



acetyl salicylic acid (aspirin)

23.82 Show the product of treating γ-butyrolactone with each of the following reagents.



γ-butyrolactone

(a) NH_3

(b) $LiAlH_4$ then H_2O

(c) NaOH, H_2O, heat

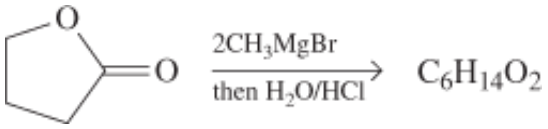
23.83 Show the product of treating *N*-methyl-γ-butyrolactam with each of the following reagents.

(a) HCl, heat

(b) NaOH, heat

(c) $LiAlH_4$ then H_2O

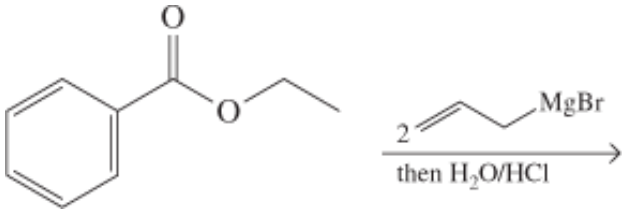
23.84 Treating γ-butyrolactone with 2 equivalents of methylmagnesium bromide, followed by hydrolysis in aqueous acid, gives a compound with the molecular formula $C_6H_{14}O_2$.



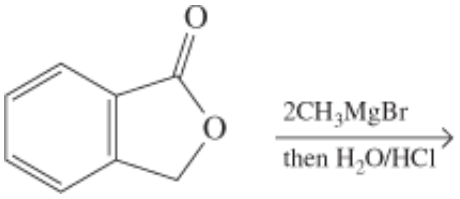
Propose a structural formula for this compound.

23.85 Complete the following reactions.

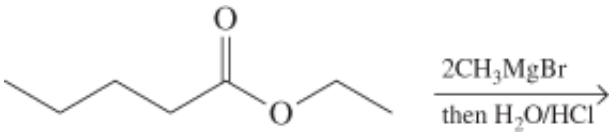
(a)



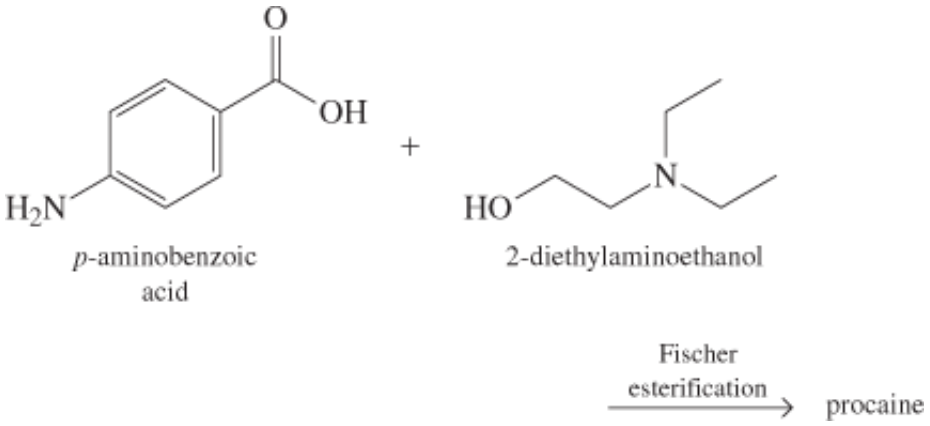
(b)



(c)

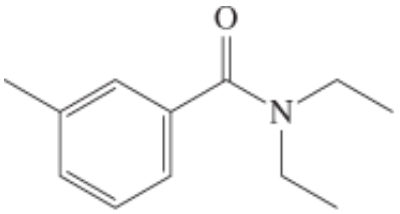


23.86 Procaine (its hydrochloride is marketed as Novocaine®) was one of the first local anaesthetics developed for infiltration and regional anaesthesia. It is synthesised by the following Fischer esterification.



Draw the structural formula of procaine.

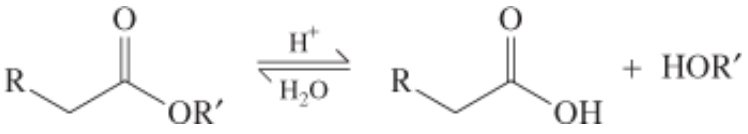
23.87 The active ingredient *N*,*N*-diethyl-*m*-toluamide (DEET) in several common insect repellents is synthesised from 3-methylbenzoic acid (*m*-toluic acid) and diethylamine.



N,*N*-diethyl-*m*-toluamide (DEET)

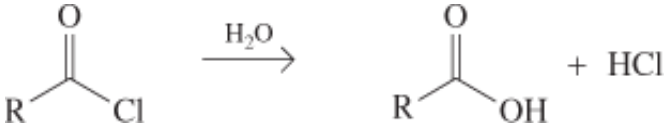
Show how this synthesis can be accomplished.

23.88 Show how an ester can react with H^+/H_2O to give a carboxylic acid and an alcohol.



(*Hint:* This is the reverse of Fischer esterification.)

23.89 In section 23.5, it was suggested that the mechanism for the Fischer esterification of carboxylic acids would be a model for many of the reactions of the functional derivatives of carboxylic acids. The reaction of an acid halide with water, is one such reaction.



Suggest a mechanism for this reaction.

23.90 What combination of ester and Grignard reagent can be used to prepare each of the following alcohols?

(a) 2-methylbutan-2-ol

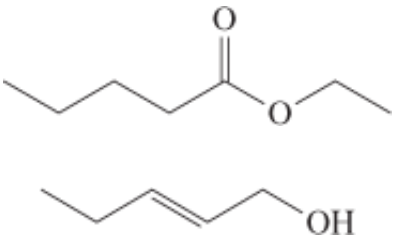
(b) 3-phenylpentan-3-ol

(c) 1,1-diphenylethanol

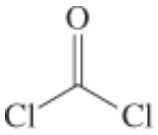
23.91 Show how to convert ethyl pent-2-enoate into each of the following compounds.

(a)

(b)



23.92 Phosgene is highly toxic and was used as a chemical weapon in World War I. It is also a synthetic precursor used in the production of many plastics.



phosgene

(a) When vapours of phosgene are inhaled, the compound rapidly reacts with any nucleophilic sites present (OH groups, NH_2 groups etc.), producing HCl gas. Draw a mechanism for this process.

(b) When phosgene is treated with ethylene glycol ($HOCH_2CH_2OH$), a compound with molecular formula $C_3H_4O_3$ is obtained. Draw the structure of this product.

23.93 The analgesic acetaminophen (paracetamol) is synthesised by treating 4-aminophenol with 1 equivalent of acetic anhydride. Write an equation for the formation of acetaminophen. (*Hint:* Remember that an —NH_2 group is a better nucleophile than an —OH group.)

23.94 The reactions of acid halides, acid anhydrides and esters with ammonia and amines are examples of the nucleophilic acyl substitution reaction. Write an equation for the reaction of each of the following.

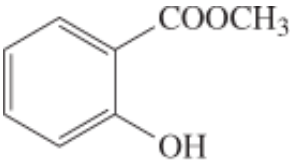
(a) an acid halide with ammonia

(b) an acid anhydride with a primary amine

(c) an ester with a secondary amine

In each case, identify the nucleophile, the leaving group and draw the structure of the tetrahedral carbonyl addition intermediate.

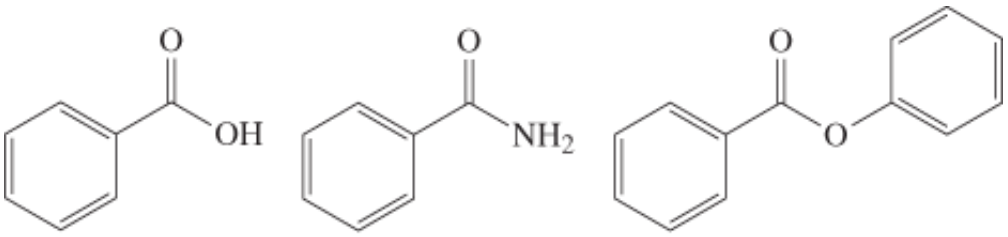
23.95 When compound *X*, $C_7H_7O_2N$, was boiled with concentrated NaOH, it dissolved readily, evolving ammonia. The resulting solution on acidification gave a white precipitate that, on refluxing with methanol and a trace of sulfuric acid, gave the characteristic smell of methyl salicylate.



methyl salicylate

Identify *X* and trace the reaction sequence involved.

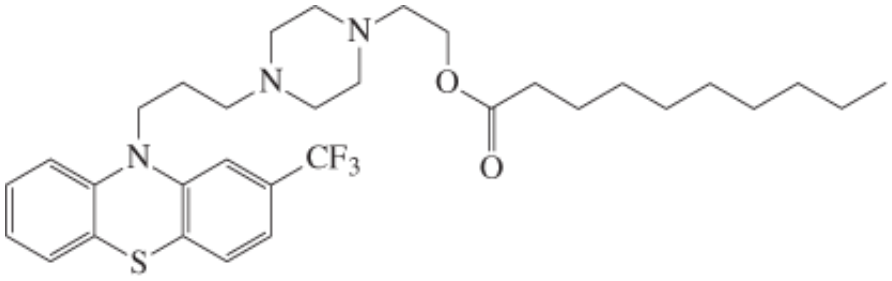
23.96 Devise chemical tests to distinguish between the following compounds, all of which are white solids.



A B C

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23.97 Fluphenazine is an antipsychotic drug that is administered as an ester prodrug via intramuscular injection.



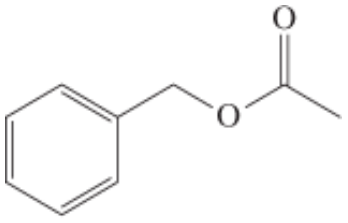
fluphenazine decanoate

The hydrophobic tail of the ester is deliberately designed to enable a slow release of the prodrug into the bloodstream, where the prodrug is rapidly hydrolysed to produce the active drug.

(a) Draw the structure of the active drug.

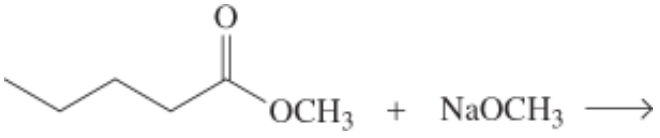
(b) Draw the structure of and assign a systematic name for the carboxylic acid that is produced as a by-product of the hydrolysis step.

23.98 Benzyl acetate is a pleasant-smelling ester found in the essential oil of jasmine flowers and is used in many perfume formulations. Starting with benzene and using any other reagents of your choice, design an efficient synthesis for benzyl acetate.



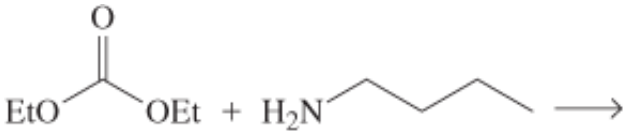
benzyl acetate

23.99 Does a nucleophilic acyl substitution occur between the ester and the nucleophile shown?



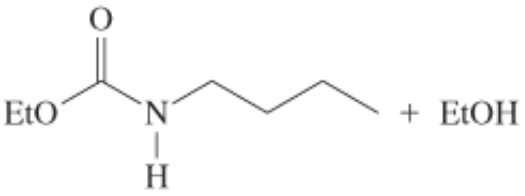
Propose an experiment that would verify your answer.

23.100 Reaction of a 1° or 2° amine with diethyl carbonate under controlled conditions gives a carbamic ester.



diethyl carbonate

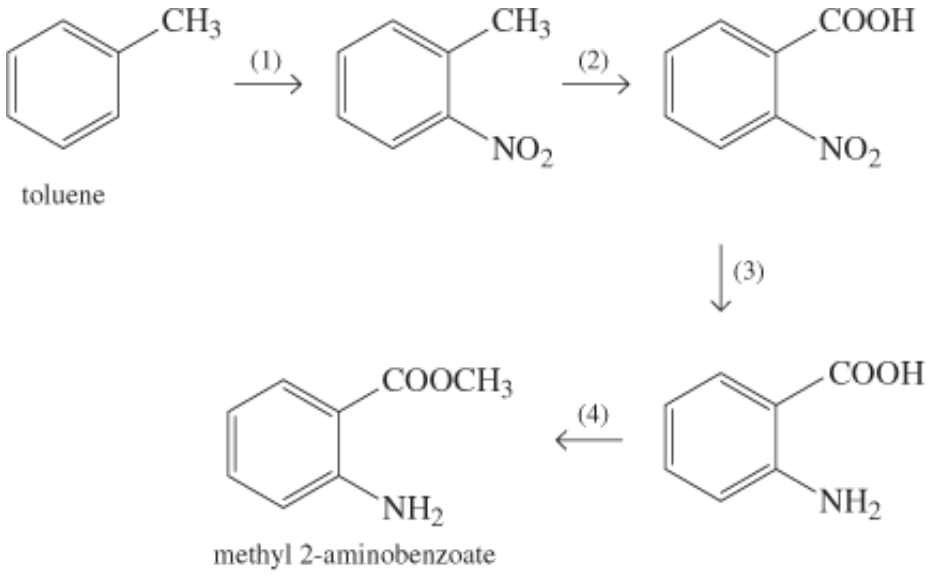
butan-1-amine (butylamine)



a carbamic ester

Propose a mechanism for this reaction.

23.101 Methyl 2-aminobenzoate, a flavouring agent with the taste of grapes, can be prepared from toluene by the following series of steps.

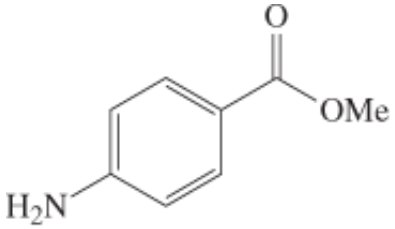


toluene

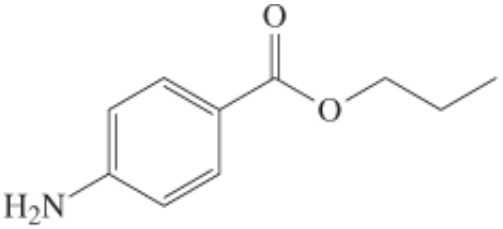
methyl 2-aminobenzoate

Show how you might bring about each step in this synthesis.

23.102 Methyl 4-aminobenzoate and propyl 4-aminobenzoate are used as preservatives in foods, beverages and cosmetics.



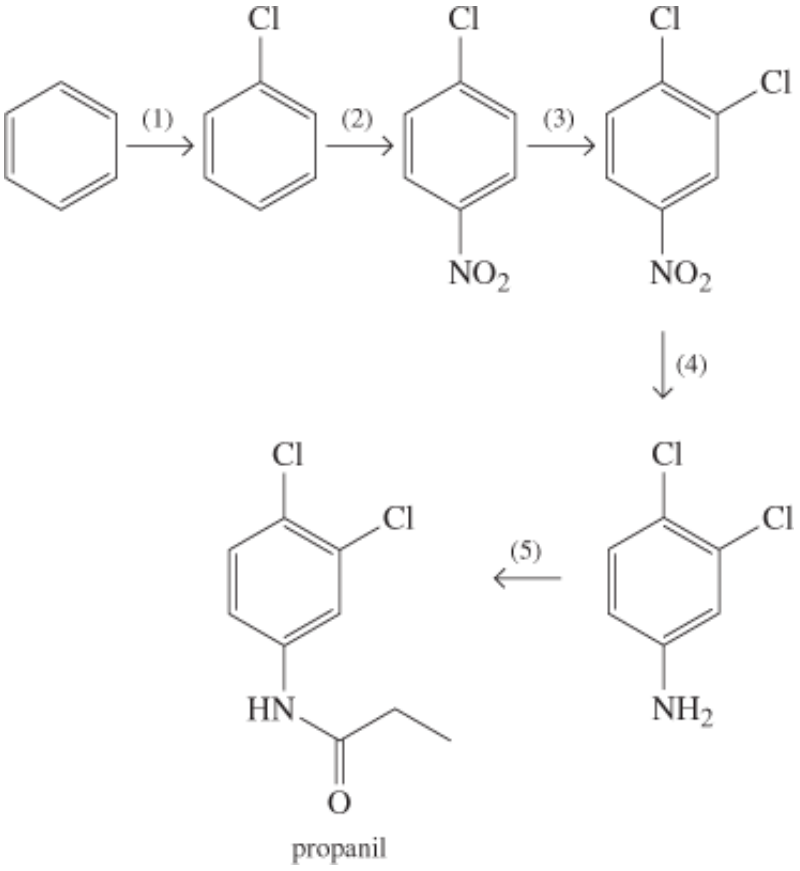
methyl 4-aminobenzoate



propyl 4-aminobenzoate

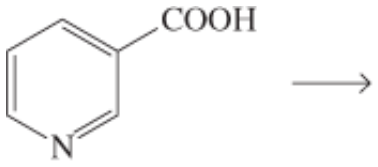
Show how the synthetic scheme in question 23.101 can be modified to give each of these compounds.

23.103 Starting materials for the synthesis of the herbicide propanil, used to kill weeds in rice paddies, are benzene and propanoic acid. Show the reagents (1) to (5) required for this synthesis.

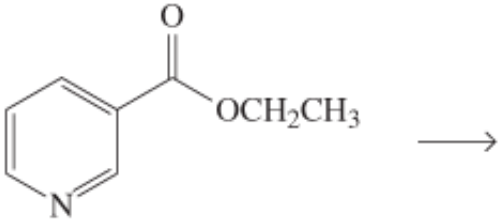


propanil

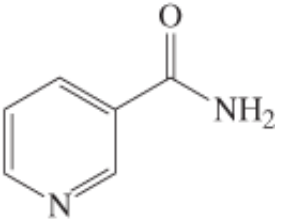
23.104 When chemists follow a reaction scheme, they need to verify that the product obtained in each step is actually what they were expecting. For the reaction scheme below, what evidence could be used to confirm that nicotinic acid has successfully been converted into ethyl nicotinate, and then that ethyl nicotinate has been converted into nicotinamide? You should provide both spectroscopic evidence (chapter 20) and simple chemical tests.



nicotinic acid
(niacin)

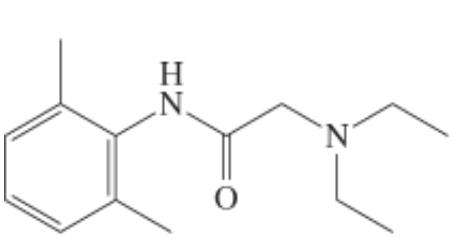


ethyl nicotinate

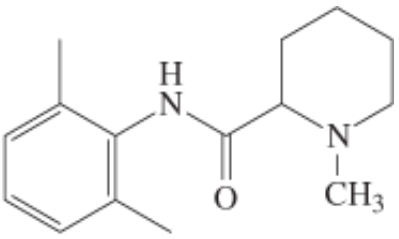


nicotinamide

23.105 The following are structural formulae of two local anaesthetics.



lidocaine
(Xylocaine®)



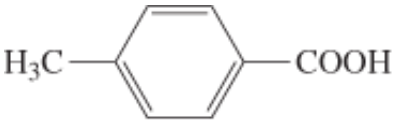
mepivacaine
(Carbocaine®)

Lidocaine was introduced in 1948 and is now the most widely used local anaesthetic for infiltration and regional anaesthesia. Its hydrochloride is marketed under the name Xylocaine. Mepivacaine (its hydrochloride is marketed as Carbocaine) acts faster than lido-caine and its effects last somewhat longer.

(a) Propose a synthesis of lidocaine from 2,6-dimethylaniline, chloroacetyl chloride ($ClCH_2COCl$) and diethylamine.

(b) Which amine and acid chloride can be reacted to give mepivacaine?

23.106 By considering the relative acidity of the following compounds, briefly describe how you would separate them. Use equations to explain the chemistry involved.



A

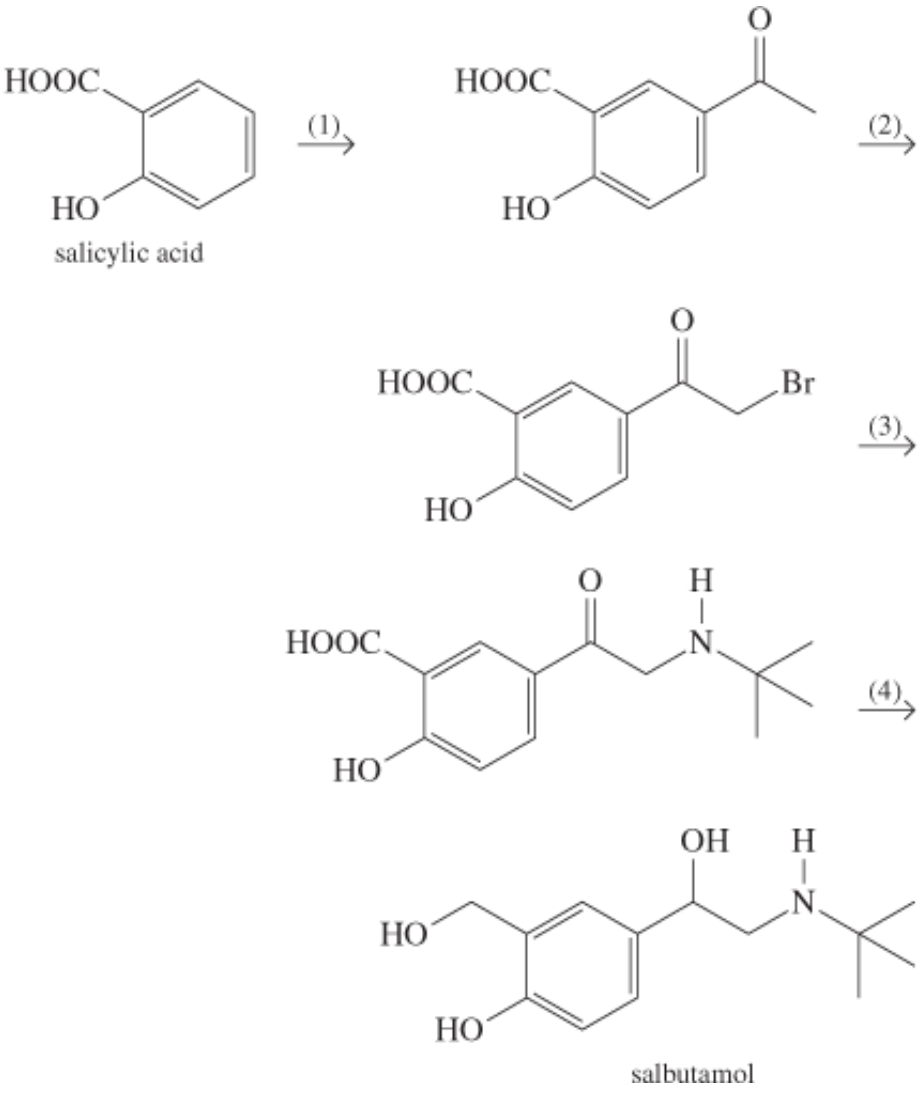


C



B

23.107 Chemists have developed several syntheses for the antiasthmatic drug salbutamol (also known as albuterol or, more commonly, Ventolin®). One of these syntheses starts with salicylic acid, the same acid that is the starting material for the synthesis of aspirin.



salicylic acid

salbutamol

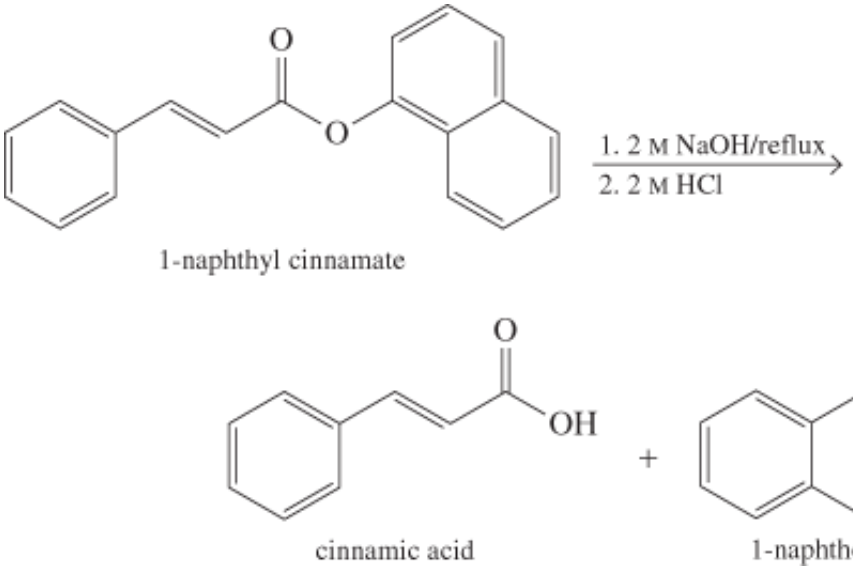
(a) Propose a reagent and a catalyst for step 1. What name is given to this type of reaction?

(b) Propose a reagent for step 2.

(c) Name the amine used to bring about step 3.

(d) Step 4 is a reduction of two functional groups. Name the functional groups reduced and name the reagent that will accomplish the reduction.

23.108 Consider the following hydrolysis reaction. Neither of the products is appreciably soluble in water. By considering the relative acidity of the products, briefly describe how you would separate the two.



1-naphthyl cinnamate

cinnamic acid

1-naphthol

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KEY TERMS

acid anhydride
acid halide
acyl group
amide
benzylic carbon
benzylic hydrogen
carboxyl group
carboxylic acid group
ester
fat
fatty acids
Fischer esterification
hardening
hydrophilic
hydrophobic
lactam
lactone
lipid
micelle
nitrile
nucleophilic acyl substitution
oil
saponification
soap
transesterification
triacylglycerol
Triglyceride
tropical oil

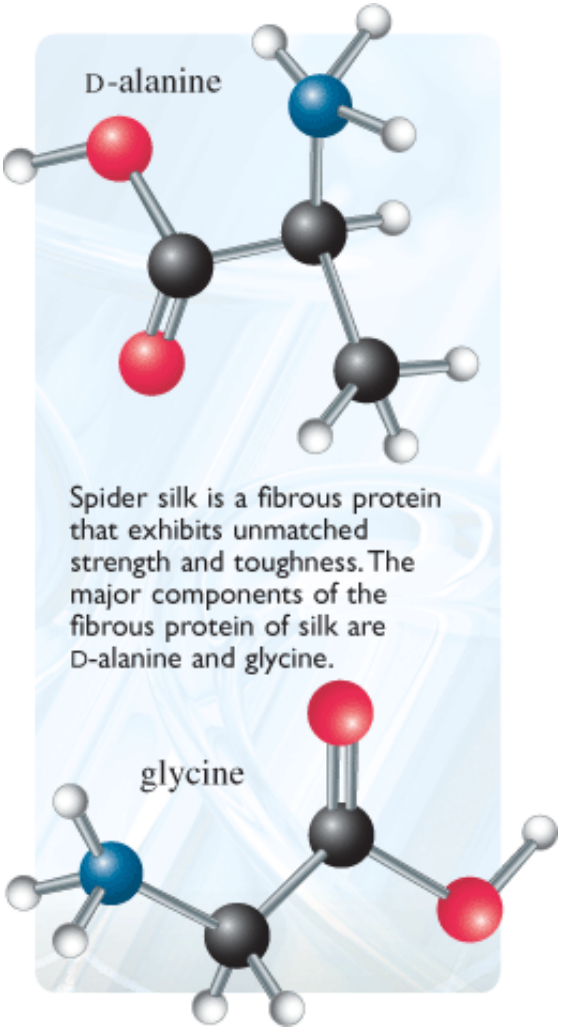
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CHAPTER

24 Amino Acids and Proteins

The properties of amino acids arise from a combination of the chemistry of amines (chapter 19) and that of carboxylic acids (chapter 23). Amino acids are important in their own right, but they also provide the building blocks of proteins. In this chapter we will look at the acid–base properties of amino acids as these control much of the nature of proteins, including many of the catalytic functions of enzymes. Understanding the chemistry of amino acids allows us in turn to understand the much more complex structure and properties of proteins. Proteins are among the most important of all biological compounds as they perform the vital functions of:

- *structure:* Structural proteins such as collagen and keratin are the chief constituents of skin, bones, hair and fingernails.
- *catalysis:* Virtually all reactions that take place in living systems are catalysed by a special group of proteins called enzymes.
- *movement:* Muscle fibres are made of proteins called myosin and actin.
- *transport:* The protein haemoglobin is responsible for the transport of oxygen from the lungs to tissues, while other proteins transport molecules across cell membranes.
- *protection:* A group of proteins called antibodies is one of the body's major defences against disease.



Spider silk is a fibrous protein that exhibits unmatched strength and toughness. The major components of the fibrous protein of silk are D-alanine and glycine.

KEY TOPICS

24.1 Amino acids
24.2 Acid–base properties of amino acids
24.3 Peptides, polypeptides and proteins
24.4 Primary structure of polypeptides and proteins
24.5 Three-dimensional shapes of polypeptides and proteins
24.6 Denaturing proteins

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24.1 Amino Acids

An **amino acid** is a compound that contains both a carboxyl group and an amino group. Although many types of amino acids are known, the **α-amino acids** are by far the most significant in the biological world because they are the building blocks from which the much larger protein molecules are constructed. Proteins, like the nucleic acids you will learn about in chapter 25, are examples of natural **polymers**. Polymers, which we will discuss in chapter 26, are very large molecules composed of many smaller molecules repeatedly linked together. The millions of different types of proteins arise from combinations of only 20 types of α-amino acid. The general structural formula of an α-amino acid is shown in figure 24.1.

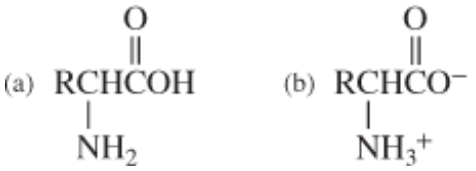


FIGURE 24.1 Representations of an α-amino acid:
(a) the (unrealistic) noncharged form and
(b) the actual internal salt (zwitterion) form.

Although figure 24.1 seems to be a typical way of writing structural formulae for amino acids, it is not accurate because it shows an acid (—COOH) and a base ($—NH_2$) within the same molecule. These acidic and basic groups react with each other to form an internal salt (a dipolarion) (figure 24.1), which is given the special name **zwitterion**. Note that a zwitterion has no net charge; it contains one positive charge and one negative charge.

Because they exist as zwitterions, amino acids have many of the properties associated with salts. They are crystalline solids with high melting points; they are fairly soluble in water but insoluble in nonpolar organic solvents such as ether and hydrocarbon solvents.

Chirality

With the exception of glycine, $H_3\overset{+}{N}CH_2COO^-$, all protein-derived amino acids have at least one stereocentre and are, therefore, chiral (see chapter 17). Figure 24.2 shows Fischer projection formulae for the enantiomers of alanine. The vast majority of carbohydrates in the biological world are of the D-series (section 22.2), whereas the vast majority of α-amino acids in the biological world are of the L-series. From the rules we developed in chapter 17, L is the *S* stereoisomer. (Note, however, that L-cysteine is the *R* stereoisomer because of the higher priority of the sulfur atom.)

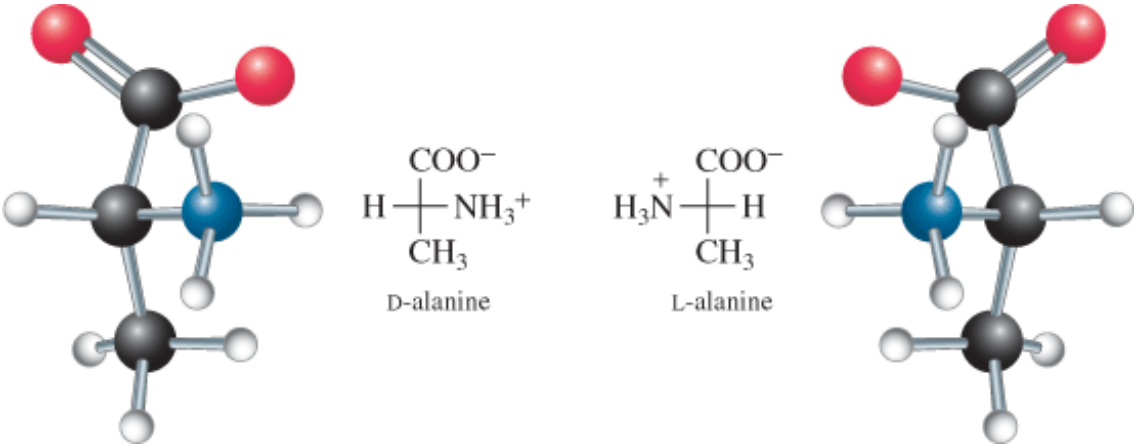


FIGURE 24.2 The enantiomers of alanine. The vast majority of α-amino acids in the biological world have the L-configuration at the α-carbon atom.

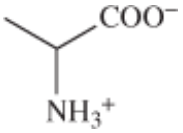
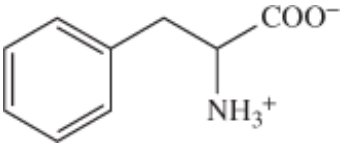
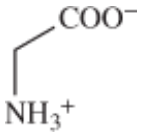
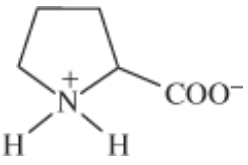
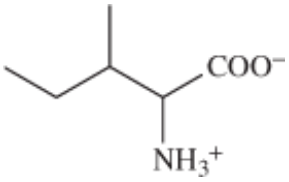
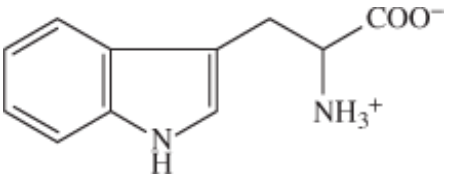
Protein-derived Amino Acids

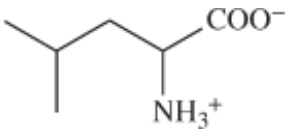
Table 24.1 gives common names, structural formulae and standard three-letter and one-letter abbreviations for the 20 common L-amino acids found in proteins. The amino acids shown are divided into four categories: those with nonpolar side chains; those with polar, but un-ionised, side chains; those with acidic side chains; and those with basic side chains. As you study the information in this table, note the following points:

1. All 20 of these protein-derived amino acids are α-amino acids, meaning that the amino group is located on the carbon atom adjacent to the carboxyl group.
2. For 19 of the 20 amino acids, the α-amino atom group is primary. Proline is different; its α-amino group is secondary.
3. With the exception of glycine, the α-carbon atom of each amino acid is a stereocentre. Although not shown in the table, all 19 chiral amino acids have the same relative configuration at the α-carbon atom. In the D,L convention, all are L-amino acids.
4. Isoleucine and threonine contain a second stereocentre. Four stereoisomers are possible for each of these amino acids, but only one of the four is found in proteins.
5. The sulfhydryl group of cysteine, the imidazole group of histidine and the phenolic hydroxyl of tyrosine are partially ionised at pH = 7.0, but the ionic form is not the major form present at that pH.

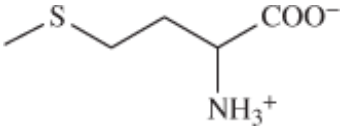
TABLE 24.1 The 20 Common Amino Acids Found in Proteins

Nonpolar Side Chains

	alanine (Ala, A)		phenylalanine (Phe, F)
	glycine (Gly, G)		proline (Pro, P)
	isoleucine (Ile, I)		tryptophan (Trp, W)
	leucine		

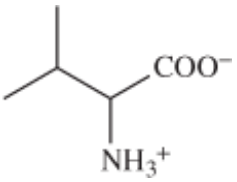


(Leu, L)



methionine

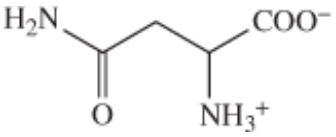
(Met, M)



valine

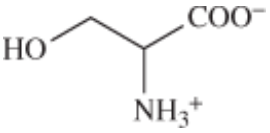
(Val,V)

Polar side chains



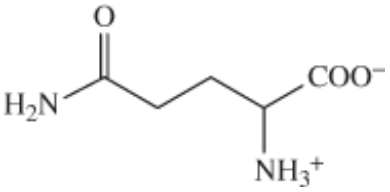
asparagine

(Asn, N)



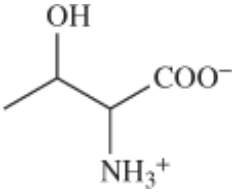
serine

(Ser, S)



glutamine

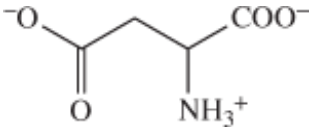
(Gln, Q)



threonine

(Thr, T)

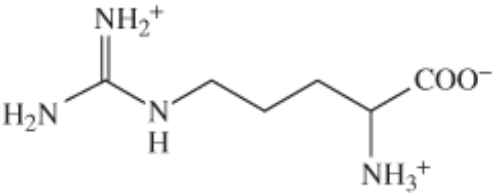
Acidic side chains



aspartic acid

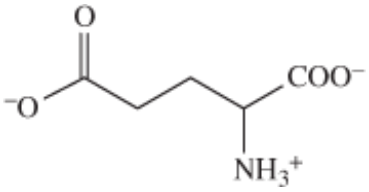
(Asp, D)

Basic side chains



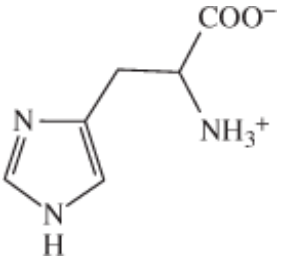
arginine

(Arg, R)



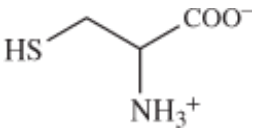
glutamic acid

(Glu, E)



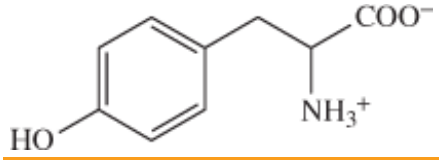
histidine

(His, H)



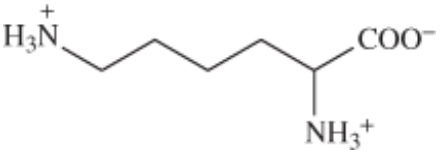
cysteine

(Cys, C)



tyrosine

(Tyr, Y)



lysine

(Lys, K)

Note: Each ionisable group is shown in the form present in highest concentration in aqueous solution at pH = 7.0.

WORKED EXAMPLE 24.1

Assessing the Structural Variations of the Common Amino Acids

Of the 20 protein-derived amino acids shown in table 24.1, how many contain (a) aromatic rings, (b) side-chain —OH groups, (c) phenolic —OH groups, (d) sulfur and (e) basic groups?

Analysis

Amino acids can look structurally complex, but it is important to understand their similarities as well as their differences. The type of side chain present has a substantial impact on the proper-ties of the amino acid, and so you will need to recognise the functional groups present in the side chain. Look for the amine and the carboxylic acid linked by a single carbon atom as the common structural unit, and then assess the nature of the functional groups present in the side chain.

Solution

(a) Phenylalanine, tryptophan, tyrosine and histidine contain aromatic rings.

(b) Serine and threonine contain side-chain hydroxyl groups.

(c) Tyrosine contains a phenolic —OH group.

(d) Methionine and cysteine contain sulfur.

(e) Arginine, histidine and lysine contain basic groups.

Is our answer reasonable?

Table 24.1 shows the structures of the groups present on the amino acids. Aromatic rings require a continuous cycle of sp^2 hybridised atoms such that the total numbers of electrons in the system equals 6 (or 10, 14, 18 etc.). Consequently, histidine contains an aromatic ring as do tryptophan and tyrosine. Note that an —OH group bound to an aromatic ring imparts consider-ably different properties from one bound to an alkyl chain, which is why we define alcohol hydroxyl groups (serine and threonine) as different from phenolic hydroxyl groups (tyrosine).

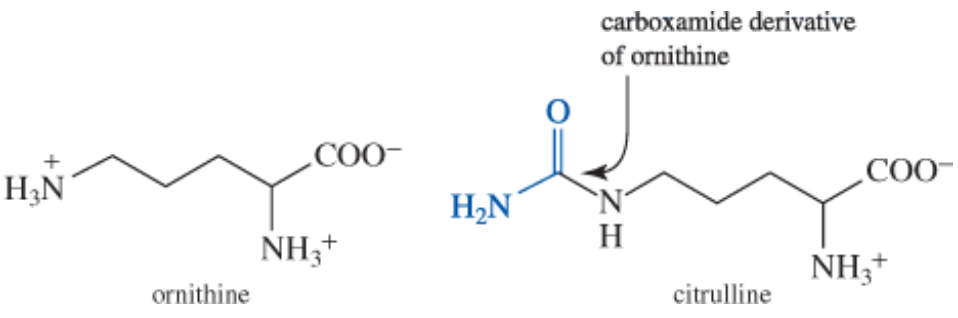
Asparagine and glutamine possess amide side chains, so these groups are not basic since the carbonyl orbitals interact with the lone electron pair on the nitrogen atom, making it unavailable to bond to hydrogen ions, H^+.

PRACTICE EXERCISE 24.1

Of the 20 protein-derived amino acids shown in table 24.1, which contain (a) no stereocentre and (b) two stereocentres?

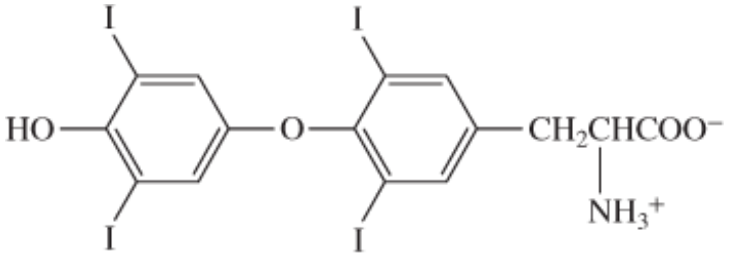
Some Other Common Amino Acids

Although the vast majority of plant and animal proteins are constructed from just these 20 α-amino acids, many examples of other kinds of amino acid can also be found in nature. Ornithine and citrulline, for example, are found predominantly in the liver and are an integral part of the urea cycle, the metabolic pathway that converts ammonia to urea:

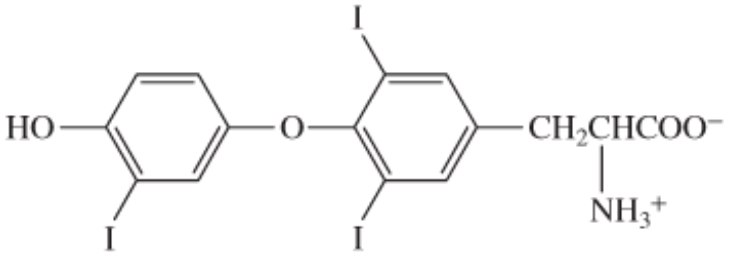


ornithine citrulline

Thyroxine and triiodothyronine, two of several hormones derived from the amino acid tyrosine, are found in thyroid tissue.



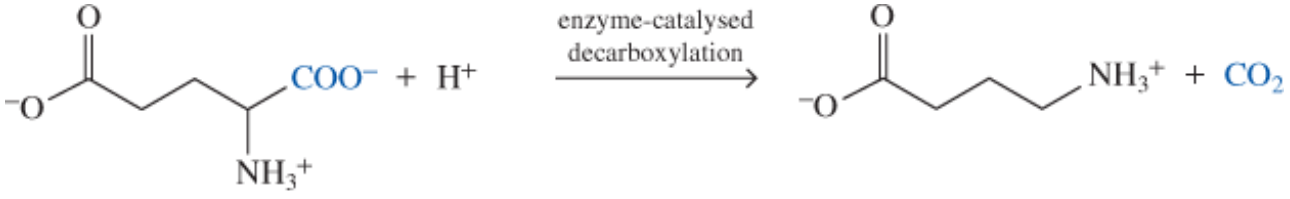
thyroxine, T_4



triiodothyronine, T_3

The principal function of these two hormones is to stimulate metabolism in other cells and tissues.

The amino acid 4-aminobutanoic acid (γ-aminobutyric acid, or GABA) is found in high concentration (0.8×10^{-3} M) in the brain, but in no significant amounts in any other mammalian tissue. GABA is synthesised in neural tissue by decarboxylation of the α-carboxyl group of glutamic acid and is a neurotransmitter in the central nervous system of invertebrates and possibly in humans as well.



glutamic acid

4-aminobutanoic acid
(γ-aminobutyric acid, GABA)

Only L-amino acids are found in proteins, and only rarely are D-amino acids a part of the metabolism of higher organisms. Several D-amino acids, however, along with their L-enantiomers, are found in lower forms of life. For example, D-alanine and D-glutamic acid are structural components of the cell walls of certain bacteria. Several D-amino acids are also present in synthetic antibiotics made from amino acids.

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24.2 Acid–base Properties of Amino Acids

Amino acids are unusual molecules in that they possess both an acidic functional group and a basic functional group in the same molecule. This means that in the biological environment they can play the role of proton (H^+) donors or proton (H^+) acceptors.

Acidic and Basic Groups of Amino Acids

Among the most important chemical properties of amino acids are their acid–base properties; all can be weak polyprotic acids because of their —COOH and —NH_3^+ groups. The exact ability of these groups to accept or donate H^+ is indicated by their pK_a values. (Recall from chapter 11 that the smaller the pK_a the more acidic is the group. At lower pH, carboxylic acids are found in the RCOOH form and amines are found in the RNH_3^+ form. At higher pH, the opposite is true; carboxylic acids are present as the salt $RCOO^-$ and amines are present as uncharged RNH_2. Figure 24.3 on p. 1061 shows how this looks at different pH). Table 24.2 gives pK_a values for each ionisable group of the 20 protein-derived amino acids.

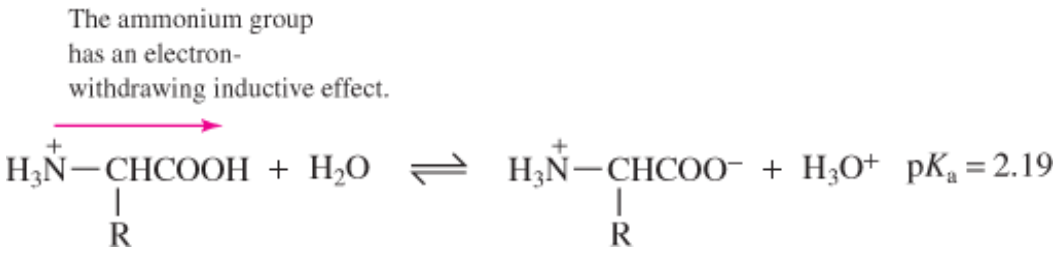
TABLE 24.2 Values of pK_a for Ionisable Groups of Amino Acids

Amino acid	pK_a of α-COOH	pK_a of α-NH_3^+	pK_a of side chain	Isoelectric point (pI)[a]
alanine	2.35	9.87	_[b]	6.11
arginine	2.01	9.04	12.48	10.76
asparagine	2.02	8.80	–	5.41
aspartic acid	2.10	9.82	3.86	2.98
cysteine	2.05	10.25	8.00	5.02
glutamic acid	2.10	9.47	4.07	3.08
glutamine	2.17	9.13	–	5.65
glycine	2.35	9.78	–	6.06
histidine	1.77	9.18	6.10	7.64
isoleucine	2.32	9.76	–	6.04
leucine	2.33	9.74	–	6.04
lysine	2.18	8.95	10.53	9.74
methionine	2.28	9.21	–	5.74
phenylalanine	2.58	9.24	–	5.91
proline	2.00	10.60	–	6.30
serine	2.21	9.15	–	5.68
threonine	2.09	9.10	–	5.60
tryptophan	2.38	9.39	–	5.88
tyrosine	2.20	9.11	10.07	5.63
valine	2.29	9.72	–	6.00

(a) See p. 1063.
(b) No ionisable side chain.

Acidity of α-carboxyl Groups

The average value of pK_a for an α-carboxyl group of a protonated amino acid is 2.19. Thus, the α-carboxyl group is a considerably stronger acid than acetic acid (pK_a = 4.74) and other low-molar-mass aliphatic carboxylic acids. This greater acidity is accounted for by the electron-withdrawing inductive effect of the adjacent —NH_3^+ group (recall that we used similar reasoning in section 23.5 to account for the relative acidities of acetic acid and its mono-, di-, and trichloroderivatives).

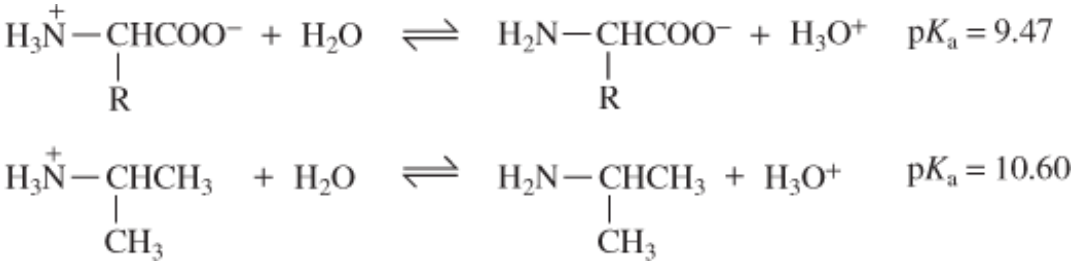


Acidity of Side-chain Carboxyl Groups

Due to the electron-withdrawing inductive effect of the α-NH_3^+ group, the side-chain carboxyl groups of protonated aspartic acid and glutamic acid are also stronger acids than acetic acid (pK_a = 4.74). Notice that this acid-strengthening inductive effect decreases with increasing distance of the —COOH group from the α-NH_3^+ group. Compare the acidities of the α-COOH group of alanine (pK_a = 2.35), the γ-COOH group of aspartic acid (pK_a = 3.86) and the δ-COOH group of glutamic acid (pK_a = 4.07).

Acidity of α-ammonium Groups

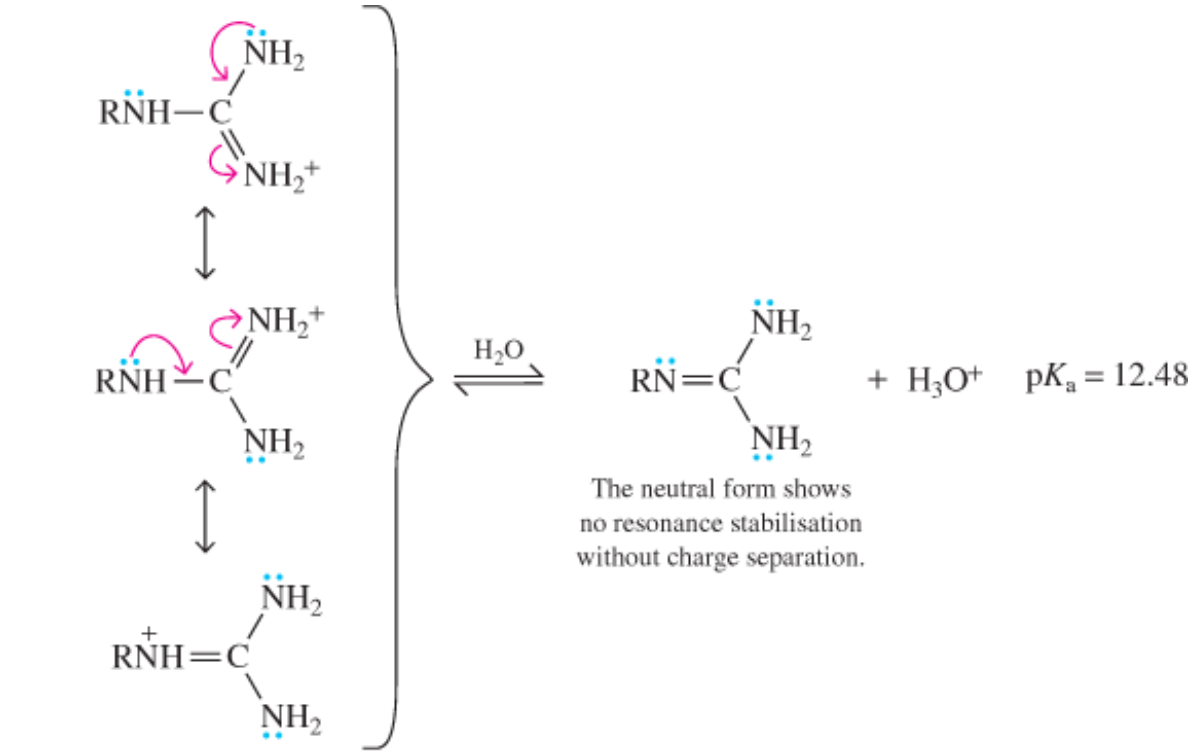
The average value of pK_a for an α-ammonium group, α-NH_3^+, is 9.47, compared with an average value of 10.76 for primary aliphatic ammonium ions (section 19.7).



Thus, the α-ammonium group of an amino acid is a slightly stronger acid than a primary aliphatic ammonium ion and, conversely, an α-amino group is a slightly weaker base than a primary aliphatic amine.

Basicity of the Guanidine Group of Arginine

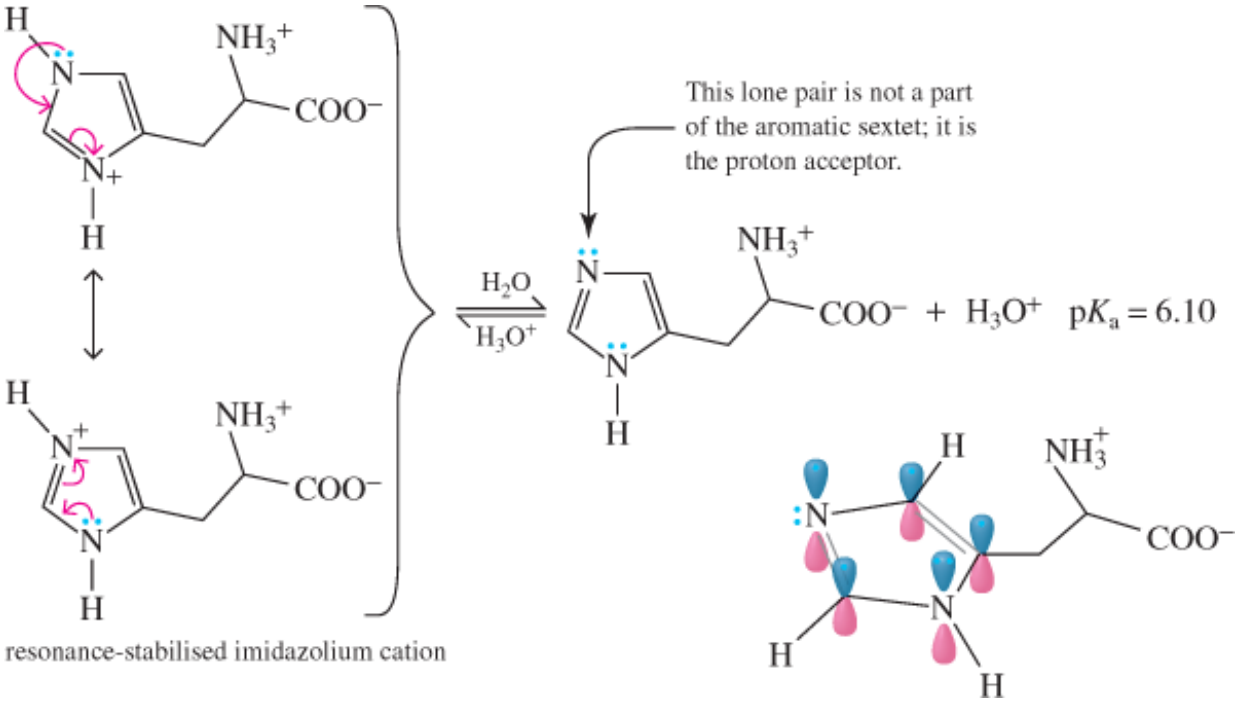
The side-chain guanidine group of arginine (—N═C$(NH_2)_2$) is a considerably stronger base than an aliphatic amine. Guanidine is the strongest base of any neutral compound. The remarkable basicity of the guanidine group of arginine is attributed to the large resonance stabilisation of the protonated form relative to the neutral form.



The protonated form of the guanidinium ion side chain of arginine is a hybrid of three contributing structures.

Basicity of the Imidazole Group of Histidine

Because the imidazole group on the side chain of histidine contains six π electrons in a planar, fully conjugated ring, imidazole is classified as a heterocyclic aromatic amine (section 19.6). The unshared pair of electrons on one nitrogen atom is a part of the aromatic sextet, whereas that on the other nitrogen atom is not. It is the pair of electrons that is not part of the aromatic sextet that is responsible for the basic properties of the imidazole ring. Protonation of this nitrogen atom produces a resonance-stabilised cation:



resonance-stabilised imidazolium cation

Titration of Amino Acids

Values of pK_a for the ionisable groups of amino acids are most commonly obtained by acid–base titration (section 11.7) and by measuring the pH of the solution as a function of added base (or added acid, depending on how the titration is done). To illustrate this experimental procedure, consider a solution containing 1.00 mole of glycine to which has been added enough strong acid so that both the amino and carboxyl groups are fully protonated. Next, the solution is titrated with 1.00 m NaOH; the volume of base added and the pH of the resulting solution are recorded and then plotted as shown in figure 24.3.

The more acidic group, and the one to react first with added sodium hydroxide, is the carboxyl group. When exactly 0.50 mole of NaOH has been added, the carboxyl group is half neutralised. At this point, the concentration of the zwitterion equals that of the positively charged ion, and the pH of 2.35 equals the pK_a value of the carboxyl group (pK_{a1}):

$$\text{At pH} = \text{p}K_{a1} \qquad [\overset{+}{\text{H}_3}\text{NCH}_2\text{COOH}] = [\overset{+}{\text{H}_3}\text{NCH}_2\text{COO}^-]$$
positive ion — zwitterion

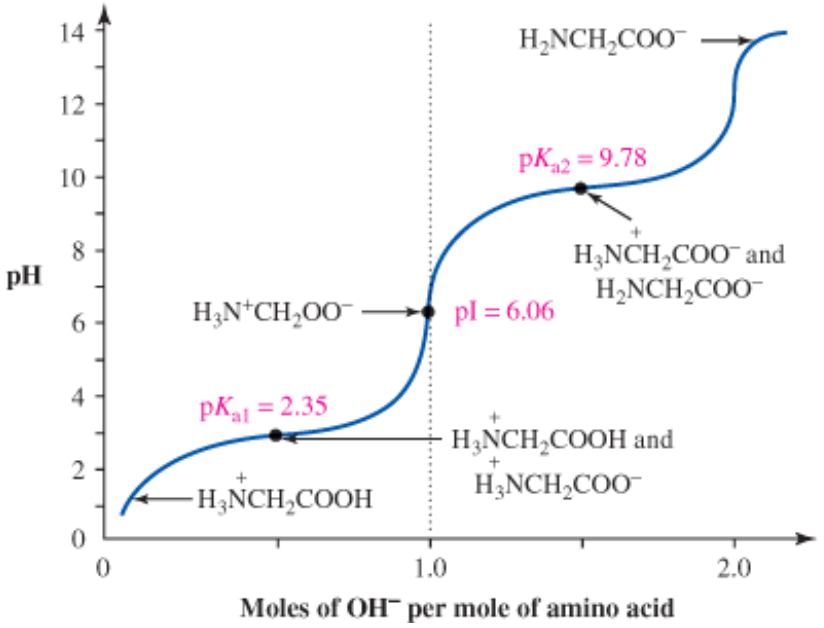


FIGURE 24.3 Titration of glycine with sodium hydroxide.

The end point of the first part of the titration is reached when 1.00 mole of NaOH has been added. At this point, the predominant species present is the zwitterion, and the observed pH of the solution is 6.06. The next section of the curve represents titration of the —NH_3^+ group. When another 0.50 mole of NaOH has been added (bringing the total to 1.50 moles), half of the —NH_3^+ groups are neutralised and converted to —NH_2. At this point, the concentrations of the zwitterion and negatively charged ion are equal, and the observed pH is 9.78, which equals the pK_a value of the ammonium group of glycine (pK_{a2}):

$$\text{At pH} = \mathbf{p}K_{\mathbf{a2}} \quad \underbrace{\left[H_3\overset{+}{N}CH_2COO^-\right]}_{\text{zwitterion}} = \underbrace{[H_3NCH_2COO^-]}_{\text{negative ion}}$$

The second end point of the titration is reached when a total of 2.00 moles of NaOH have been added and glycine is converted entirely to an anion.

Amino Acid Charge at Physiological pH

Knowing the pK_a of the functional groups allows us to understand the nature of the amino acid in a physiological context. Recall from chapter 11 that pK_a refers to the relationship between the equilibrium concentrations of the undissociated acid (HA) and the conjugate base (A^-). It is important to understand the implications of this for amino acids at the pH conditions found in biological environments. For instance, if an amino acid has a pK_a of 2, then $K_a = 10^{-2}$. The ratio of HA to A^- is derived from the Henderson–Hasselbalch equation:

$$K_a = \frac{[H_3O^+][RCOO^-]}{[RCOOH]}$$

Physiological systems are buffered and remain at a controlled pH close to 7, so $[H_3O^+] = 10^{-7}$ in these environments. Substituting into this equation gives:

$$K_a = 10^{-2} = \frac{10^{-7}[RCOO^-]}{[RCOOH]}$$

and rearranging gives:

$$\frac{10^{-2}}{10^{-7}} = 10^5 = \frac{[RCOO^-]}{[RCOOH]}$$

Consequently, the ratio of dissociated $RCOO^-$ to undissociated RCOOH is 100 000 : 1 (i.e. there is very little RCOOH present), and we can say that all of the amino acid is effectively present in the charged $RCOO^-$ form. If the pK_a value of the amino acid is equal to the pH, there is a 50 : 50 mixture of the two components:

$$K_a = 10^{-7} = \frac{10^{-7}[RCOO^-]}{[RCOOH]}$$

and rearranging gives:

$$\frac{10^{-7}}{10^{-7}} = 1 = \frac{[RCOO^-]}{[RCOOH]}$$

When the pK_a value is 1 log unit below physiological pH (pH = 7), the ratio is 90 : 10; if it is 2 log units below the pH, the ratio is 99 : 1. We can use this relationship to control the charge of the amino acid by controlling the pH. If we make the pH of the solution containing the amino acid 2 log units above its pK_a value, we know that the amino acid is essentially present (99%) in its dissociated form. To aid your understanding, table 24.3 shows the ratios of undissociated acids, HA, compared with the conjugate base, A^-, at physiological pH for various pK_a values.

TABLE 24.3 Ratios of Undissociated Amino Acids, HA, Compared with the Conjugate Base, A^-, at Physiological pH for Various pK_a Values

pK_a	4	5	6	7	8	9	10
A^-	99.9	99	90	50	10	1	0.1
HA	0.1	1	10	50	90	99	99.1

Using this analysis, it is clear why, at physiological pH, all amino-acid and side-chain carboxylic acid groups are ionised and found in the $RCOO^-$ form. Furthermore, at physiological pH, all amino, side-chain amino and guanidino groups are protonated. However, tyrosine's phenol group is not ionised, cysteine's thiol group is largely (but not completely) un-ionised, and histidine's side chain is largely (but not completely) protonated.

Isoelectric Point

Titration curves, such as that for glycine (figure 24.3), enable us to determine pK_a values for the ionisable groups of an amino acid. The pK_a values in turn allow us to determine the ratio of charged to uncharged groups in a molecule. Titration curves also enable us to determine another important property: the **isoelectric point (pI)** —the pH at which most of the molecules of the amino acid in solution have a net charge of 0. The isoelectric points for common amino acids are given in table 24.2. By examining the titration curve (figure 24.3), you can see that the isoelectric point for glycine falls halfway between the pK_a values for the carboxyl groups and the ammonium ion:

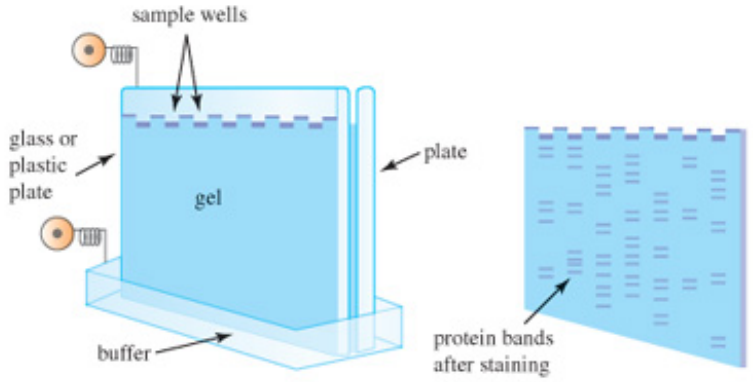
$$\begin{aligned} pI &= \frac{1}{2}(pK_a \text{ of } \alpha\text{-COOH} + pK_a \text{ of } \alpha\text{-}NH_3^+) \\ &= \frac{1}{2}(2.35 + 9.78) \\ &= 6.06 \end{aligned}$$

At pH = 6.06, the predominant form of glycine molecules is the zwitterion; furthermore, at this pH, the concentration of positively charged glycine molecules equals the concentration of negatively charged glycine molecules.

Given a value for the isoelectric point of an amino acid, it is possible to estimate the charge on that amino acid at any pH. For example, the charge on tyrosine at pH = 5.63 (the isoelectric point of tyrosine) is 0. A small fraction of tyrosine molecules is positively charged at pH = 5.00 (0.63 of a log unit less than its pI), and virtually all are positively charged at pH = 3.63 (2.00 log units less than its pI). As another example, the net charge on lysine is 0 at pH = 9.74. At pH values smaller than 9.74, an increasing fraction of lysine molecules is positively charged.

Electrophoresis

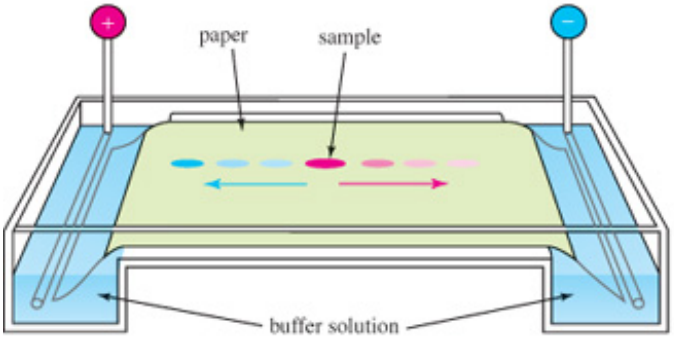
Electrophoresis, the process of separating compounds on the basis of their electric charges, is used to isolate and identify the components present in mixtures of amino acids and proteins. Electrophoretic separations most commonly use polyacrylamide gels and the technique is referred to as PAGE, for *poly**a**c*rylamide *gel**e*lectrophoresis. A typical electrophoresis separation set-up is shown in figure 24.4a,b.



(a)



(b)



(c)

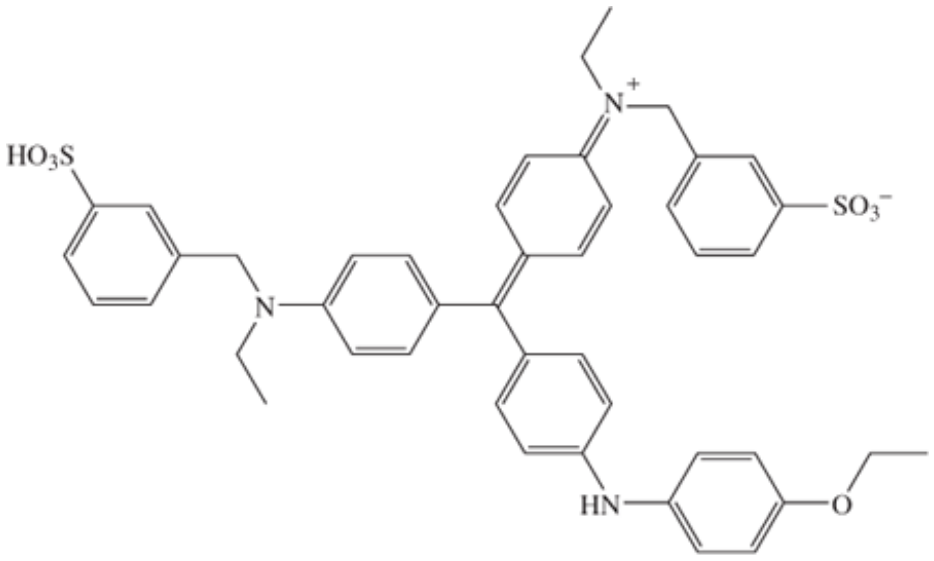
FIGURE 24.4 Electrophoresis of a mixture of:

(a) and

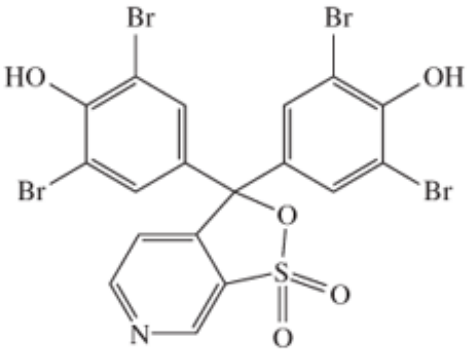
(b) proteins by SDS-PAGE and

(c) amino acids by paper electrophoresis. During SDS-PAGE, proteins with the highest molecular weight carry the most charge and move towards the positive electrode most quickly. During paper electrophoresis, depending on the pH of the solution, amino acids with a negative charge move towards the positive electrode, and those with a positive charge move towards the negative electrode; those at their isoelectric point do not move.

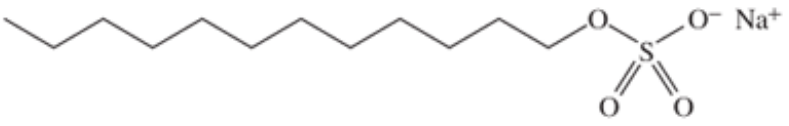
The amino acids are colourless, but a blue dye, bromophenol blue, is added to aid in loading the mixture and to indicate when the process has been completed. When an electrical potential is applied to the gel, amino acids migrate towards the electrode; molecules with a high charge density move more rapidly than those with a lower charge density. Any molecule already at its isoelectric point remains at the origin. PAGE can be done on unmodified mixtures (native-PAGE), where separation is based on charge and molecular mass, or the proteins can be denatured (section 24.6) using *s*odium *d*odecyl *s*ulphate, a strong detergent (SDS-PAGE). The detergent leaves the protein with a similar linear structure and an overall negative charge. Separation then depends only on molecular weight. After the separation is complete, the gel may be treated with a dye such as Coomassie Brilliant Blue that transforms each component into a coloured band, making the separation visible. One advantage of native-PAGE over SDS-PAGE is that proteins are not altered in the separation process and may later be detected on the basis of specific enzyme interactions or subjected to further analytical techniques such as mass spectrometry (section 20.2).



Coomassie Brilliant Blue



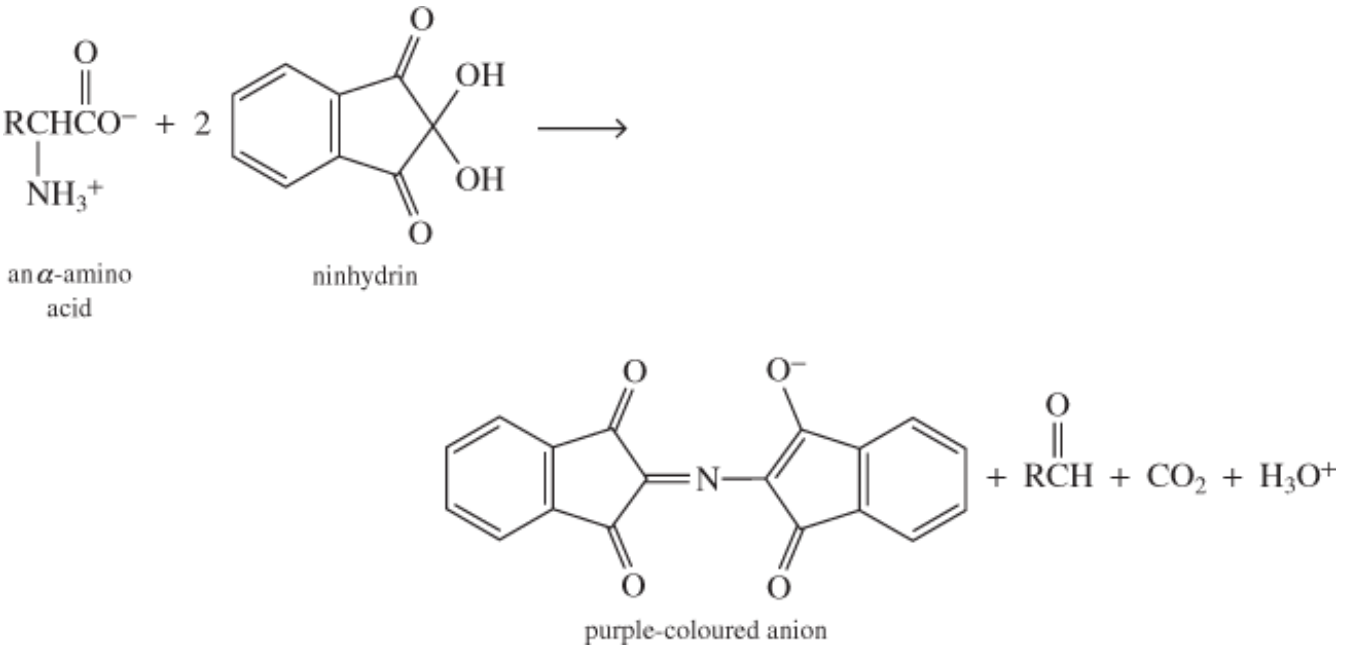
bromophenol blue



sodium dodecyl sulphate

Electrophoresis can also be performed using other polymers, starch, agar and even paper. With paper electrophoresis a paper strip saturated with an aqueous buffer of predetermined pH serves as a bridge between two electrode vessels (figure 24.4c). When an electrical potential is applied to the electrode vessels, the amino acids migrate towards the electrode carrying the charge opposite to their own. As previously, molecules with a high charge density move more rapidly than those with a lower charge density, and any molecule already at its isoelectric point remains at the origin.

After the electrophoresis process is complete, the separated components need to be detected, or visualised. Often this involves treatment with a dye that transforms each amino acid or protein into a coloured compound. Other approaches involve ‘blotting’, which transfers the separated compounds to another surface which may contain reactive dyes or enzyme-linked coloured responses. For mixtures of amino acids, treatment with ninhydrin (1,2,3-indanetrione monohydrate) is often used. Ninhydrin reacts with α-amino acids to produce an aldehyde, carbon dioxide and a purple-coloured anion:



This reaction is commonly used in both qualitative and quantitative analyses of amino acids. Of the 20 protein-derived α-amino acids, 19 have primary amino groups and give the same purple-coloured ninhydrin-derived anion. Proline, a secondary amine, gives a different, orange-coloured, compound.

WORKED EXAMPLE 24.2

Analysing Amino Acids Based on their Charge

The isoelectric point of tyrosine is 5.63. Towards which electrode does tyrosine migrate during paper electrophoresis at pH = 7.0?

Analysis

Negatively charged materials move towards the positive electrode and positively charged species move towards the negative electrode. You can determine the direction of movement during electrophoresis if you know the charge on the amino acid.

Solution

During paper electrophoresis at pH = 7.0 (more basic than its isoelectric point), tyrosine has a net negative charge so migrates towards the positive electrode.

Is our answer reasonable?

If the pH of a solution is equal to the pK_a value of an ionisable group, the group is present as a 50 : 50 mixture of charged and uncharged species. The situation becomes more complicated when there are several ionisable groups present, but the isoelectric point gives a measure of the pH required for most of the molecules to be uncharged. Here, the pH of the solution at 7.0 is more basic than the isoelectric point, so the molecule should be negatively charged.

PRACTICE EXERCISE 24.2

The isoelectric point of histidine is 7.64. Towards which electrode does histidine migrate during paper electrophoresis at pH = 7.0?

WORKED EXAMPLE 24.1

Separation of a Mixture of Amino Acids Based on their Charge

The electrophoresis of a mixture of lysine, histidine and cysteine is carried out at pH = 7.64. Describe the behaviour of each amino acid under these conditions.

Analysis

Negatively charged materials move towards the positive electrode and positively charged species move towards the negative electrode. If you know the pH of the solution and the values of the isoelectric point for the amino acids involved, you can determine the charges present and the direction in which the species will move.

Solution

The isoelectric point of histidine is 7.64. At this pH, histidine has a net charge of 0 and so it does not move from the origin. The pI of cysteine is 5.02; at pH = 7.64 (more basic than its isoelectric point), cysteine has a net negative charge and so it moves towards the positive electrode. The pI of lysine is 9.74; at pH = 7.64 (more acidic than its isoelectric point), lysine has a net positive charge and so it moves towards the negative electrode.

Is our answer reasonable?

This separation can work only if the molecules present have different isoelectric points. Here the isoelectric points are 5.02, 7.64 and 9.74 so, at pH = 7.64, we have an uncharged molecule, a negatively charged molecule and a positively charged molecule.

PRACTICE EXERCISE 24.3

Describe the behaviour of a mixture of glutamic acid, arginine and valine during paper electrophoresis at pH = 6.0.

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24.3 Peptides, Polypeptides and Proteins

In 1902, Emil Fischer proposed that proteins were long chains of amino acids joined together by amide bonds between the α-carboxyl group of one amino acid and the α-amino group of another. For these amide bonds, Fischer proposed the special name **peptide bond**. Figure 24.5 shows the peptide bond formed between serine and alanine in the molecule serylalanine.

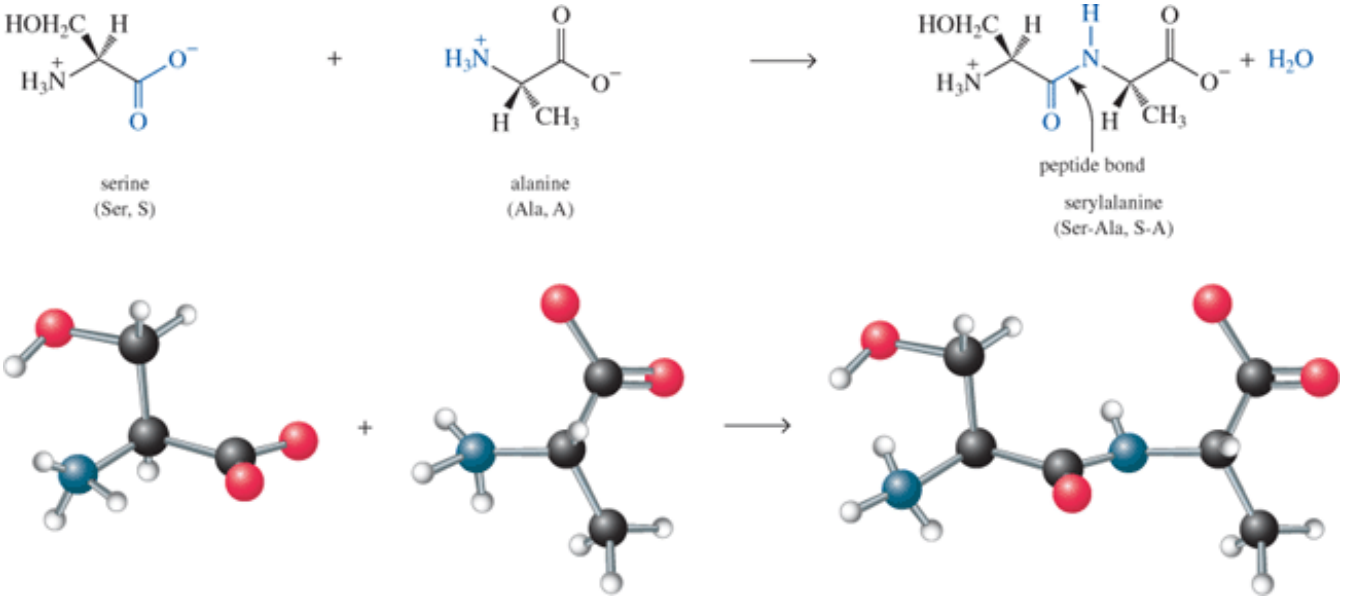
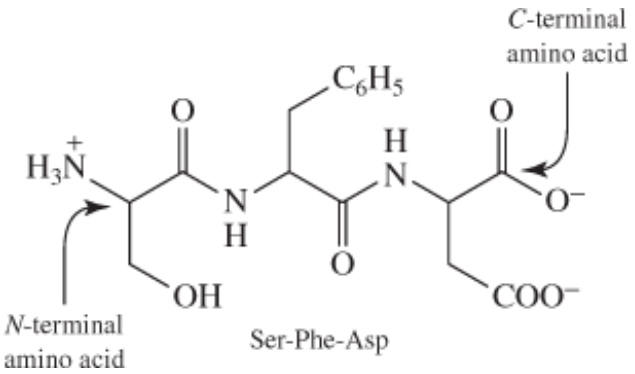


FIGURE 24.5 The peptide bond in serylalanine.

Peptide is the name given to a short polymer of amino acids. We classify peptides by the number of amino acid units in their chains. A molecule containing two amino acids joined by an amide bond is called a **dipeptide**. Those containing three to ten amino acids are called **tripeptides**, **tetrapeptides**, **pentapeptides** and so on. Molecules containing more than ten but fewer than 20 amino acids are called **oligopeptides**. Those containing 20 or more amino acids are called **polypeptides**. **Proteins** are biological macromolecules with a molar mass of 5000 u (more than about 40 amino acids) or greater and consisting of one or more polypeptide chains. The distinctions in this terminology are not at all precise.

By convention, polypeptides are written from left to right, beginning with the amino acid with the free —NH_3^+ group and proceeding towards the amino acid with the free —COO^- group. The amino acid with the free —NH_3^+ group is called the ***N*-terminal amino acid**, and that with the free —COO^- group is called the ***C*-terminal amino acid**:



WORKED EXAMPLE 24.4

Representing the Structures of Peptides

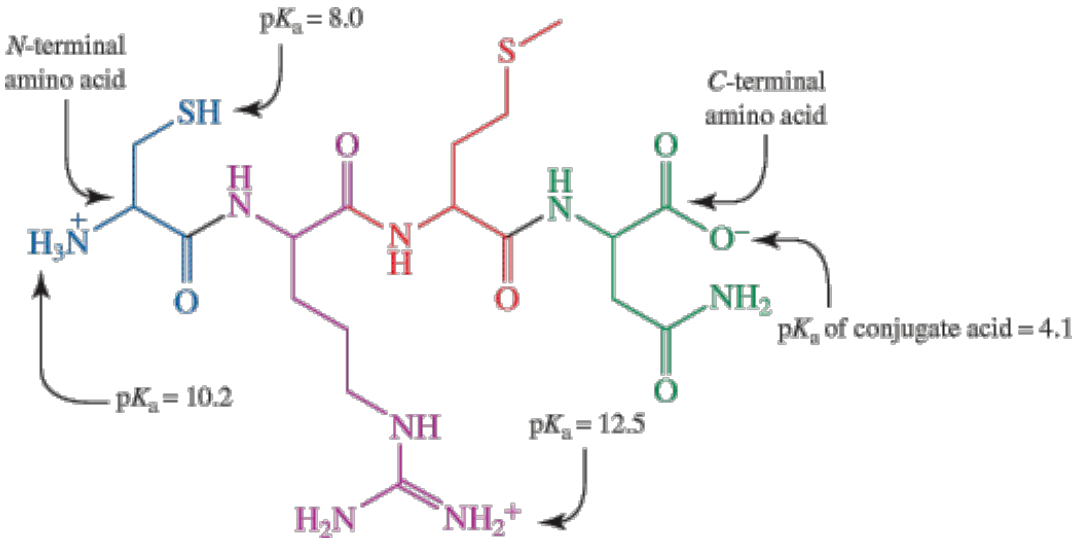
Draw the structural formula for Cys-Arg-Met-Asn. Label the *N*-terminal amino acid and the *C*-terminal amino acid. What is the net charge on this tetrapeptide at pH = 6.0?

Analysis

As peptide structures can be quite complicated, it is important to represent them in as simple and common a form as possible. Start with Cys at the left-hand end —this will be the *N*-terminal amino acid. Form a peptide bond between the carboxyl carbon atom of this and the amino group of the next amino acid, Arg. Continue along the chain in this fashion until you come to the end amino acid, Asn. This will be the *C*-terminal amino acid. The net charge can be calculated by analysis of the pK_a data for all of the acidic and basic groups present in the peptide.

Solution

The backbone of Cys-Arg-Met-Asn, a tetrapeptide, is a repeating sequence of nitrogen– α-carbon–carbonyl. The following is its structural formula:



At pH = 6.0, the basic groups present are strong enough bases (pK_a of their conjugate acids = 10.2 and 12.5) to be protonated, and the acidic group is a strong enough acid (pK_a = 4.1) to dissociate to give the conjugate base. The thiol is not acidic enough (pK_a = 8.0) to dissociate. The net charge on this tetrapeptide at pH = 6.0 is therefore +1.

Is our answer reasonable?

Linking amino acids to make a peptide removes the effect of many of the carboxylic acid and amine groups on the charge at a particular pH. You should note that a peptide (or amide) linkage is not basic, so the nitrogen atom in this part of the molecule will not be able to be protonated and become charged. Only the terminal amine and carboxylic acid, as well as their side-chain groups, govern the overall charge on a peptide.

PRACTICE EXERCISE 24.4

Draw the structural formula for Lys-Phe-Ala.

Label the *N*-terminal amino acid and the *C*-terminal amino acid. What is the net charge on this tripeptide at pH = 6.0?

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24.4 Primary Structure of Polypeptides and Proteins

The **primary (1°) structure** of a polypeptide or protein is the sequence of amino acids in its polypeptide chain. In this sense, the primary structure is a complete description of all covalent bonding in a polypeptide or protein.

In 1953, Frederick Sanger (figure 24.6) of Cambridge University, England, reported the primary structure of the two polypeptide chains of the hormone insulin. This was a remarkable achievement in analytical chemistry; it also clearly established that all the molecules of a given protein have the same amino acid composition and the same amino acid sequence. Today, the amino acid sequences of over 20 000 different proteins are known, and the number is growing rapidly.



FIGURE 24.6 Frederick Sanger was awarded the Nobel Prize in chemistry in 1958 for his work on insulin. He was awarded a *second* Nobel Prize in chemistry in 1980 for his work on determining the base sequences in DNA.

Amino Acid Analysis

The first step in determining the primary structure of a polypeptide is hydrolysis and quantitative analysis of its amino acid composition. Recall from section 23.5 (p. 1025) that amide bonds are resistant to hydrolysis. Typically, samples of protein are hydrolysed in 6 m HCl in sealed glass vials at 110 °C for 24 to 72 hours. (This hydrolysis can be done in a microwave oven in a shorter time.) After the polypeptide is hydrolysed, the resulting mixture of amino acids is analysed by ion-exchange chromatography. In this process, the mixture of amino acids is passed through a specially packed column. Each of the 20 amino acids requires a different time to pass through the column. Amino acids are detected by reaction with ninhydrin as they emerge from the column (section 24.2), followed by absorption spectroscopy. Current procedures for the hydrolysis of polypeptides and the analysis of amino acid mixtures have been refined to the point where it is possible to determine the amino acid composition from as little as 50 nanomoles (50×10^{-9} mole) of a polypeptide. Figure 24.7 shows the analysis of a polypeptide hydrolysate by ion-exchange chromatography. Note that, during hydrolysis, the side-chain amide groups of asparagine and glutamine are hydrolysed, and these amino acids are

detected as aspartic acid and glutamic acid. For each glutamine or asparagine hydrolysed, an equivalent amount of ammonium chloride is formed.

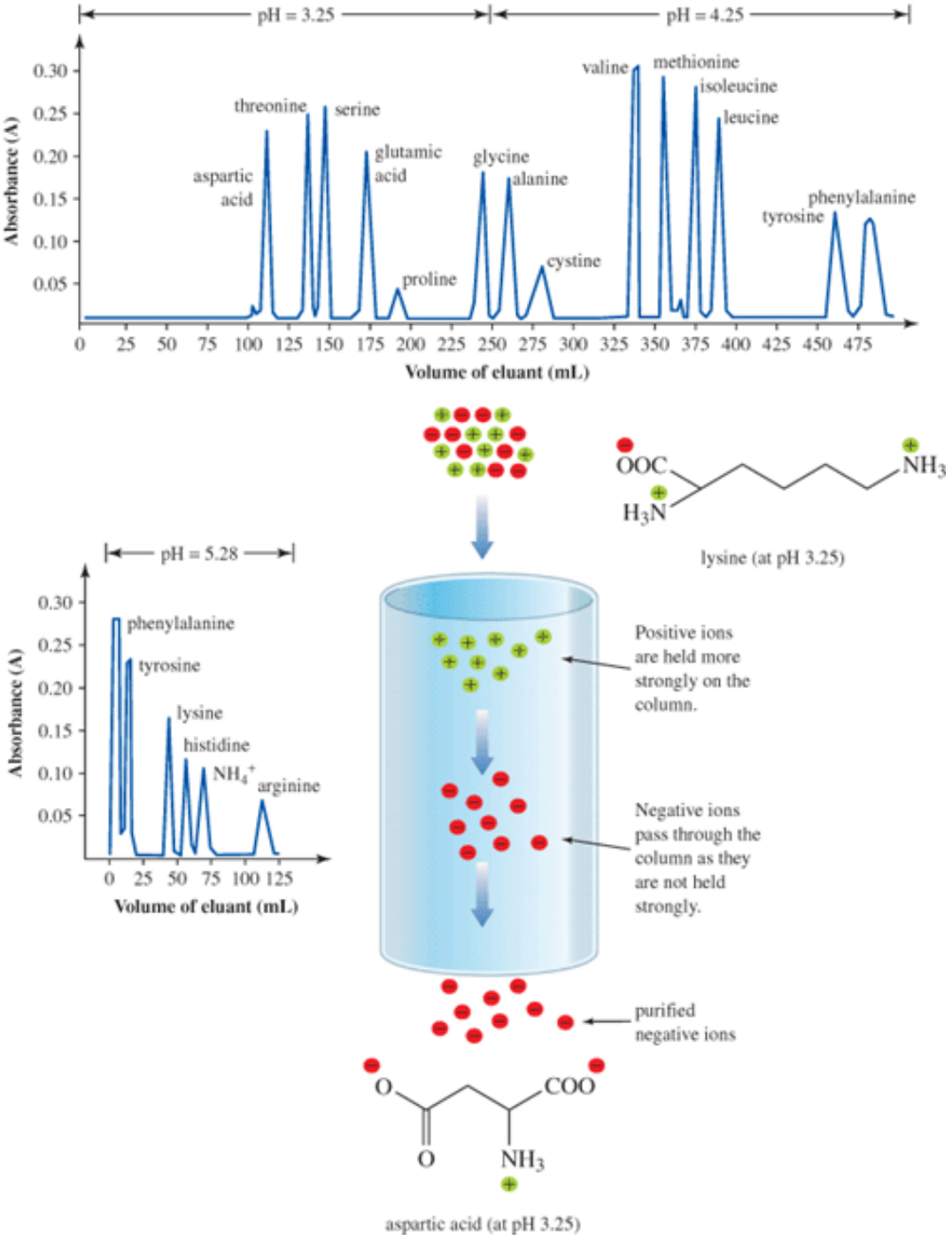


FIGURE 24.7 Analysis of a mixture of amino acids by ion-exchange chromatography using Amberlite IR-120, a sulfonated polystyrene resin. The resin contains phenyl-$SO_3^-Na^+$ groups. The amino acid mixture is applied to the column at low pH (3.25), conditions under which the acidic amino acids (Asp, Glu) are weakly bound to the resin and the basic amino acids (Lys, His, Arg) are tightly bound. Sodium citrate buffers of two different concentrations and three different values of pH are used to elute the amino acids from the column. Cysteine is determined as cystine, Cys-S-S-Cys, the disulfide of cysteine.

Sequence Analysis

Once the amino acid composition of a polypeptide has been determined, the next step is to determine the order in which the amino acids are joined in the polypeptide chain. The most common sequencing strategy is to cleave the polypeptide at specific peptide bonds, determine the sequence of each fragment,

and then match overlapping fragments to arrive at the sequence of the polypeptide.

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24.5 Three-dimensional Shapes of Polypeptides and Proteins

Many of the properties of polypeptides and proteins are governed by the precise three-dimensional shape of these complex molecules. The complexity of the shape arises from the nature of the peptide bond.

Geometry of a Peptide Bond

In the late 1930s, Linus Pauling (Nobel Prize in chemistry, 1954) began a series of studies aimed at determining the geometry of a peptide bond. One of his first discoveries was that a peptide bond is planar. As shown in figure 24.8, the four atoms of a peptide bond and the two α-carbon atoms joined to it all lie in the same plane.

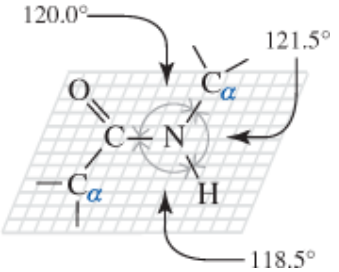
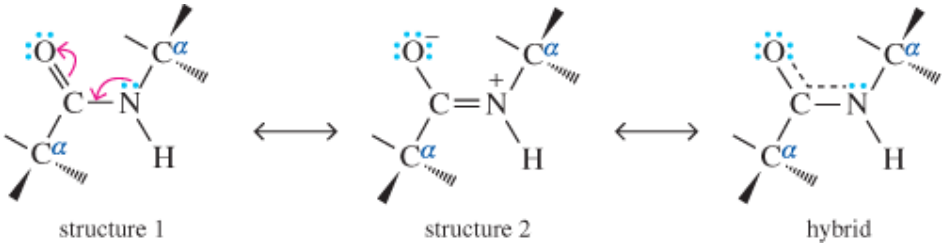


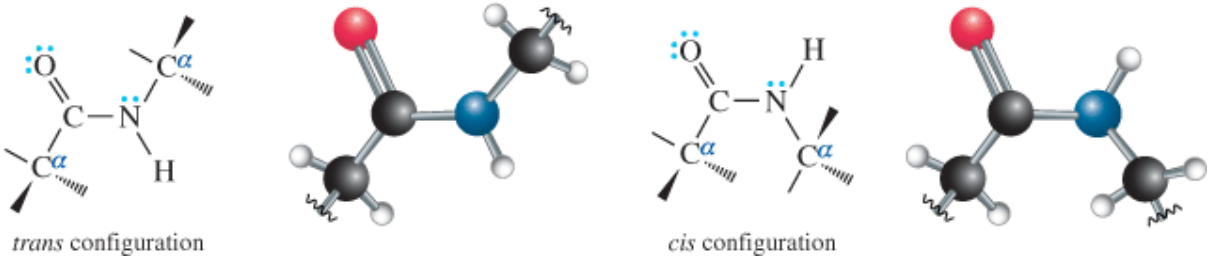
FIGURE 24.8 Planarity of a peptide bond. Bond angles around the carbonyl carbon atom and the amide nitrogen atom are approximately 120°.

Had you been asked in chapter 5 to describe the geometry of a peptide bond, you probably would have predicted bond angles of 120° around the carbonyl carbon atom and 109.5° around the amide nitrogen atom. This prediction agrees with the observed bond angles of approximately 120° around the carbonyl carbon atom. It does not agree, however, with the observed bond angles of 120° around the amide nitrogen. To account for this geometry, Pauling proposed that a peptide bond is more accurately represented as a resonance hybrid of these two contributing structures.



Contributing structure 1 shows a carbon–oxygen double bond, and structure 2 shows a carbon– nitrogen double bond. The hybrid, of course, is neither of these; in the real structure, the carbon–nitrogen bond has considerable double-bond character. Accordingly, in the hybrid, the six-atom group shown in the two resonance structures is planar.

Because of the partial double-bond character, two configurations are possible for the atoms of a planar peptide bond. In one, the two α-carbon atoms are *cis* to each other; in the other, they are *trans* to each other. The *trans* configuration is more favourable because, in the *trans* configuration, the α-carbon atoms with the bulky groups bonded to them are further from each other than they are in the *cis* configuration. Virtually all peptide bonds in naturally occurring proteins studied to date have the *trans* configuration.



Secondary Structure

Secondary (2°) structure is the ordered arrangement (conformation) of amino acids in localised regions of a polypeptide or protein molecule. The first studies of polypeptide conformations were carried out by Linus Pauling and Robert Corey, beginning in 1939. They assumed that, in conformations of greatest stability, all atoms in a peptide bond lie in the same plane and there is hydrogen bonding between the N—H of one peptide bond and the C═O of another, as shown in figure 24.9.

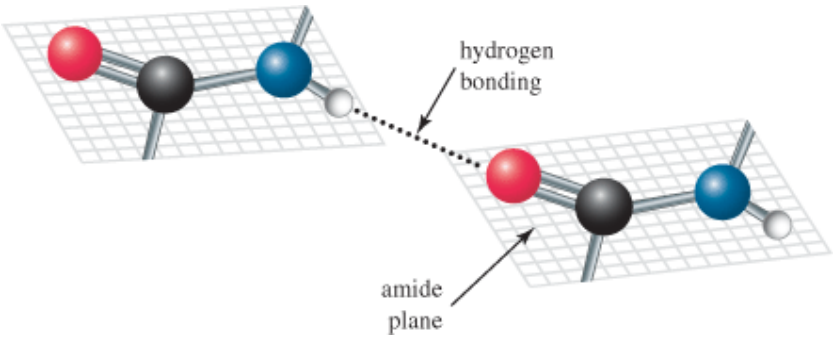


FIGURE 24.9 Hydrogen bonding between amide groups.

On the basis of model building, Pauling proposed that two types of secondary structure should be particularly stable: the α-helix and the antiparallel β-pleated sheet.

The α-helix

In an **α-helix** pattern, shown in figure 24.10, a polypeptide chain is coiled in a spiral. As you study this section of the α-helix, note the following:

1. The helix is coiled in a clockwise, or right-handed, manner. *Right-handed* means that if you *d* turn the helix clockwise, it twists away from you. In this sense, a right-handed helix is analogous to the right-handed thread of a common wood or machine screw.
2. There are 3.6 amino acids per turn of the helix.
3. Each peptide bond is *trans* and planar.
4. The N—H group of each peptide bond points roughly downwards, parallel to the axis of the helix, and the C═O of each peptide bond points roughly upwards, also parallel to the axis of the helix.
5. The carbonyl group of each peptide bond is hydrogen bonded to the N—H group of the peptide bond four amino acid units away from it. Hydrogen bonds are shown as dashed lines.
6. All R groups point outwards from the helix.

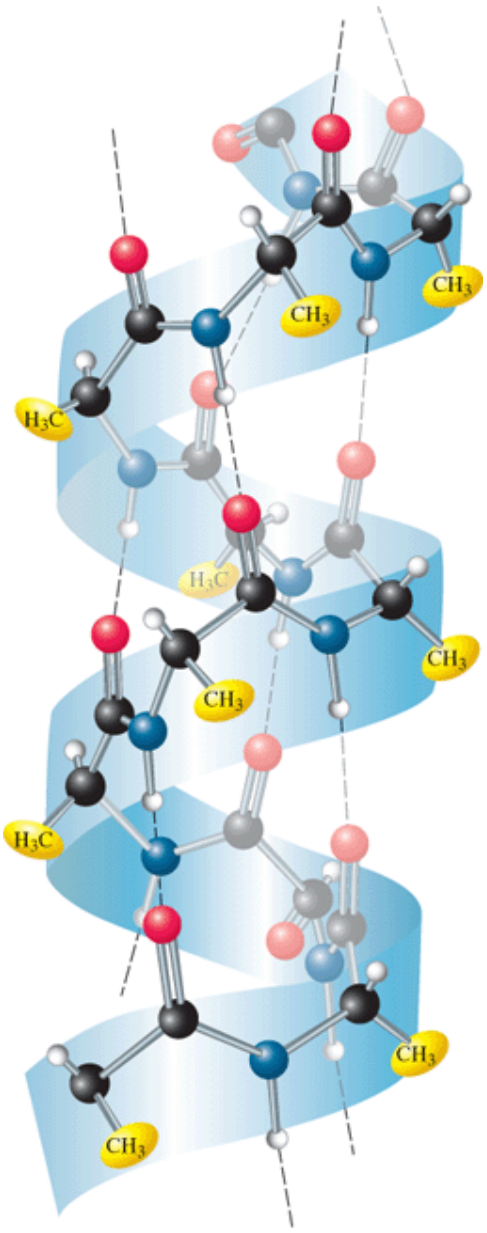


FIGURE 24.10 An α-helix. The polypeptide chain is repeating units of L-alanine. (Dashed lines indicate hydrogen bonding.)

Almost immediately after Pauling proposed the α-helix conformation, other researchers proved the presence of α-helix conformations in keratin, the protein of hair and wool. It soon became obvious that the α-helix is one of the fundamental folding patterns of polypeptide chains.

Chemistry Research

Antimicrobial Peptides

Professor Frances Separovic, University of Melbourne

Some antibiotics literally deliver a killer blow when they fight disease, according to research by biophysical chemists at the University of Melbourne. These antibiotics destroy bacteria by effectively 'punching' holes in their cell membranes. This can upset the osmotic balance so that water flows in, and the bacteria swell and eventually burst. A University of Melbourne, School of Chemistry research team discovered this while studying the structure of antibiotic peptides and how they kill cells.

Peptides are small proteins that play a key role in biochemistry. For example, amphibians and bacteria produce antimicrobial peptides as protection against disease, some of which can act as antibiotics. Many of these peptides destroy cell membranes but the mechanism is not well understood.

According to research team leader Professor Frances Separovic, most studies have looked at peptide antibiotics in solution instead of observing their action directly in cell membranes. Together with collaborators at the University of Adelaide, Professor Separovic has been studying antimicrobial peptides in membranes and in live bacteria using NMR spectroscopy, a technique for determining molecular structure. These antibiotic peptides act as though they punch holes in cell membranes.

Professor Separovic says early studies of the antibiotic peptide gramicidin A in solution showed it to be composed of two tightly intertwined strands. However, her studies of the peptide *in situ* within a model cell membrane revealed a different picture. Rather than the double helix found in solution, two molecules of the peptide form a single helical strand on top of one another within the membrane, forming a hole that serves as an ion channel. Ions and water flow in or out of the cell so that the cell swells and finally bursts. This research was the first to determine the molecular structure of a peptide within a membrane bilayer.

Other scientists are now using the gramicidin ion channel (figure 24.11) as part of a biosensor (figure 24.12). Professor Separovic says the technique involves linking receptors for particular chemicals, such as drugs, to the peptide. If the drug is present, it binds to the receptor, prevents the formation of an ion channel and reduces the ion current through the membrane, which the sensor can detect.

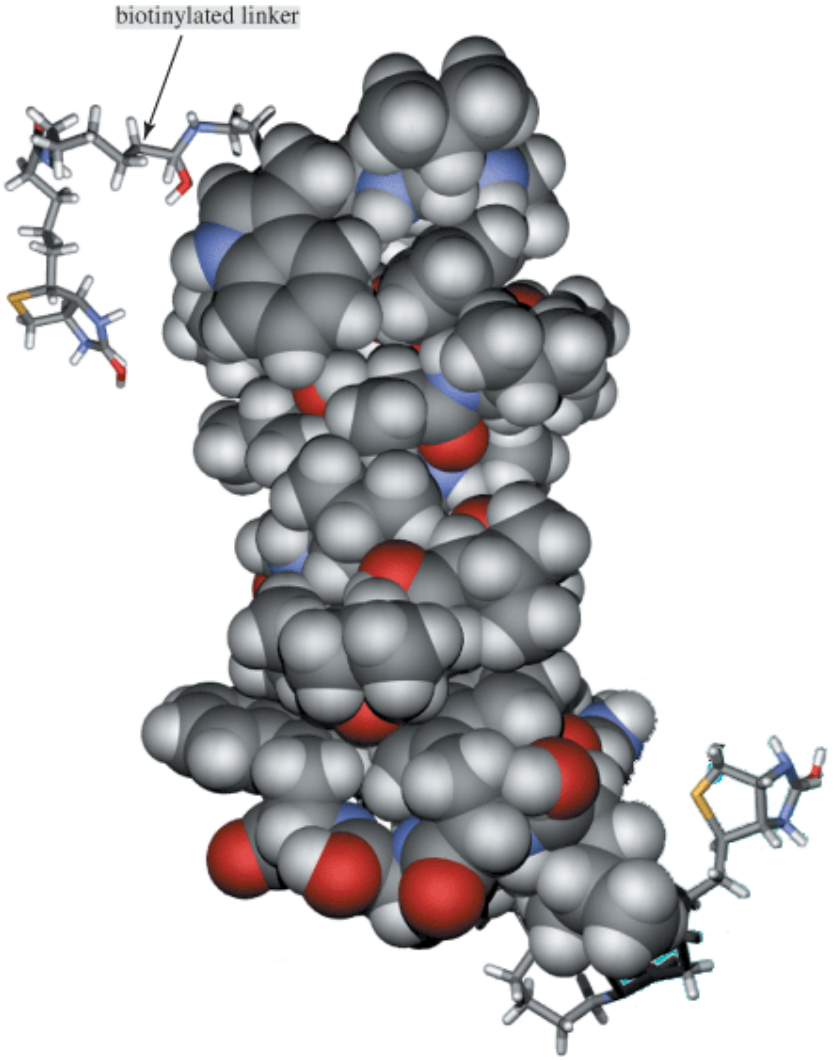


FIGURE 24.11 Gramicidin A ion channel with biotinylated linker attached.

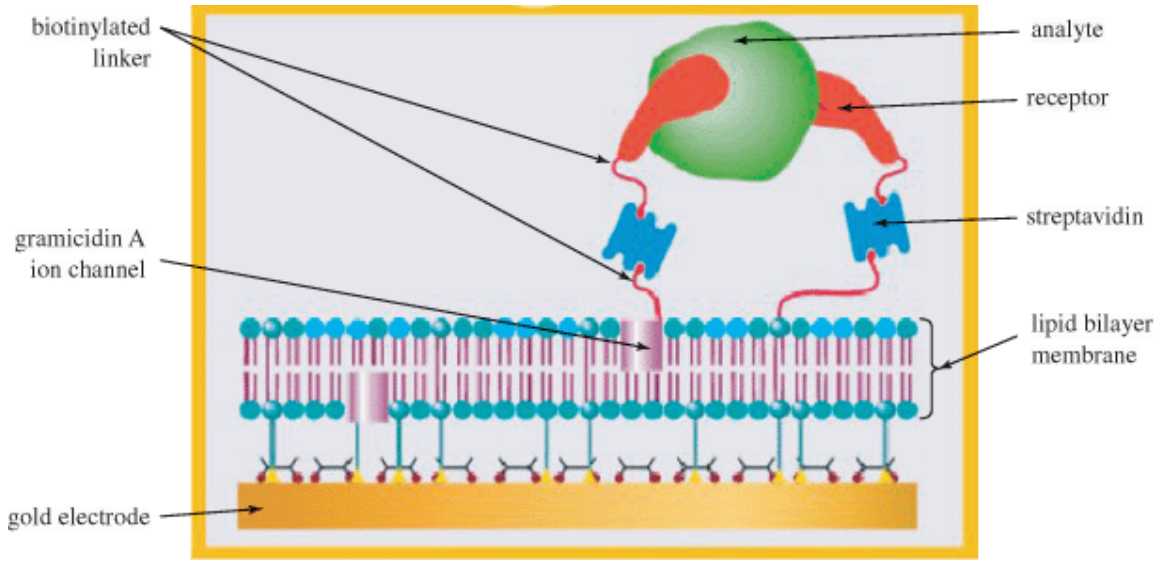


FIGURE 24.12 Graphical representation of an ion channel switch biosensor. The pink 'barrel' with red linker attached is one half of a biotinylated gramicidin A channel in a lipid bilayer membrane attached to a gold electrode. When an analyte molecule (green) binds to the receptor (red), the ion current is reduced and the electrode 'senses' its presence.

The β-pleated Sheet

An antiparallel **β-pleated sheet** consists of an extended polypeptide chain with neighbouring sections of the chain running in opposite (antiparallel) directions. In a parallel β-pleated sheet, the neighbouring sections run in the same direction. In contrast to the α-helix arrangement, N—H and C═O groups lie in the plane of the sheet and are roughly perpendicular to the long axis of the sheet. The C═O group of each peptide bond is hydrogen bonded to the N—H group of a peptide bond of a neighbouring section of the chain (figure 24.13).

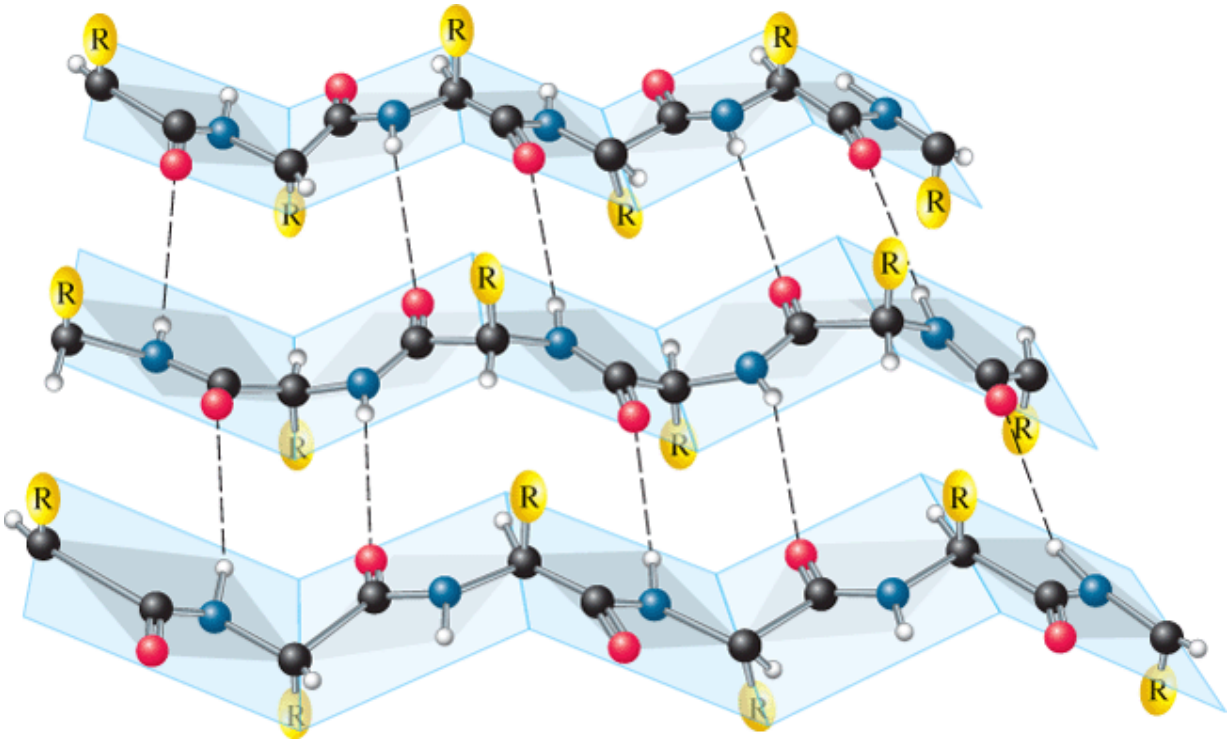


FIGURE 24.13 Three polypeptide chains running in opposite (antiparallel) directions in a β-pleated sheet conformation (dashed lines indicate hydrogen bonding; yellow shapes represent side chains).

As you study this section of β-pleated sheet, note the following:

1. The three sections of the polypeptide chain lie adjacent to each other and run in opposite (anti-parallel) directions.
2. Each peptide bond is planar, and the α-carbon atoms are *trans* to each other.
3. The C═O and N—H groups of peptide bonds from adjacent sections point at each other and are in the same plane, so that hydrogen bonding is possible between adjacent sections.
4. The R groups on any one chain alternate, first above, then below, the plane of the sheet, and so on.

The β-pleated sheet conformation is stabilised by hydrogen bonding between N—H groups of one section of the chain and C═O groups of an adjacent section. By comparison, the α-helix is stabilised by hydrogen bonding between N—H and C═O groups within the same polypeptide chain.

Tertiary Structure

Tertiary (3°) structure is the overall folding pattern and arrangement in space of all atoms in a single polypeptide chain. No sharp dividing line exists between secondary and tertiary structures. Secondary structure refers to the spatial arrangement of amino acids close to one another on a polypeptide chain, whereas tertiary structure refers to the three-dimensional arrangement of all atoms in a polypeptide chain. Among the most important factors in maintaining 3° structure are disulfide bonds, hydrophobic interactions, hydrogen bonding and salt linkages.

Disulfide bonds play an important role in maintaining tertiary structure. Disulfide bonds are formed between side chains of two cysteine units by oxidation of their thiol groups (—SH) to form a disulfide bond (section 19.5). Treatment of a disulfide bond with a reducing agent regenerates the thiol groups:

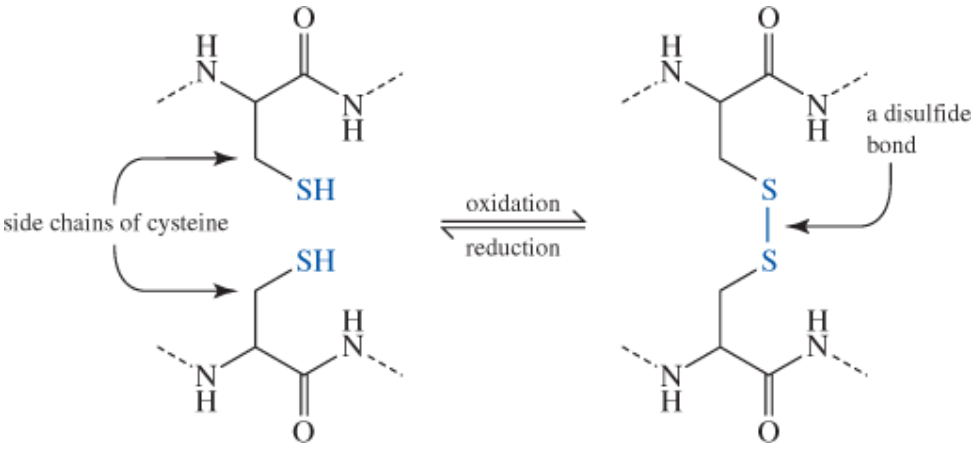


Figure 24.14 shows the amino acid sequence of human insulin. This protein consists of two polypeptide chains: an A chain of 21 amino acids and a B chain of 30 amino acids. The A chain is bonded to the B chain by two interchain disulfide bonds. An intrachain disulfide bond also connects the cysteine units at positions 6 and 11 of the A chain.



FIGURE 24.14 Human insulin. The A chain of 21 amino acids and B chain of 30 amino acids are connected by interchain disulfide bonds between A7 and B7 and between A20 and B19. In addition, a single intrachain disulfide bond occurs between A6 and A11.

As an example of 2° and 3° structure, let us look at the three-dimensional structure of myoglobin, a protein found in skeletal muscle and particularly abundant in diving mammals, such as whales (figure 24.15), dolphins and seals. Myoglobin and its structural relative, haemoglobin, are the oxygen transport and storage molecules of vertebrates. Haemoglobin binds molecular oxygen in the lungs and transports it to myoglobin in muscles. Myoglobin stores molecular oxygen until it is required for metabolic oxidation.



FIGURE 24.15 Like all humpback whales, Migaloo relies on myoglobin as a storage form of oxygen.

Myoglobin consists of a single polypeptide chain of 153 amino acids. Myoglobin also contains a single haem unit. Haem consists of one Fe^{2+} ion, coordinated in a square planar array with the four nitrogen atoms of a molecule of porphyrin (figure 24.16).

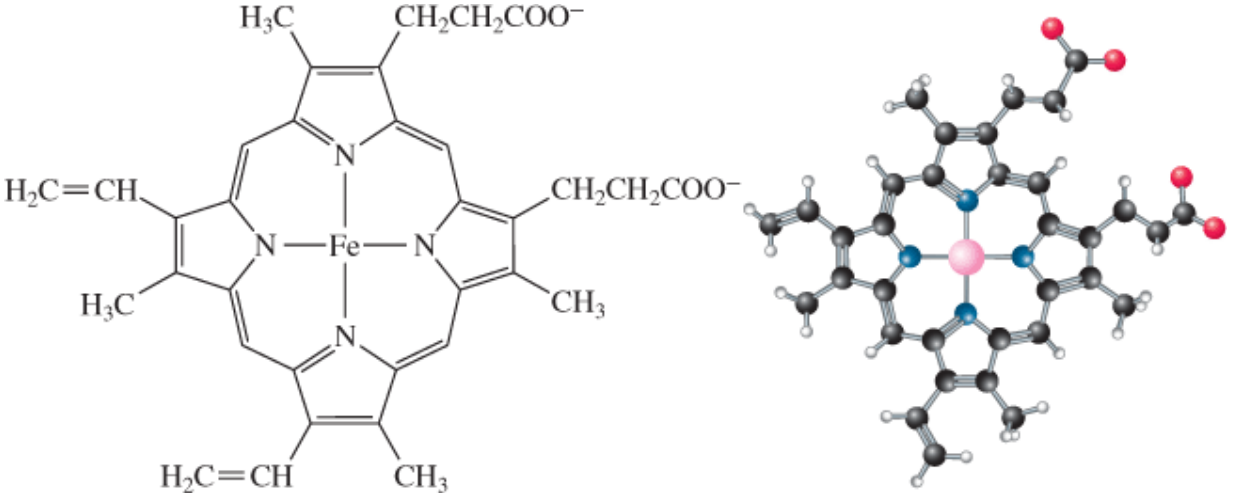


FIGURE 24.16 Representations of the structure of haem found in myoglobin and haemoglobin.

Determination of the three-dimensional structure of myoglobin represented a milestone in the study of molecular architecture. For their contribution to this research, John C Kendrew and Max F Perutz, both of Britain, shared the 1962 Nobel Prize in chemistry. The secondary and tertiary structures of myoglobin are shown in figure 24.17. The single polypeptide chain is folded into a complex, almost boxlike shape.

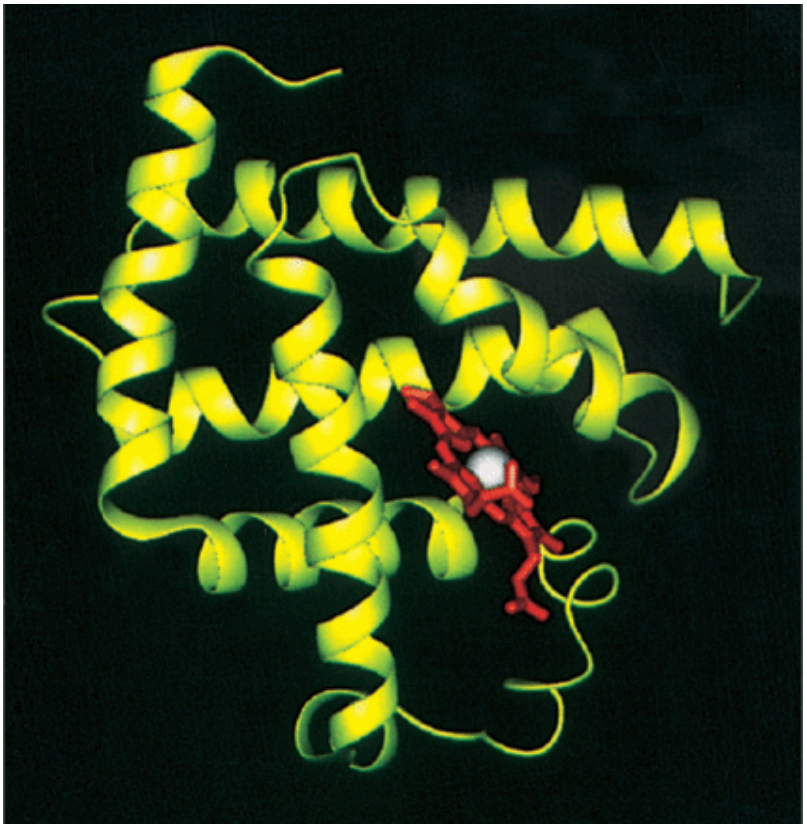


FIGURE 24.17 Ribbon model of myoglobin. The polypeptide chain is shown in yellow, the haem ligand in red and the Fe atom as a white sphere.

There are several important structural features of the three-dimensional shape of myoglobin:

1. The backbone consists of eight relatively straight sections of α-helix, each separated by a bend in the polypeptide chain. The longest section of α-helix has 24 amino acids, the shortest has seven. Some 75% of the

amino acids are found in these eight regions of α-helix.

2. Hydrophobic side chains of phenylalanine, alanine, valine, leucine, isoleucine and methionine are clustered in the interior of the molecule, where they are shielded from contact with water. **Hydrophobic interactions** are a major factor in directing the folding of the polypeptide chain of myoglobin into this compact, three-dimensional shape.
3. The outer surface of myoglobin is coated with hydrophilic side chains, such as those of lysine, arginine, serine, glutamic acid, histidine and glutamine, which interact with the aqueous environment by **hydrogen bonding**. The only polar side chains that point to the interior of the myoglobin molecule are those of two histidine units, which point inwards towards the haem group.
4. Oppositely charged amino acid side chains close to each other in the three-dimensional structure interact by electrostatic attractions called **salt linkages**. An example of a salt linkage is the attraction of the side chains of lysine ($—NH_3^+$) and glutamic acid ($—COO^-$).

The tertiary structures of hundreds of proteins have also been determined. It is clear that proteins contain α-helix and β-pleated sheet structures, but that wide variations exist in the relative amounts of each. Lysozyme, with 129 amino acids in a single polypeptide chain, has only 25% of its amino acids in α-helix regions. Cytochrome, with 104 amino acids in a single polypeptide chain, has no α-helix structure, but does contain several regions of β-pleated sheet. Yet, whatever the proportions of α-helix, β-pleated sheet or other periodic structure, virtually all nonpolar side chains of water-soluble proteins are directed towards the interior of the molecule, whereas polar side chains are on the surface of the molecule, in contact with the aqueous environment.

WORKED EXAMPLE 24.1

Recognising Peptide Side Chains that Influence Tertiary Structure

The side chains of which of the following amino acids can form hydrogen bonds with the side chain of threonine?

(a) valine
(b) asparagine
(c) phenylalanine
(d) histidine
(e) tyrosine
(f) alanine

Analysis

Hydrogen bonds occur between heteroatoms that possess lone pairs of nonbonding electrons and polarised N—H or O—H bonds. Threonine has an —OH group on the side chain, which is a strong hydrogen bonding group. It should be able to form hydrogen bonds with any group containing lone pairs of N—H or O—H bonds.

Solution

The side chain of threonine contains a hydroxyl group that can participate in hydrogen bonding in two ways:

1. Its oxygen atom has a partial negative charge and can function as a hydrogen bond acceptor.
2. Its hydrogen atom has a partial positive charge and can function as a hydrogen bond donor.

Therefore, the side chain of threonine can form hydrogen bonds with the side chains of tyrosine, asparagine and histidine.

PRACTICE EXERCISE 24.5

The side chains of which amino acids can form salt linkages with the side chain of lysine at pH = 7.4?

Quaternary Structure

Most proteins with molar mass greater than 50 000 u consist of two or more noncovalently linked polypeptide chains. The arrangement of protein monomers into an aggregation is known as **quaternary (4°) structure**. A good example is haemoglobin (figure 24.18), a protein that consists of four separate polypeptide chains: two α-chains of 141 amino acids each and two β-chains of 146 amino acids each.

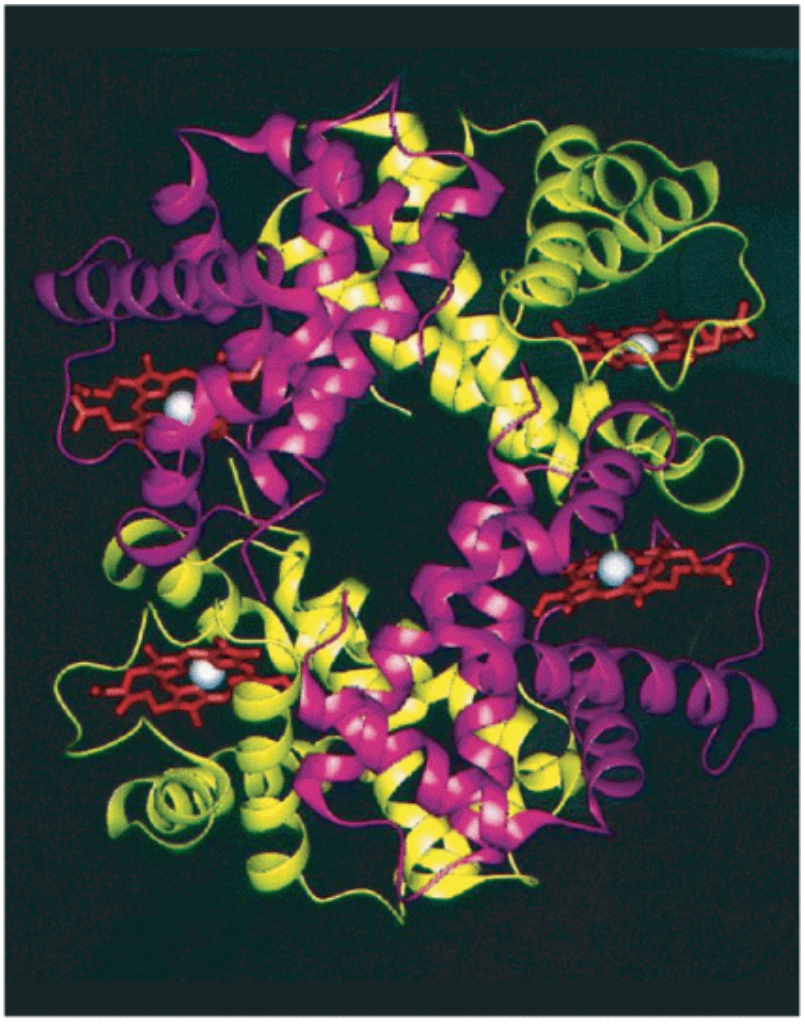


FIGURE 24.18 Ribbon model of haemoglobin. The α-chains are shown in purple, the β-chains in yellow, the haem ligands in red and the Fe atoms as white spheres.

The separate polypeptides pack together and are held in this arrangement by the same type of interactions seen within the tertiary structures: hydrogen bonds, salt bridges and hydrophobic interactions. For proteins in aqueous environments, aggregations in quaternary structures are stabilised mainly by hydrophobic interactions. Thus, separate polypeptide chains fold into compact three-dimensional shapes to expose polar side chains to the aqueous environment; in most cases, however, this still leaves some hydrophobic sections of the proteins in contact with water. By aggregating to form quaternary structures, they are protected from exposure.

Chemistry Research

Protein Folding, Unfolding and Molecular Chaperones

Professor John Carver, University of Adelaide

Proteins are synthesised as unfolded linear chains of amino acids (U) that fold via the folding pathway (figure 24.19) into the correct (native (N)) three-dimensional structure. Along this pathway, the protein adopts a variety of partially folded, intermediate states (I) with some elements of secondary structure in place. Under conditions of cellular stress, such as elevated temperature, infection and oxidation, the reverse process, protein unfolding (from the native folded state), occurs via these intermediate states. These intermediates have their hydrophobic core exposed to solution and, if present for long enough, may aggregate via the off-folding pathways shown. Much research activity has been generated lately because the unfolding of specific proteins is associated with many diseases, particularly those of ageing such as Alzheimer's, Parkinson's and cataract. In the case of Alzheimer's disease, the unfolding, aggregation and precipitation of a small protein, the amyloid β-peptide (Aβ), are believed to be responsible for the disease. Aβ forms highly ordered structures known as amyloid fibrils and is the principal component of the protein deposits (plaques) found in Alzheimer's disease. Thus, understanding the unfolding and aggregation of Aβ, and other disease-related proteins that form similar aggregates, will help determine the fundamental processes and chemistry associated with these diseases and development of therapeutics for their treatment and prevention.

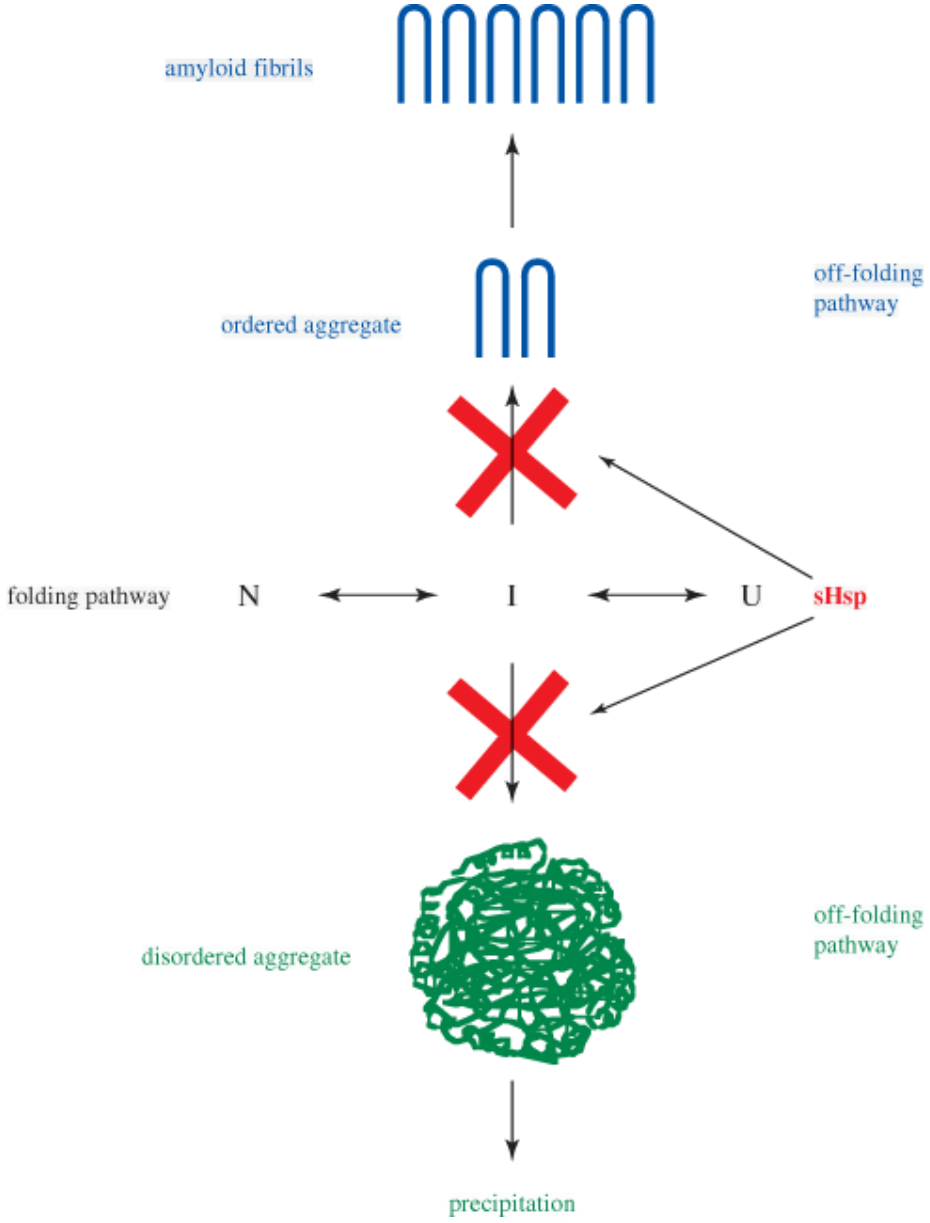


FIGURE 24.19 Protein folding and unfolding. Off-folding pathways give rise either to disordered aggregates that may precipitate or to highly ordered amyloid fibrils, which are the major components of the protein deposits (plaques) found in diseases such as Alzheimer's and Parkinson's. Small heat-shock proteins (sHsps) prevent both types of protein aggregation by interacting with intermediate states (I) early along their off-folding pathways. N and U indicate the native and unfolded states of the protein, respectively.

In vivo, the folding and unfolding of proteins is regulated by a diverse group of proteins known as molecular

chaperones. When referring to protein folding, the term ‘chaperone’ is most appropriate as, by analogy with a human chaperone, the function of a molecular chaperone is to facilitate correct intimate association of a polypeptide chain but not to remain part of the final functional, folded form of the protein. The well-studied bacterial chaperone, GroEL, forms a very large cylindrical aggregate with a central cavity into which the folding target protein is sequestered. In this isolated environment, the protein can fold without the possibility of illicit interactions with other cellular components that may lead to an incorrectly folded state. When the protein is folded, it is released from the GroEL cavity.

Our studies have concentrated mainly on small heat-shock proteins (sHsps), a ubiquitous class of molecular chaperones that are specifically involved in preventing the unfolding and aggregation of target proteins. Under conditions of cellular stress, their synthesis is enhanced greatly and they therefore act as one of the primary cellular defence mechanisms. Because of their inherent ability to prevent target protein aggregation, these heat-shock proteins are potential therapeutics in the treatment of protein aggregation diseases such as Alzheimer's disease. Indeed, sHsps are commonly found associated with the *in vivo* protein deposits that characterise these diseases. The micrographs in figure 24.20 show that one sHsp, αB-crystallin, prevents *in vitro* amyloid fibril formation by the protein α-synuclein, the major component of Lewy body deposits in Parkinson's disease.

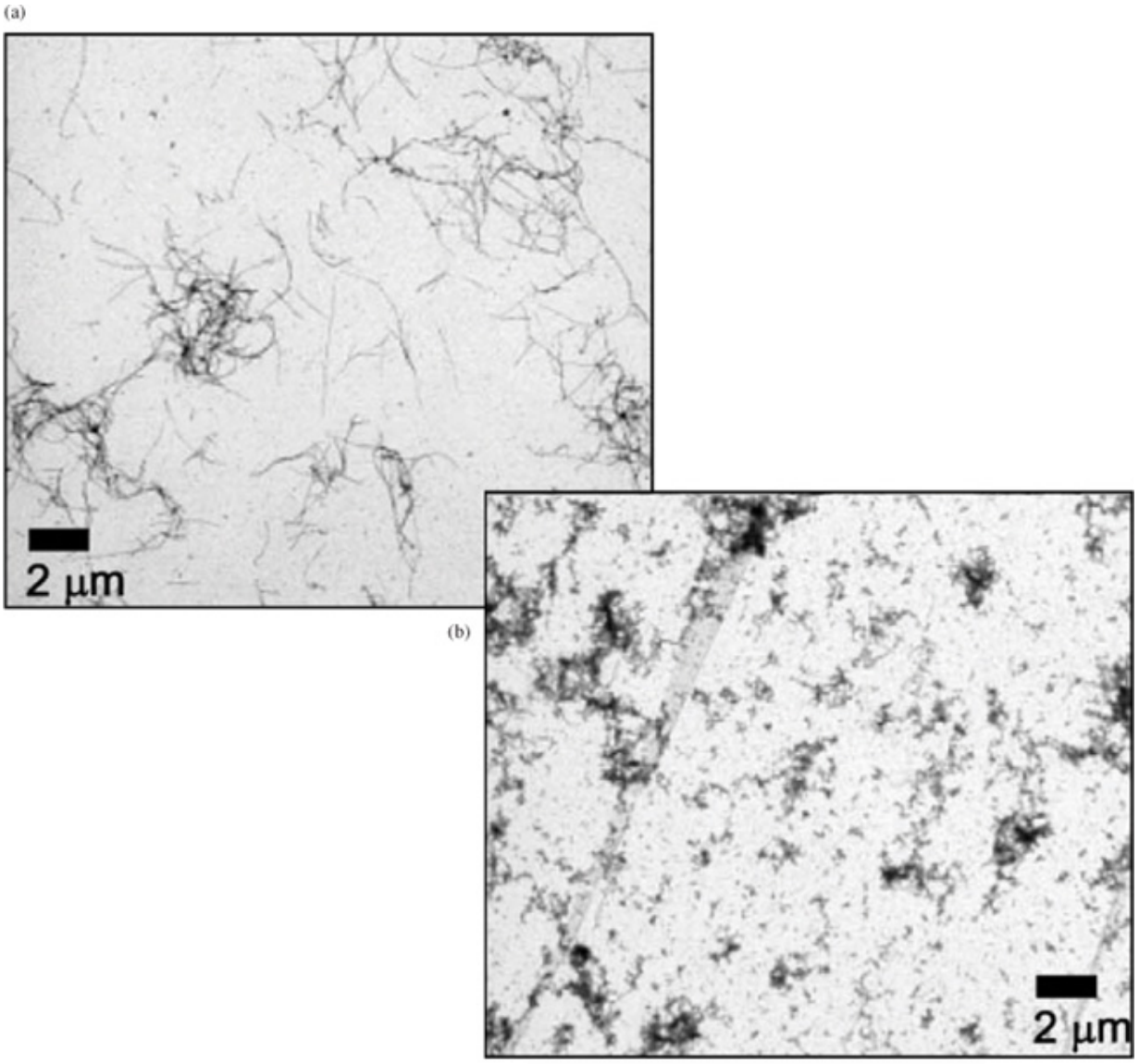


FIGURE 24.20 Transmission electron micrographs of the inhibition of α-synuclein amyloid fibril formation by the small heat-shock protein αB-crystallin.

(a) At neutral pH, α-synuclein spontaneously forms fibrils.

(b) However, in the presence of αB-crystallin, fibril formation is prevented; disordered aggregates are formed instead.

Our work adopts a highly interdisciplinary approach by using a variety of complementary biophysical, protein chemical, cell biological and spectroscopic techniques to investigate the structure, function and interactions of sHsps. For example, our NMR spectroscopic studies have shown that they have a highly flexible and unstructured region at their extreme *C*-terminus, which is crucial in chaperone function and in maintaining the protein's structural integrity.

If two or more proteins assemble so that the hydrophobic sections match up, these components are then shielded from the aqueous environment. The numbers of subunits for several proteins that are known to form quaternary structures are shown in table 24.4.

TABLE 24.4 Quaternary Structure of Selected Proteins

Protein	Number of subunits
alcohol dehydrogenase	2
aldolase	4
haemoglobin	4
lactate dehydrogenase	4
insulin	6
glutamine synthetase	12
tobacco mosaic virus protein disc	17

On the other hand, about one-third of all proteins are actually present in the nonaqueous environment of cell membranes. Proteins that are incorporated in cell membranes are called **integral membrane proteins** because they traverse a membrane bilayer partially or completely. To keep the protein stable in the nonpolar environment of a lipid bilayer, these proteins form quaternary structures in which the outer surface is largely nonpolar and can interact favourably with the lipid environment. The integral membrane proteins aggregate because most of the polar groups turn inwards away from the nonpolar environment, thus forming the quaternary structures and shielding these groups

from the lipids. Figure 24.21 represents the four levels of organisational structure found in proteins.

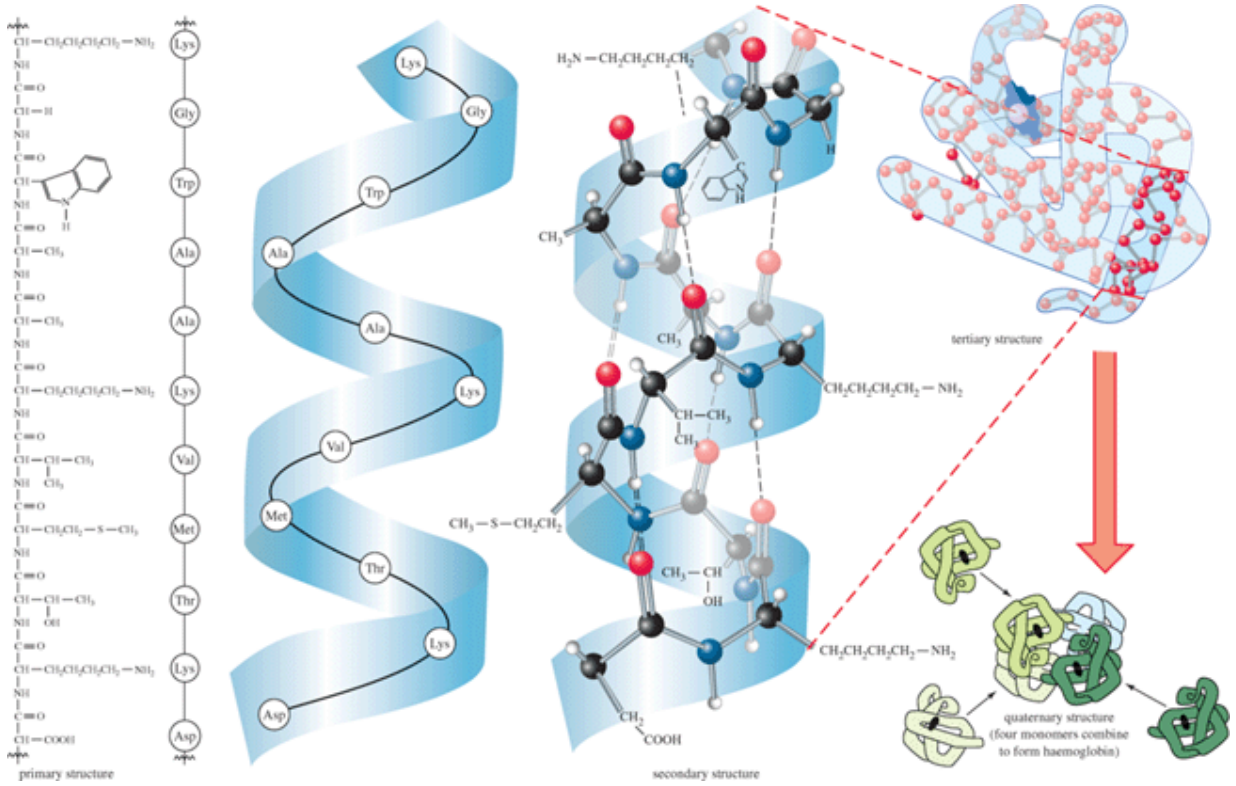


FIGURE 24.21 Primary, secondary, tertiary and quaternary structures of a protein.

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24.6 Denaturing Proteins

The functions and properties of proteins arise from a combination of the secondary, tertiary and quaternary structures that give a protein its particular shape and conformation. Any physical or chemical agent that interferes with these stabilising structures changes the conformation of the protein and often removes the protein's functionality. We call this process **denaturation**.

Heat, for example, breaks apart hydrogen bonds, so boiling a protein destroys its α-helical and β-pleated sheet structures. The polypeptide chains of globular proteins unfold when heated; the unravelled proteins can then bind strongly to each other and precipitate or coagulate. This is what happens when an egg is boiled and the 'liquid' white is turned into a 'solid'.

Similar transformations can be achieved by the addition of denaturing chemicals. For example, aqueous urea, $H_2N—CO—NH_2$, forms strong hydrogen bonds, so it can disrupt other hydrogen bonds and cause globular proteins to unfold. Ethanol denatures proteins by coagulation. Detergents change protein conformation by disturbing the hydrophobic interactions, whereas acids, bases and salts interfere with ionic salt bridges in the tertiary and quaternary structures. Other chemical agents such as reducing agents can break the key disulfide bonds (—S—S—) holding tertiary structures together. Additionally, heavy metal ions (Pb^{2+}, Hg^{2+}, Cd^{2+} etc.) attack thiol groups (—S—H) to form new salt bridges and disrupt other salt bridges. Table 24.5 outlines some common denaturing factors and the regions of the protein that are affected.

TABLE 24.5 Protein Denaturing Agents and their Modes of Action

Denaturing agent	Affected region
heat	H bonds
6 m urea	H bonds
detergents	hydrophobic regions
acids/bases	salt bridges and H bonds
salts	salt bridges
reducing agents	disulfide bonds
heavy metals	disulfide bonds/thiols/salt bridges
alcohol	hydration layers

Chemistry Research

Putting the Heat on Poisonous Proteins

In 2006, Australia and New Zealand were declared by the World Organisation for Animal Health to be two of only four countries in the world that are free of mad cow disease. So-called mad cow disease is the name given to bovine spongiform encephalopathy (BSE), a debilitating disease that causes strange behaviour in cattle and eventually death. Consuming meat from animals affected by BSE is also harmful to humans. It has been shown that eating contaminated meat can lead to a variant of the disease, called Creutzfeldt Jakob disease (CJD). BSE and CJD arise from the presence of a specific type of misfolded protein called a prion. It is believed that these small, robust proteins can survive the digestion process and become incorporated into the brain, where they lead to similar misfolding of the brain's proteins. They do this by acting as a template around which the larger brain proteins wrap, possibly becoming locked in these incorrect structures by a free radical or some other nonreversible chemical reaction.

Australia and New Zealand owe their BSE-free status to the fact that they did not follow the US and UK's lead in feeding cattle with protein supplements sourced from sheep and chickens. A similar disease called scrapie has been known in sheep for over 200 years. However, BSE and CJD have only recently become a problem due to a change in the regulations controlling the way protein supplements from sheep were treated. In a terrible example of the dangers that arise when economics overrules science, laws were changed in the 1980s to allow sheep protein to be treated at a lower temperature than previously. You have learned in this chapter

that heat denatures proteins, and it is thought that treatment at the lower temperature, while cheaper, allowed prion proteins from scrapie to be transferred to cattle. From there, the prions were transferred into the human population, possibly via poorly cooked mince containing offal.

Interestingly, Australia and New Zealand are free of scrapie, not because of higher standards, but more likely because of the free-range practices used for raising cattle. Australia and New Zealand can be thankful for this as CJD has already killed more than 150 people worldwide. Unfortunately, many more sufferers are expected to emerge, as it has been estimated that more than 400 000 cattle infected with BSE entered the human food chain in the 1980s.

Australia has a reputation of harbouring the deadliest creatures, including sharks, snakes and crocodiles. Even the timid platypus (figure 24.22) can deliver a powerful sting through a claw on its hind foot. New Zealand does not have as many dangerous creatures but it does have the katipo or red katipo (*Latrodectus katipo*), which is a venomous spider found in many parts of New Zealand. It is a widow spider and is related to Australia's redback spider (figure 24.23) and the USA's black widow spiders.



FIGURE 24.22 Platypus.



FIGURE 24.23 Redback spider.

Interestingly, many of the venoms injected by spiders, such as the redbacks and katipos, are a cocktail of proteins that interfere with nerve transmission and cellular function. Platypus venoms (figure 24.24), snake venoms and even the stinging agents from the box jellyfish (figure 24.25) found in northern Australian waters are all similar in that they contain potent mixes of poisonous proteins, enzymes and polypeptides. While antivenoms exist for katipo, redback spider and many snake venoms, no such treatment is available for jellyfish stings. These stings cause tremendous pain, leave significant scars and have led to a number of deaths. Over the years, there have been several recommended initial treatments for such stings, including salt-bridge disrupting solutions of inorganic ions, including Stingose® and mild acid (vinegar). Currently, the recommended first aid treatment for jellyfish stings is hot water —as hot as the victim can stand. Proteins, enzymes and polypeptides must retain specific structures to maintain activity, so any action that disrupts their structure will lower or prevent their effects. Like the heat treatment needed to denature scrapie prions, hot water denatures jellyfish toxins to some extent and the heat may also penetrate into the affected area, helping to alleviate the effects of this painful sting.

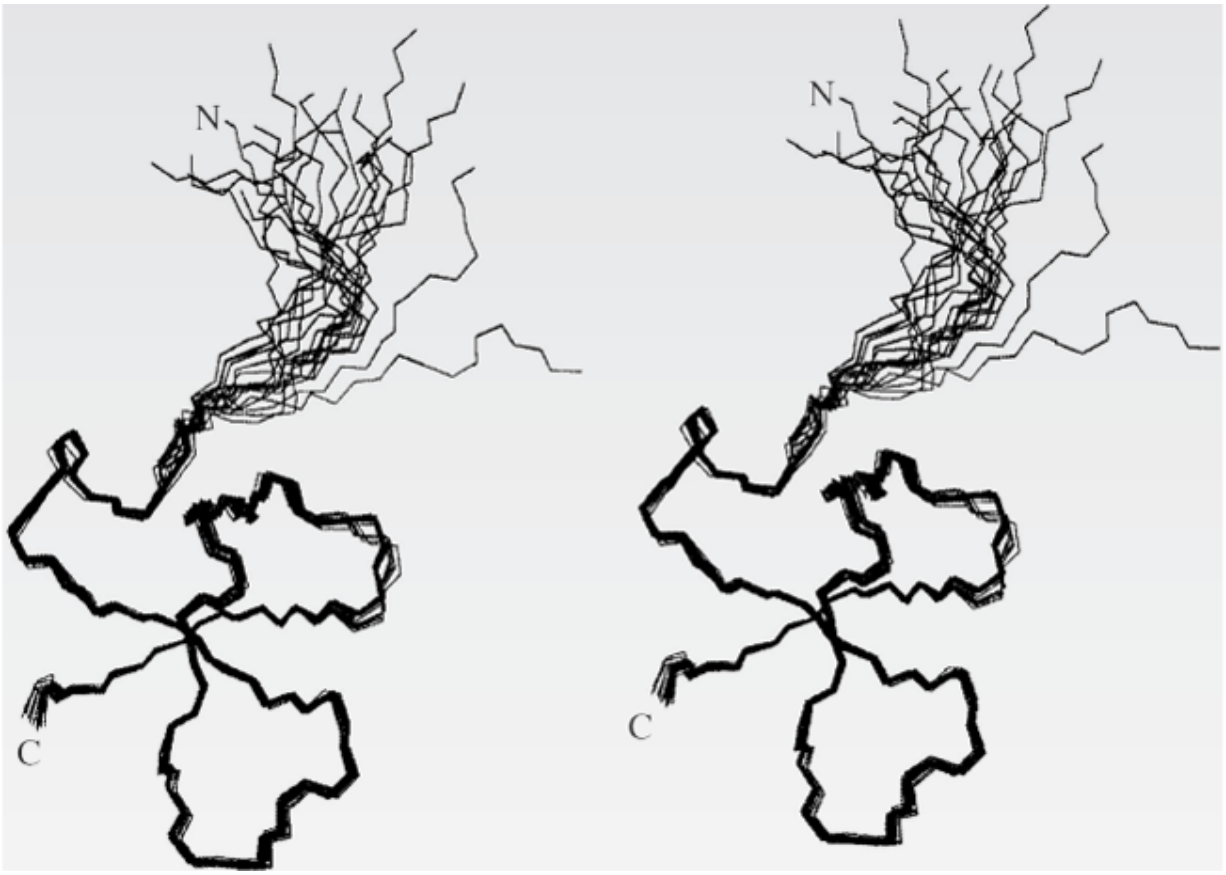


FIGURE 24.24 Stereoview of the active conformations of one of the proteins present in platypus venom (see pp. 44–5 for help in viewing this three-dimensional image). Reproduced with permission from Allan M Torres et al., *Journal of Biochemistry*, vol. 341, 1999, 785–94. © The Biochemistry Society

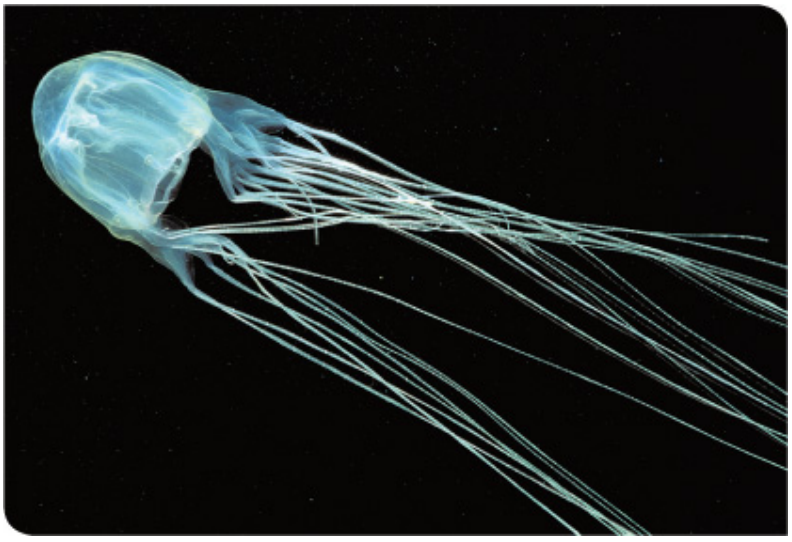


FIGURE 24.25 Box jellyfish.

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SUMMARY

Amino Acids

An α-amino acid is a compound with an amino group adjacent to a carboxyl group. Amino acids exist as zwitterions, or internal salts, at physiological pH. With the exception of glycine, all protein-derived amino acids are chiral. In the D,L convention, all are L-amino acids. Isoleucine and threonine contain two stereocentres. The 20 protein-derived amino acids can be divided into four categories: nine with nonpolar side chains; four with polar, but un-ionised, side chains; four with acidic side chains; and three with basic side chains.

Acid–base Properties of Amino Acids

The isoelectric point, pI, of an amino acid, polypeptide or protein is the pH at which it has no net charge. Electrophoresis is the process of separating compounds on the basis of their electric charge. Compounds with a high charge density move more rapidly than those with a lower charge density. Any amino acid or protein in a solution with a pH that equals the pI of the compound remains at the origin.

Peptides, Polypeptides and Proteins

A peptide bond is the special name given to the amide bond formed between α-amino acids. A polypeptide is a biological macromolecule containing 20 or more amino acids joined by peptide bonds. By convention, the sequence of amino acids in a polypeptide is written from the *N*-terminal amino acid to the *C*-terminal amino acid.

Primary Structure of Polypeptides and Proteins

The primary (1°) structure of a polypeptide is the sequence of amino acids in its polypeptide chain.

Three-dimensional Shapes of Polypeptides and Proteins

A peptide bond is planar; that is, the four atoms of the amide bond and the two α-carbon atoms of a peptide bond lie in the same plane. Bond angles around the amide nitrogen atom and the carbonyl carbon atom are approximately 120°. Secondary (2°) structure is the ordered arrangement (conformation) of amino acids in localised regions of a polypeptide or protein. Two types of secondary structure are the α-helix and the β-pleated sheet. Tertiary (3°) structure is the overall folding pattern and arrangement in space of all atoms in a single polypeptide chain. Quaternary (4°) structure is the arrangement of individual poly peptide chains into a noncovalently bonded aggregate.

Denaturing Proteins

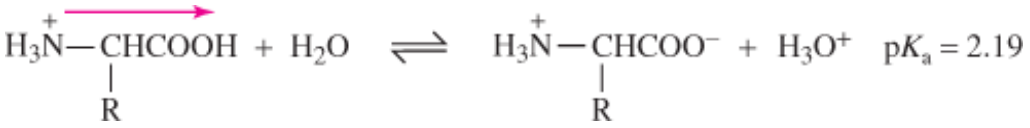
Denaturation is the loss of a protein's properties due to the application of chemicals or physical conditions that interfere with its 2°, 3° and 4° structures.

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KEY CONCEPTS AND EQUATIONS

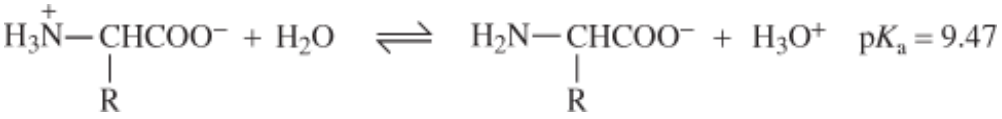
Acidity of α-carboxyl groups *(section 24.2)*

An α-COOH ($pK_a \approx 2.19$) of a protonated amino acid is a considerably stronger acid than acetic acid ($pK_a = 4.74$) or other low-molar-mass aliphatic carboxylic acids, due to the electron-withdrawing inductive effect of the α-NH_3^+ group.



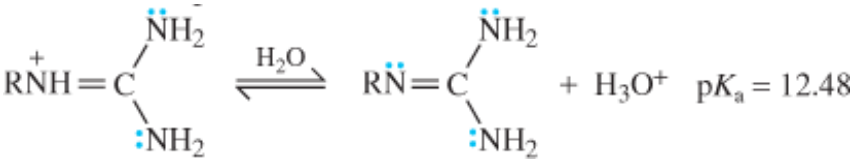
Acidity of α-ammonium groups *(section 24.2)*

An α-NH_3^+ group ($pK_a \approx 9.47$) is a slightly stronger acid than a primary aliphatic ammonium ion ($pK_a \approx 10.76$):



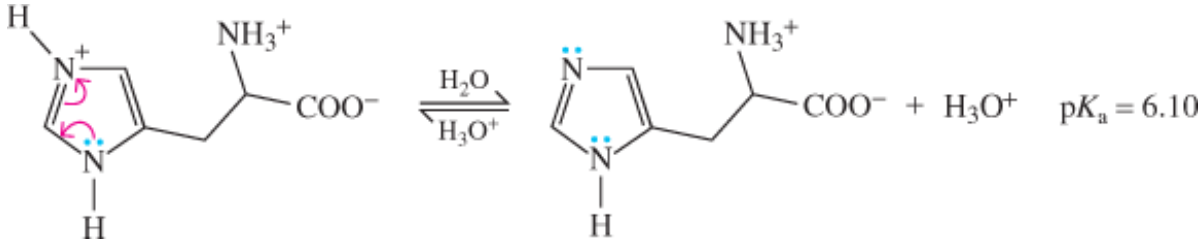
Basicity of the guanidine group of arginine *(section 24.2)*

The protonated form of the arginine side chain forms readily because of substantial resonance stabilisation.



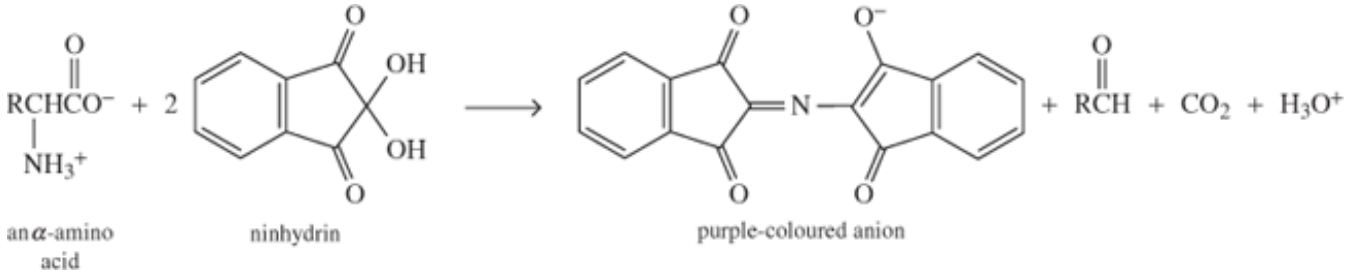
Basicity of the imidazole group of histidine *(section 24.2)*

Protonation of the nitrogen atom of imidazole produces a resonance-stabilised cation.



Reaction of an α-amino acid with ninhydrin *(section 24.2)*

Treating an α-amino acid with ninhydrin gives a purple-coloured solution.



Treating proline with ninhydrin gives an orange-coloured solution.

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REVIEW QUESTIONS

Amino Acids

24.1 Which amino acid does each of the following abbreviations stand for?

(a) Phe
(b) Ser
(c) Asp
(d) Gln
(e) His
(f) Gly
(g) Tyr

24.2 Define the term ‘zwitterion’.

24.3 Draw zwitterion forms of the following amino acids.

(a) valine
(b) phenylalanine
(c) glutamine

24.4 Why are Glu and Asp often called acidic amino acids?

24.5 Why is Arg often called a basic amino acid? Which two other amino acids are also basic amino acids?

24.6 What is the meaning of the alpha as it is used in α-amino acid?

24.7 Several β-amino acids exist. A unit of β-alanine, for example, is contained within the structure of coenzyme A. Write the structural formula of β-alanine.

24.8 What is the difference in structure between tyrosine and phenylalanine?

24.9 Classify the following amino acids as nonpolar, polar, neutral, acidic or basic.

(a) arginine
(b) leucine
(c) glutamic acid
(d) asparagine
(e) tyrosine
(f) phenylalanine
(g) glycine

24.10 Why does glycine have no d or l form?

Acid–base Properties of Amino Acids

24.11 Draw the structural formula for the form of each of the following amino acids that is most prevalent at pH = 1.0.

(a) threonine
(b) arginine
(c) methionine
(d) tyrosine

24.12 Draw the structural formula for the form of each of the following amino acids that is most prevalent at pH = 10.0.

(a) leucine

(b) valine

(c) proline

(d) aspartic acid

24.13 Write the zwitterion form of alanine and show the reaction of 1 mole of alanine with each of the following.

(a) 1.0 mol NaOH

(b) 1.0 mol HCl

24.14 Write the form of lysine most prevalent at pH = 1.0, and then show the product of the reaction of 1 mole of lysine with each of the following. (See table 24.2 for pK_a values of the ionisable groups in lysine.)

(a) 1.0 mol NaOH

(b) 2.0 mol NaOH

(c) 3.0 mol NaOH

24.15 Write the form of aspartic acid most prevalent at pH = 1.0, and then show the reaction of 1 mole of aspartic acid with the following. (See table 24.2 for pK_a values of the ionisable groups in aspartic acid.)

(a) 1.0 mol NaOH

(b) 2.0 mol NaOH

(c) 3.0 mol NaOH

24.16 Given pK_a values for ionisable groups from table 24.2, sketch curves for the titration of

(a) glutamic acid with NaOH and

(b) histidine with NaOH.

24.17 Draw a structural formula for the product formed when alanine is treated with each of the following reagents.

(a) aqueous NaOH

(b) aqueous HCl

(c) CH_3CH_2OH, H_2SO_4

(d) $(CH_3CO)_2O$, $NaOOCCH_3$

24.18 Do the following compounds migrate to the cathode or the anode on electrophoresis at the specified pH?

(a) histidine at pH = 6.8

(b) lysine at pH = 6.8

(c) glutamic acid at pH = 4.0

(d) glutamine at pH = 4.0

(e) Glu-Ile-Val at pH = 6.0

(f) Lys-Gln-Tyr at pH = 6.0

24.19 At what pH would you carry out an electrophoresis to separate the amino acids in each of the following mixtures?

(a) Ala, His, Lys

(b) Glu, Gln, Asp

(c) Lys, Leu, Tyr

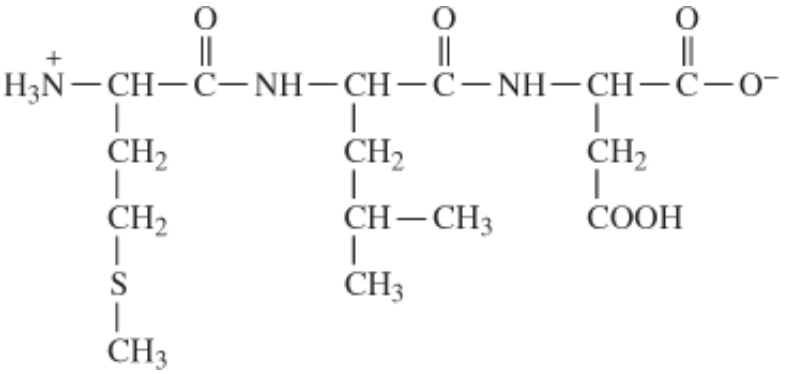
Peptides, Polypeptides and Proteins

24.20 What is the name of the bond that links amino acids in a polypeptide or protein?

24.21 How many carbon atoms always separate the nitrogen atoms in a protein or polypeptide?

24.22 Draw all of the structures possible for a tripeptide made from threonine, arginine and methionine.

24.23 Consider the following tripeptide.



(a) Use the three-letter abbreviations for amino acids to represent the tripeptide.

(b) Which amino acid is the *C*-terminal end and which is the *N*-terminal end?

Primary Structure of Polypeptides and Proteins

24.24 Based on your knowledge of the chemical properties of amino acid side chains, suggest a substitution for leucine in the primary structure of a protein that would probably not change the character of the protein very much.

24.25 If a protein contains four SH groups, how many different disulfides are possible if only a single disulfide bond is formed? How many arrangements of different disulfide bonds are possible if two disulfide bonds are formed?

24.26 How many different tetrapeptides can be made in each of the following cases.

(a) The tetrapeptide contains one unit each of Asp, Glu, Pro and Phe.

(b) All 20 amino acids can be used, but each only once.

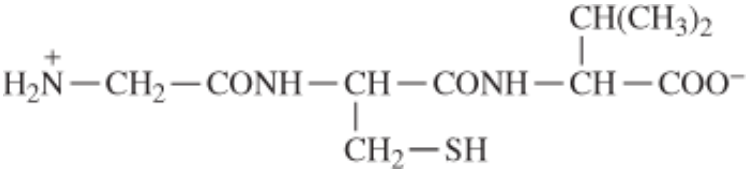
24.27 Draw a structural formula of each of the following tripeptides. Mark each peptide bond, the *N*-terminal amino acid and the *C*-terminal amino acid.

(a) Phe-Val-Asn

(b) Leu-Val-Gln

24.28 Estimate the pI of each tripeptide in question 24.27.

24.29 Consider the following tripeptide.



Which amino acids would be formed upon hydrolysis (digestion)?

Three-dimensional Shapes of Polypeptides and Proteins

24.30 Examine the α-helix conformation (p. 1070). Are amino acid side chains arranged all inside the helix, all outside the helix or randomly?

24.31 Distinguish between intermolecular and intramolecular hydrogen bonding between the backbone groups on polypeptide chains. In which type of secondary structure do you find intermolecular hydrogen bonds? In which type do you find intramolecular hydrogen bonding?

Denaturing Proteins

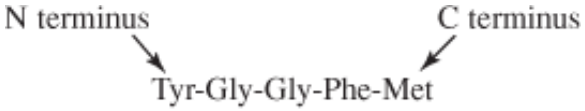
24.32 Enzymes are examples of proteins. Why do enzymes lose some of their activity at higher than physiological temperatures?

24.33 When an egg is boiled, the yolk changes colour and consistency but, when it is cooled to its original temperature, it does not regain its original nature. Explain.

24.34 It is essential to wear safety glasses in the laboratory. Explain why the eye must be protected from even minor amounts of acid or base.

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24.35 Methionine enkephalin is a pentapeptide that is produced by the body to control pain. From the sequence of its amino acid residues, draw a line structure of methionine enkephalin.



methionin enkephalin

24.36 The configuration of the stereocentre in α-amino acids is most commonly specified using the D,L convention. The configuration can also be identified using the *R*,*S* convention. Does the stereocentre in L-serine have the *R* or the *S* configuration?

24.37 Assign an *R* or *S* configuration to the stereocentre in each of the following amino acids.

(a) L-phenylalanine

(b) L-glutamic acid

(c) L-methionine

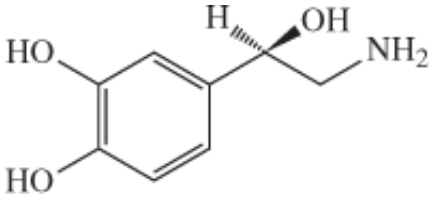
24.38 The amino acid threonine has two stereocentres. The stereoisomer found in proteins has the configuration (2*S*,3*R*) around the two stereocentres. Draw a Fischer projection of this stereoisomer and a three-dimensional representation.

24.39 Apart from threonine, which amino acid (or acids) contain more than one stereocentre?

24.40 Although only L-amino acids occur in proteins, D-amino acids are often a part of the metabolism of lower organisms. The antibiotic actinomycin D, for example, contains a unit of D-valine, and the antibiotic bacitracin A contains units of D-asparagine and D-glutamic acid. Draw Fischer projections and three-dimensional representations for these three D-amino acids.

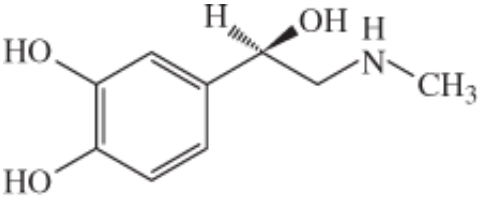
24.41 Both norepinephrine and epinephrine are synthesised from the same protein-derived amino acid.

(a)



norepinephrine
(noradrenaline)

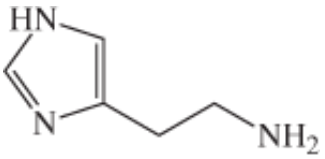
(b)



epinephrine
(adrenaline)

From which amino acid are the two compounds synthesised, and what types of reactions are involved in their biosynthesis?

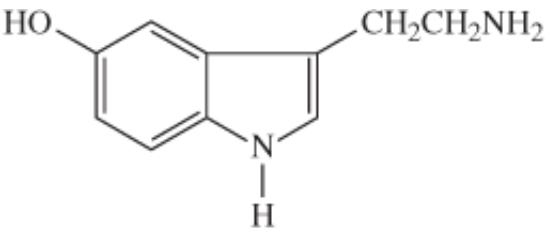
24.42 Histamine is synthesised from one of the 20 protein-derived amino acids. Suggest which amino acid is the biochemical precursor of histamine, and name the type of organic reaction(s) (e.g. oxidation, reduction, decarboxylation, nucleophilic substitution) involved in its conversion to histamine.



histamine

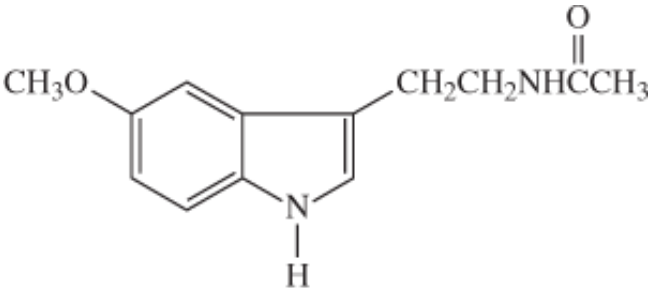
24.43 From which amino acid are serotonin and melatonin synthesised and what types of reactions are involved in their biosynthesis?

(a)



serotonin

(b)



melatonin

24.44 Enzymes are usually proteins and catalyse common organic reactions. Why are amino acids such as histidine, aspartic acid and serine more commonly found near the catalytic site of the enzyme but amino acids such as leucine and valine appear less often in these locations?

24.45 Why is histidine considered a basic amino acid when the pK_a value of the protonated form of its side chain is 6.1?

24.46 Account for the fact that the isoelectric point of glutamine (pI = 5.65) is higher than the isoelectric point of glutamic acid (pI = 3.08).

24.47 Enzyme-catalysed decarboxylation of glutamic acid gives 4-aminobutanoic acid. Estimate the pI of 4-aminobutanoic acid.

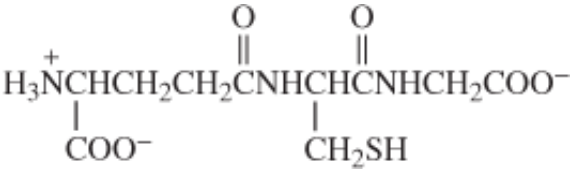
24.48 Guanidine and the guanidino group present in arginine are two of the strongest biochemical bases known. Account for their basicity.

24.49 At pH = 7.4, the pH of blood plasma, do the majority of protein-derived amino acids bear a net negative charge or a net positive charge?

24.50 Examine the amino acid sequence of human insulin (figure 24.14) and note how many Asp, Glu, His, Lys and Arg amino acids occur in this molecule. Do you expect human insulin to have an isoelectric point nearer that of the acidic amino acids (pI = 2.0 –3.0), the neutral amino acids (pI = 5.5– 6.5) or the basic amino acids (pI = 9.5 -11.0)?

24.51 Glutathione (GSH), one of the most common tripeptides in animals, plants and bacteria, is a scavenger of oxidising agents.

glutathione



In reacting with oxidising agents, glutathione is converted to GSSG.

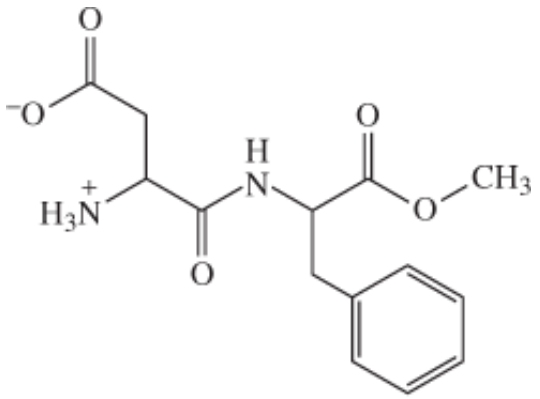
(a) Name the amino acids in this tripeptide.

(b) What is unusual about the peptide bond formed by the *N*-terminal amino acid?

(c) Is glutathione a biological oxidising agent or a biological reducing agent?

(d) Write a balanced equation for the reaction of glutathione with molecular oxygen, O_2, to form GSSG and H_2O. Is molecular oxygen oxidised or reduced in this reaction?

24.52 The following is the structural formula for the artificial sweetener aspartame.



aspartame

(a) Name the two amino acids in this molecule.

(b) Estimate the isoelectric point of aspartame.

(c) Draw structural formulae for the products of the hydrolysis of aspartame in 1 m HCl.

24.53 Proline is often described as an α-helix terminator; that is, it is usually in the random-coil secondary structure following an α-helical portion of a protein chain. Why does proline not fit easily into an α-helix structure?

24.54 Many plasma proteins found in an aqueous environment are globular in shape. Which of the following amino acid side chains would you expect to find on the surface of a globular protein, in contact with the aqueous environment, and which would you expect to find inside, shielded from the aqueous environment? Explain your answers.

(a) Leu

(b) Arg

(c) Ser

(d) Lys

(e) Phe

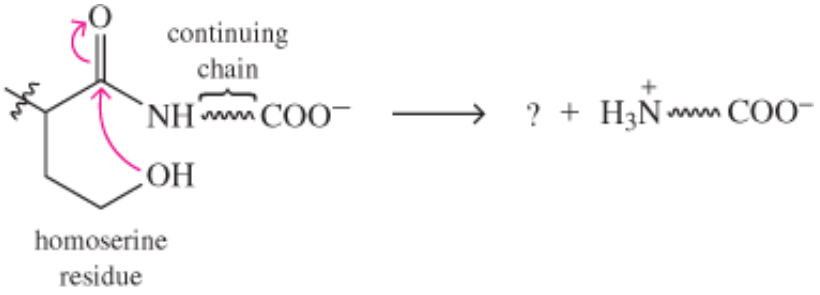
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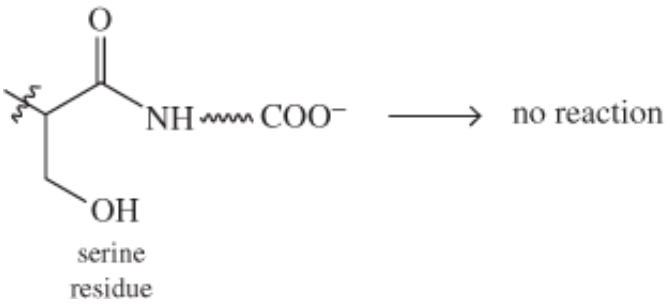
ADDITIONAL EXERCISES

24.55 Heating can disrupt the 3° structure of a protein. Explain the chemical processes that occur upon heating a protein.

24.56 Some amino acids cannot be incorporated into proteins because they are self-destructive. As shown on the right, homoserine, for example, can use its side-chain —OH group in an intramolecular, nucleophilic acyl substitution to cleave the peptide bond and form a cyclic structure on one end of the chain.

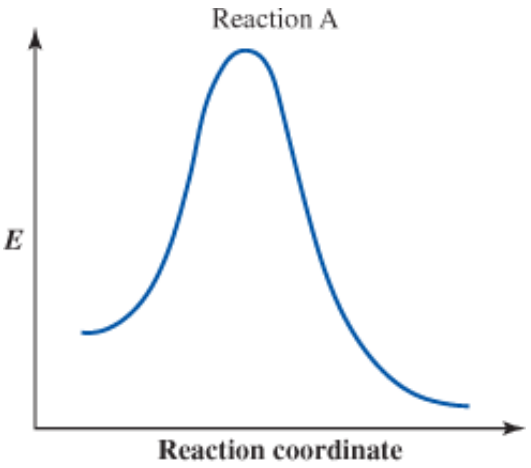
Draw the cyclic structure formed and explain why serine does not suffer the same fate, as shown on the right.

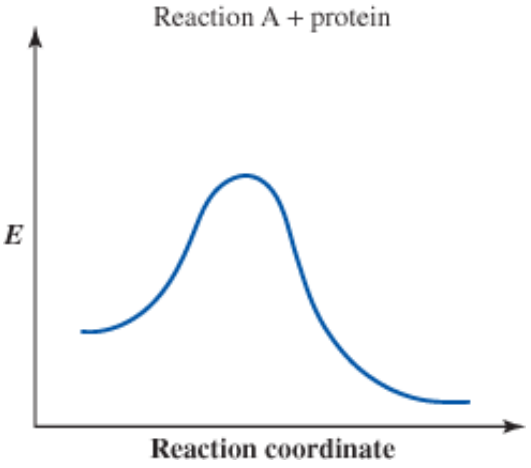




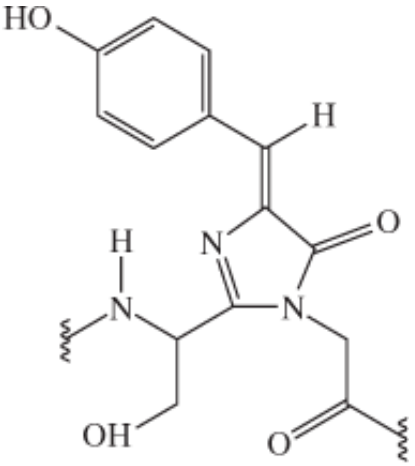
24.57 Would you expect a decapeptide of only isoleucine residues to form an α-helix? Explain.

24.58 Which type of protein would you expect to have the following effect?





24.59 Green fluorescent protein (GFP), first isolated from bioluminescent jellyfish, is a protein containing 238 amino acid residues. The discovery of GFP has revolutionised the field of fluorescence microscopy, which enables biochemists to monitor the biosynthesis of proteins. The 2008 Nobel Prize in chemistry was awarded to Martin Chalfie, Osamu Shimomura and Roger Tsien for the discovery and development of GFP. The structural subunit of GFP responsible for fluorescence, called the fluorophore, results when three amino acid residues undergo cyclisation. Identify the three amino acids that go into the biosynthesis of this fluorophore.



fluorophore

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KEY TERMS

α-amino acids
α-helix
β-pleated sheet
amino acid
C-terminal amino acid
denaturation
dipeptide
Disulfide bonds
Electrophoresis
hydrogen bonding
Hydrophobic interactions
integral membrane proteins
isoelectric point (pI)
N-terminal amino acid
oligopeptides
pentapeptides
Peptide
peptide bond
polymers
polypeptides
primary (1°) structure
Proteins
quaternary (4°) structure
salt linkages
Secondary (2°) structure
Tertiary (3°) structure
tetrapeptides
tripeptides
zwitterion

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CHAPTER

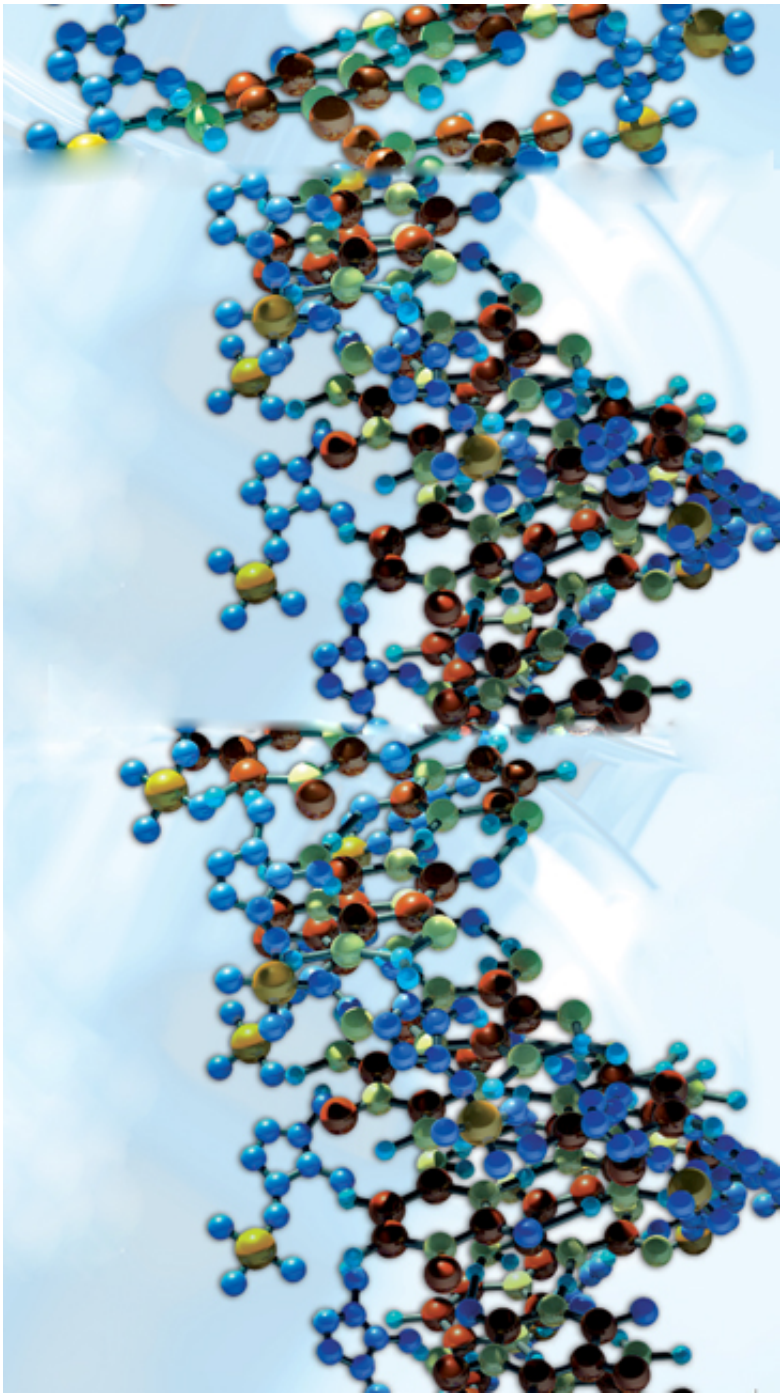
25 The Chemistry of DNA

Deoxyribonucleic acid (DNA) is an enormous molecule that stores our genetic information. This information makes us who we are and helps to determine many of our outward characteristics, such as eye, hair and skin colour, height and weight, to name but a few. Nature has chosen DNA as our genetic material as it is a relatively robust molecule and does not readily undergo undesirable chemical reactions. However, damage to the DNA molecule can occur under some circumstances, and this can lead to cancer. Skin cancer is the most common form of cancer in Australia and New Zealand. It is most often caused by the damaging effect of ultraviolet light in sunlight on DNA in the skin, which leads to mutations and cancerous cell growth (shown at right). The dark pigment melanin helps to protect human skin by absorbing ultraviolet light. Fairskinned people, such as those of Anglo-Celtic origin who make up the largest fraction of the Australian and New Zealand populations, do not develop much melanin in their skin and so are more at risk of sun damage. In fact, the incidence of skin cancer in New Zealand and Australia is the highest in the world; two in three New Zealanders and one in two Australians will develop a skin cancer at some time in their lives.

In this chapter, we will look at the DNA molecule (model shown at right) in detail to gain an understanding of its structure and function. We start by examining the structure of the building blocks of DNA and how these are covalently bonded together to form the molecule. Then we explore how genetic information is encoded by molecules of DNA, the function of the three types of ribonucleic acids and, finally, how the primary structure of a DNA molecule is determined.



James Stevenson/SPL



KEY TOPICS

25.1 Nucleosides and nucleotides

25.2 The structure of deoxyribonucleic acid (DNA)

25.3 Ribonucleic acid (RNA)

25.4 The genetic code

25.1 Nucleosides and Nucleotides

Genetic information is stored in molecules of **nucleic acid**: deoxyribonucleic acid (**DNA**) and ribonucleic acid (**RNA**). A cell's DNA encodes the information that determines the nature of the cell and controls its growth and division; it also contains instructions for the biosynthesis of enzymes and other proteins that are essential for the functioning of the cell. RNA is involved in the synthesis of proteins. Nucleic acids consist of three types of simpler building-block molecules:

1. aromatic molecules, consisting of one or two fused rings where some carbon atoms are replaced by nitrogen (such compounds are also called *heterocyclic*), which can act as bases (sections 19.6 and 19.7)
2. monosaccharides (pentoses), which are five-membered carbohydrates (section 22.2)
3. phosphate, as phosphate esters of the pentoses.

Figure 25.1 shows the five heterocyclic aromatic amine bases most common in nucleic acids. Uracil, cytosine and thymine are called pyrimidine bases after the parent base. Guanine and adenine are called purine bases. The bases, except for adenine, exist as an equilibrium of enol and amide tautomers (see section 21.6). Of these forms, the most stable is the cyclic amide. Such cyclic amides are called lactams. However, the enol tautomer (called a lactim) most clearly demonstrates the aromatic nature of the base. Pyrimidine and purine bases are aromatic in nature because they contain six π and ten π electrons, respectively (see p. 726), which satisfies the $(4n + 2)$ π electron Hückel rule.

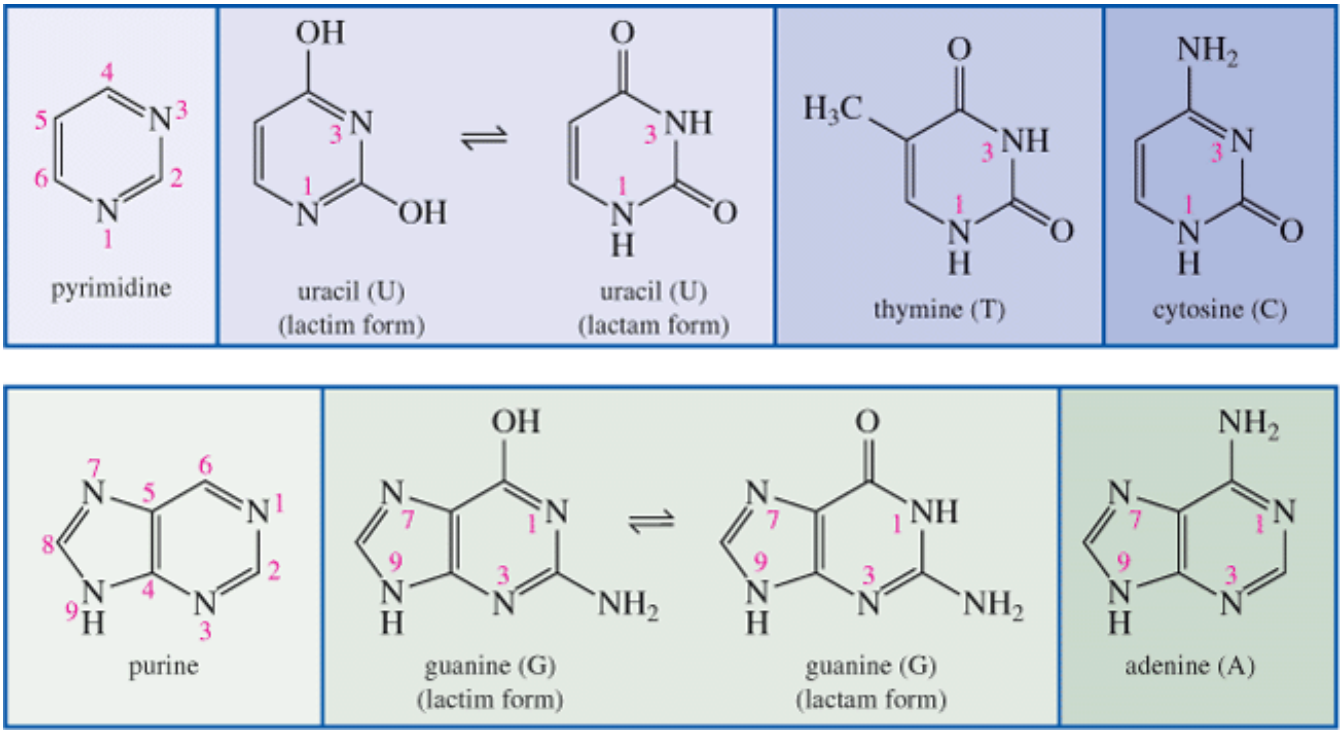


FIGURE 25.1 Names and one-letter abbreviations for the heterocyclic aromatic amine bases most common in DNA and RNA. Bases are numbered according to the patterns of pyrimidine and purine, the parent compounds. The tautomeric (lactim) enol forms of uracil and guanine are given to show their structural resemblance to the pyrimidine and purine parents, respectively.

A **nucleoside** is a compound containing a pentose, such as D-ribose and 2-deoxy-D-ribose, bonded to a purine or pyrimidine base by a β-*N*-glycosidic bond (section 22.4). The monosaccharide component of DNA is 2-deoxy-D-ribose (the '2-deoxy' refers to the absence of a hydroxyl group at the 2 position), and that of RNA is D-ribose. The glycosidic bond is between C(1′) (the anomeric carbon atom) of ribose or 2-deoxyribose and N(1) of a pyrimidine base or N(9) of a purine base. Figure 25.2a,b shows the structural formula of uridine, a nucleoside derived from ribose and uracil. Atom numbers on the monosaccharide rings are primed to distinguish them from atom numbers on the heterocyclic base. Figure 25.2c shows thymidine, which contains 2′-deoxyribose as the monosaccharide component.

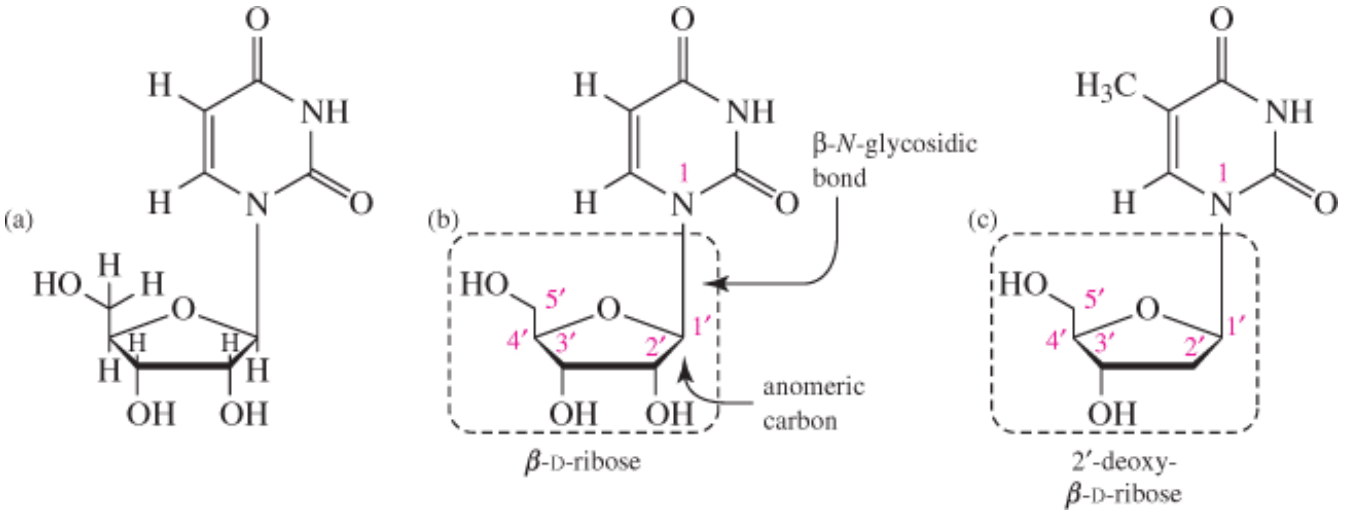


FIGURE 25.2 Uridine, a nucleoside

(a) drawn showing all hydrogen atoms.

(b) For convenience, the hydrogen atoms of C—H bonds are usually omitted. Atom numbers on the monosaccharide rings are primed to distinguish them from atom numbers on the heterocyclic base.

(c) Thymidine possesses 2′-deoxyribose as the monosaccharide component.

The names of the nucleosides, which correspond to each of the bases, are compiled in table 25.1.

TABLE 25.1 Nomenclature of nucleosidesq

Base	Name of nucleoside
uracil	uridine
thymine	thymidine
cytosine	cytidine
guanine	guanosine
adenine	adenosine

A **nucleotide** is a nucleoside in which a molecule of phosphoric acid is esterified with a free hydroxyl group of the monosaccharide at the 3′ or the 5′ hydroxyl group. A nucleotide is named by giving the name of the parent nucleoside, followed by the word ‘monophosphate’. The position of the phosphoric ester is specified by the number of the carbon atom to which it is bonded. Figure 25.3 shows the structural formulae of adenosine 5′-monophosphate, 2′-deoxyadenosine 5′-monophosphate and 2-deoxyadenosine 3′-monophosphate. Monophosphoric esters are diprotic acids with pK_a values of approximately 1 and 6 (see section 11.4). Therefore, at a pH of 7, the phosphoric monoester is ionised, giving the nucleotide a charge of 2-.

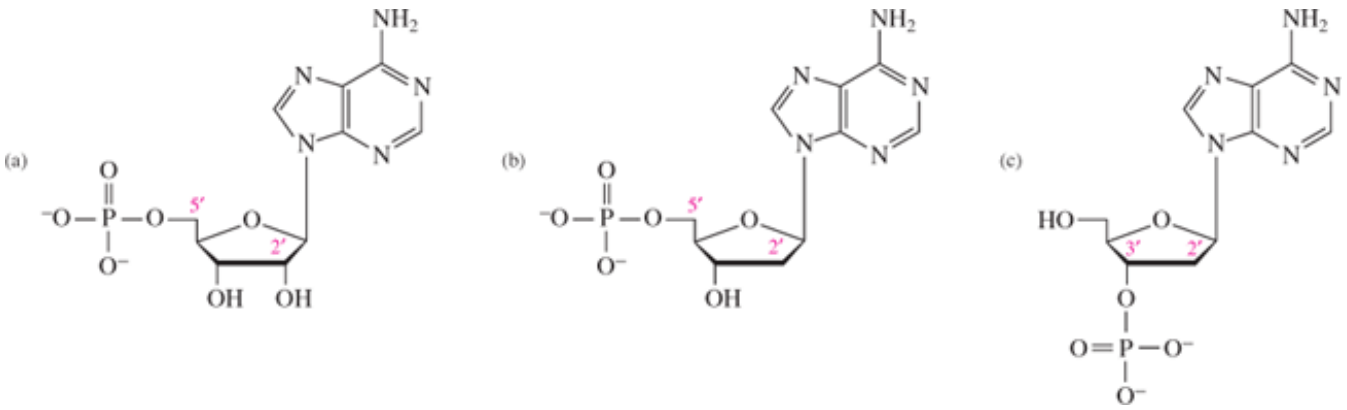


FIGURE 25.3 The nucleotides
(a) adenosine 5′-monophosphate,
(b) 2′-deoxyadenosine 5′-monophosphate and
(c) 2-deoxyadenosine 3′-monophosphate. The phosphate group is ionised at pH 7.0, giving these nucleotides a charge of 2-.

Nucleoside monophosphates can be further phosphorylated to form nucleoside diphosphates and nucleoside triphosphates. Figure 25.4 shows the structural formula of adenosine 5′-triphosphate (ATP). ATP is a phosphorylating agent (that is, it donates phosphate to other molecules) in many biochemical processes, where it acts as an energy source.

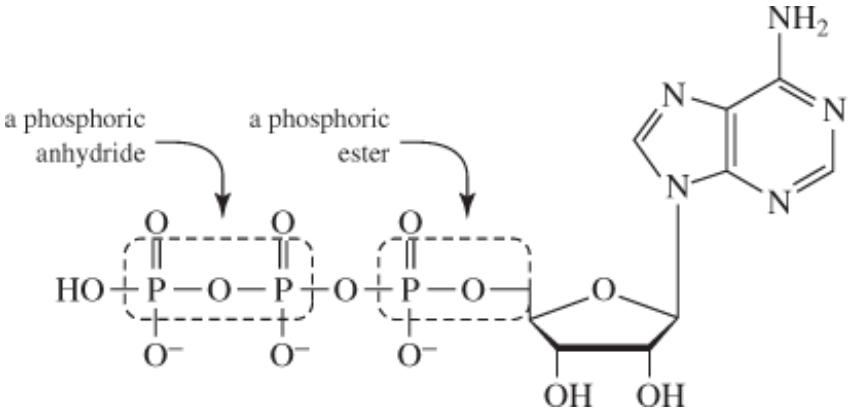


FIGURE 25.4 Adenosine triphosphate (ATP^{3-}).

Nucleoside diphosphates and triphosphates are also polyprotic acids and are extensively ionised at pH 7.0. The values of pK_a for the first three ionisation steps for adenosine triphosphate are less than 5.0. The value of pK_{a4} is approximately 7.0. Therefore, at pH 7.0, approximately 50% of adenosine triphosphate is present as ATP^{4-} and 50% is present as ATP^{3-}.

WORKED EXAMPLE 25.1

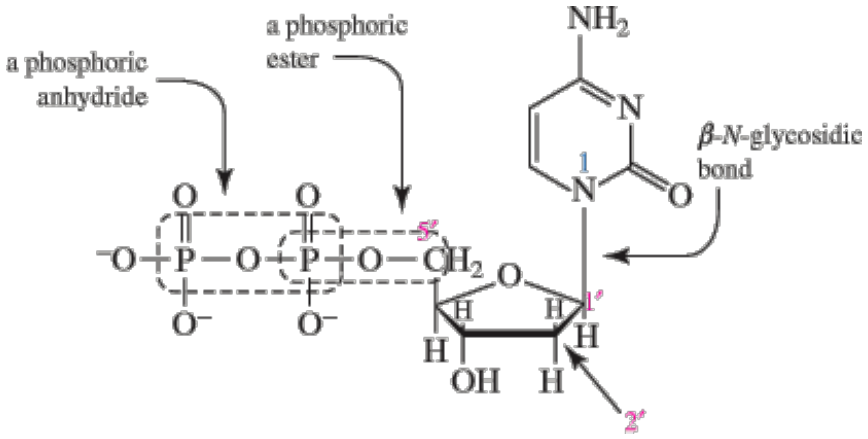
Drawing Structural Formulae for Nucleotides

Draw the structural formula for 2′-deoxycytidine 5′-diphosphate in its tri-anionic form (charge = 3-).

Analysis

Cytidine is formed by a β-*N*-glycosidic bond between N(1) of cytosine and C(1′) of the cyclic hemiacetal form of 2-deoxy-D-ribose. The 5′ hydroxyl of the pentose is bonded to a phosphate group by an ester bond, and this phosphate is in turn bonded to a second phosphate group by an anhydride bond.

Solution



PRACTICE EXERCISE 25.1

Draw the structural formula of 2′-deoxythymidine 3′-monophosphate in its di-anionic form.

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25.2 The Structure of Deoxyribonucleic Acid (DNA)

In chapter 24, we saw that the four levels of structural complexity in polypeptides and proteins are primary, secondary, tertiary and quaternary. There are three levels of structural complexity in nucleic acids, and, although these levels are somewhat comparable to those in polypeptides and proteins, they also differ in significant ways.

Primary Structure: the Covalent Backbone

Deoxyribonucleic acids consist of a backbone of alternating units of 2′-deoxyribose and phosphate in which the 3′-hydroxyl of one deoxyribose unit is joined by a phosphodiester bond to the 5′-hydroxyl of another deoxyribose unit (figure 25.5). A purine or pyrimidine base — adenine, guanine, thymine or cytosine — is bonded to each 2′-deoxyribose unit by a β-*N*-glycosidic bond. The **primary structure** of a DNA molecule is the order of heterocyclic bases along the 2′-deoxyribose-phosphodiester backbone. The **5′ end** is the end of a poly-nucleotide at which the 5′ —OH group of the terminal 2′-deoxyribose is free. The **3′ end** of the polynucleotide is the end at which the 3′ —OH group of the terminal 2′-deoxyribose is free. By convention, the sequence of bases is read from the 5′ end to the 3′ end. For example, in figure 25.5, the sequence is, therefore, TCAG.

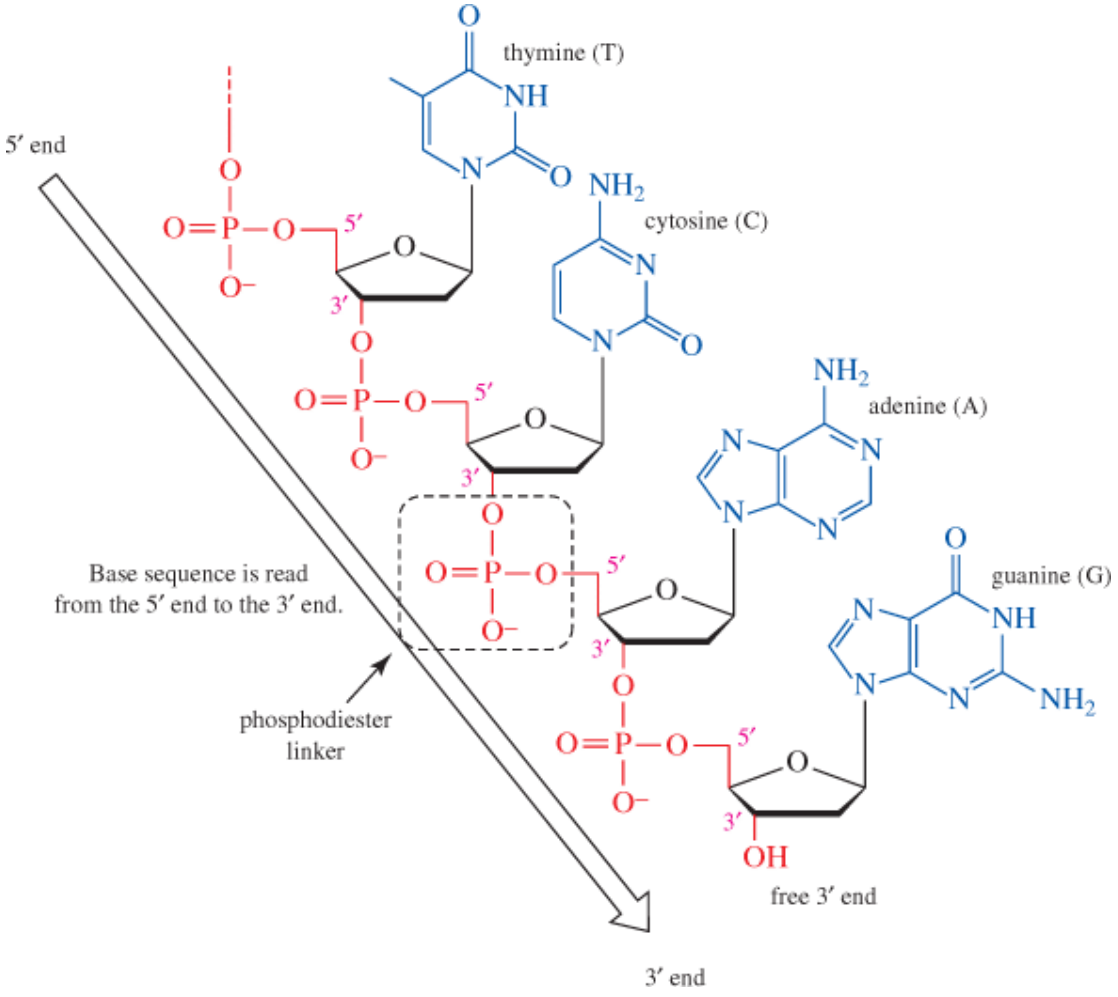


FIGURE 25.5 A tetranucleotide section, TCAG, of a single-stranded DNA showing the phosphate backbone (red), deoxyribose units (black) and nucleobases (blue). The end of the polynucleotide has a ribose unit with a free —OH group at either the 3′ or 5′ position. This example shows a section with a free 3′ end.

WORKED EXAMPLE 25.2

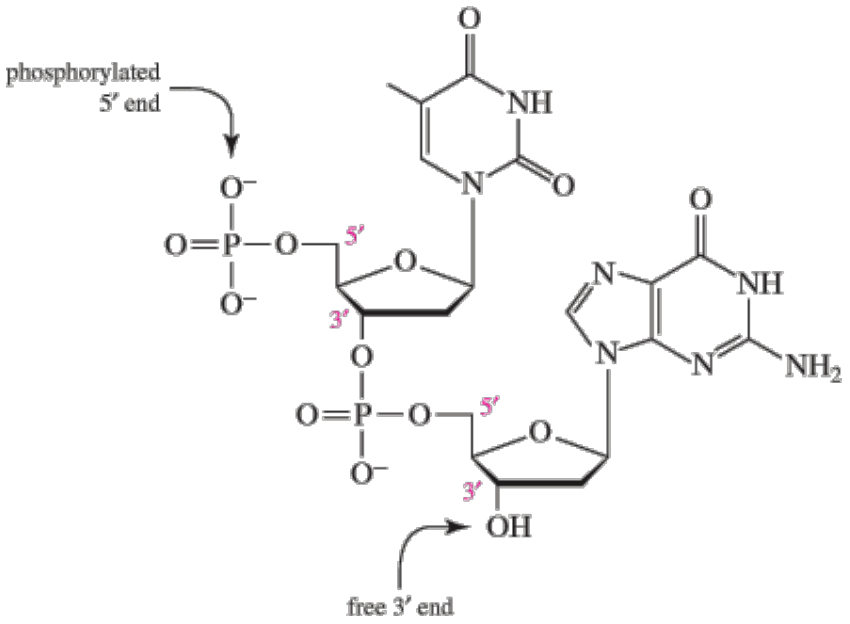
Drawing Structural Formulae for Sections of DNA

Draw the structural formula of the DNA dinucleotide TG that is phosphorylated at the 5′ end only.

Analysis

Since the sequence of bases is always read from the 5′ end to the 3′ end, a thymidine is connected via a phosphodiester bond to guanosine at the 5′ end of the latter. The 3′ end of the guanosine has a free —OH group.

Solution



PRACTICE EXERCISE 25.2

Draw the structural formula for a section of DNA that contains the base sequence CTG and is phosphorylated at the 3′ end only.

Secondary Structure: the Double Helix

By the early 1950s, it was clear that DNA molecules consist of chains of alternating units of deoxyribose and phosphate joined by 3′,5′-phosphodiester bonds, with a base attached to each 2′-deoxyribose unit by a β-*N*-glycosidic bond. In 1953, the American biologist James D Watson and the British physicist Francis HC Crick proposed a double-helix model for the **secondary structure** of DNA.

The Watson–Crick model (see figure 25.6) was based on molecular modelling and two lines of experimental observations: chemical analyses of DNA base compositions and mathematical analyses of X-ray diffraction patterns of crystals of DNA. Watson, Crick and the New Zealand-born Maurice Wilkins shared the 1962 Nobel Prize in physiology or medicine for ‘their discoveries concerning the molecular structure of nucleic acids, and its significance for information transfer in living material’. Although Rosalind Franklin (figure 25.7) also took part in this research, her name was omitted from the Nobel list because of her death in 1958 at the age of 37. The Nobel Foundation does not make awards posthumously.

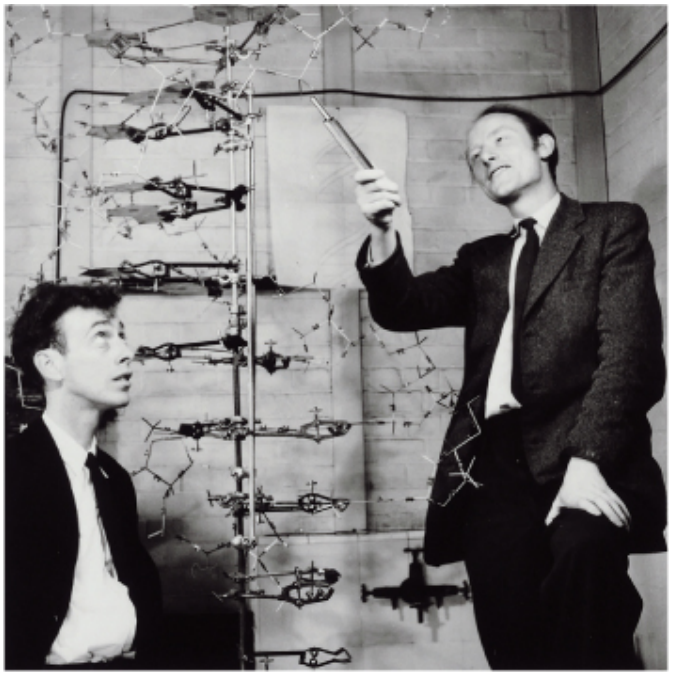


FIGURE 25.6 James Watson and Francis Crick with their DNA model. SPL/A Barrington



FIGURE 25.7 Rosalind Franklin (1920 -1958): In 1951, she joined the Biophysical Laboratory at King's College, London, where she began her work on the application of X-ray diffraction methods to the study of DNA. She is credited with discoveries that established the density of DNA, its helical conformation and other significant aspects. Her work was thus important to the model of DNA developed by Watson and Crick. She died of ovarian cancer in 1958 at the age of 37 and, because a Nobel Prize is never awarded posthumously, she did not share the 1962 Nobel Prize in physiology or medicine with Watson, Crick and Wilkins. Although the relation between Watson, Crick and Franklin was initially strained, Watson later said that 'we later came to appreciate … the struggles the intelligent woman faces to be accepted by the scientific world which often regards women as mere diversions from serious thinking'. Photo Researchers/Inc-Photo

Base Composition

At one time, it was thought that the four principal bases occurred in the same ratios in all organisms and was repeated in a regular pattern along the 2′-deoxyribose-phosphodiester backbone of DNA. However, more precise determinations of their composition by Erwin Chargaff revealed that the bases do not occur in the same ratios (table 25.2).

TABLE 25.2 Comparison of DNA from several organisms — base composition, in mole percent

	Purines		Pyrimidines				
Organism	A	G	C	T	A/T[(a)]	G/C[(b)]	Purines/pyrimidines[(c)]
human	30.9	19.8	19.9	29.4	1.05	0.99	1.03
sheep	29.3	21.4	21.0	28.3	1.04	1.02	1.03
yeast	31.3	17.1	18.7	32.9	0.95	0.91	0.94
E. coli	24.7	25.7	26.0	23.6	1.05	0.99	1.02

(a) Ratio of mole percentages of adenine and thiamine
(b) Ratio of mole percentages of guanine and cytosine
(c) Ratio of mole percentages of purines and pyrimidines

Researchers used the data in table 25.2 and related data to conclude (Chargaff's rules) that, within experimental error:

1. The mole-percent base composition of DNA in any organism is the same in all cells of the organism and is characteristic of the organism.
2. The mole percentages of adenine (a purine base) and thymine (a pyrimidine base) are equal. The mole percentages of guanine (a purine base) and cytosine (a pyrimidine base) are also equal.
3. The mole percentages of purine bases (A + G) and pyrimidine bases (C + T) are equal and have a 1 : 1 ratio.

Analyses of X-ray Diffraction Patterns

Fundamental information about the structure of DNA emerged when X-ray diffraction photographs (see section 7.5) taken by Rosalind Franklin were analysed. The diffraction patterns revealed that, even though the base composition of DNA isolated from different organisms varies, DNA molecules themselves are remarkably uniform in thickness. They are long and fairly straight, with an outside diameter of approximately 2.0 nm and not more than 12 atoms thick. Further-more, the crystallographic pattern repeats every 3.4 nm. This presented one of the chief problems to be solved: How could the molecular dimensions of DNA be so regular, even though the relative percentages of the various bases differ so widely? With this accumulated information, the stage was set for the development of a hypothesis about DNA structure.

The Watson–Crick Double Helix

The heart of the Watson–Crick model is the postulate that a molecule of DNA is a *complementary* **double helix** consisting of two antiparallel polynucleotide strands coiled in a right-handed manner around the same axis. As illustrated in the ribbon models in figure 25.8, chirality is associated with a double helix like enantiomers (see chapter 17); left-handed and right-handed double helices are related by reflection.



FIGURE 25.8 A DNA double helix has an associated chirality. Right-handed and left-handed double helices of otherwise identical DNA chains are nonsuperimposable mirror images.

To account for the observed base ratios and uniform thickness of DNA, Watson and Crick postulated that purine and pyrimidine bases project inwards to the axis of the helix and always pair in a specific manner. According to scale models, the dimensions of an adenine–thymine base pair are almost identical to the dimensions of a guanine–cytosine base pair, and the length of each pair is consistent with the core thickness of a DNA strand (figure 25.9). Thus, if the purine base in one strand is adenine, its complement in the antiparallel strand must be thymine. Similarly, if the purine in one strand is guanine, its complement in the antiparallel strand must be cytosine. In other words, if the sequence of one strand is known, the sequence of the other strand can be inferred. The base pairs are held together by hydrogen bonds (see section 6.8) between a lone pair of electrons on a carbonyl oxygen atom or an imine nitrogen atom in one base and a proton of an amino group in the other base.

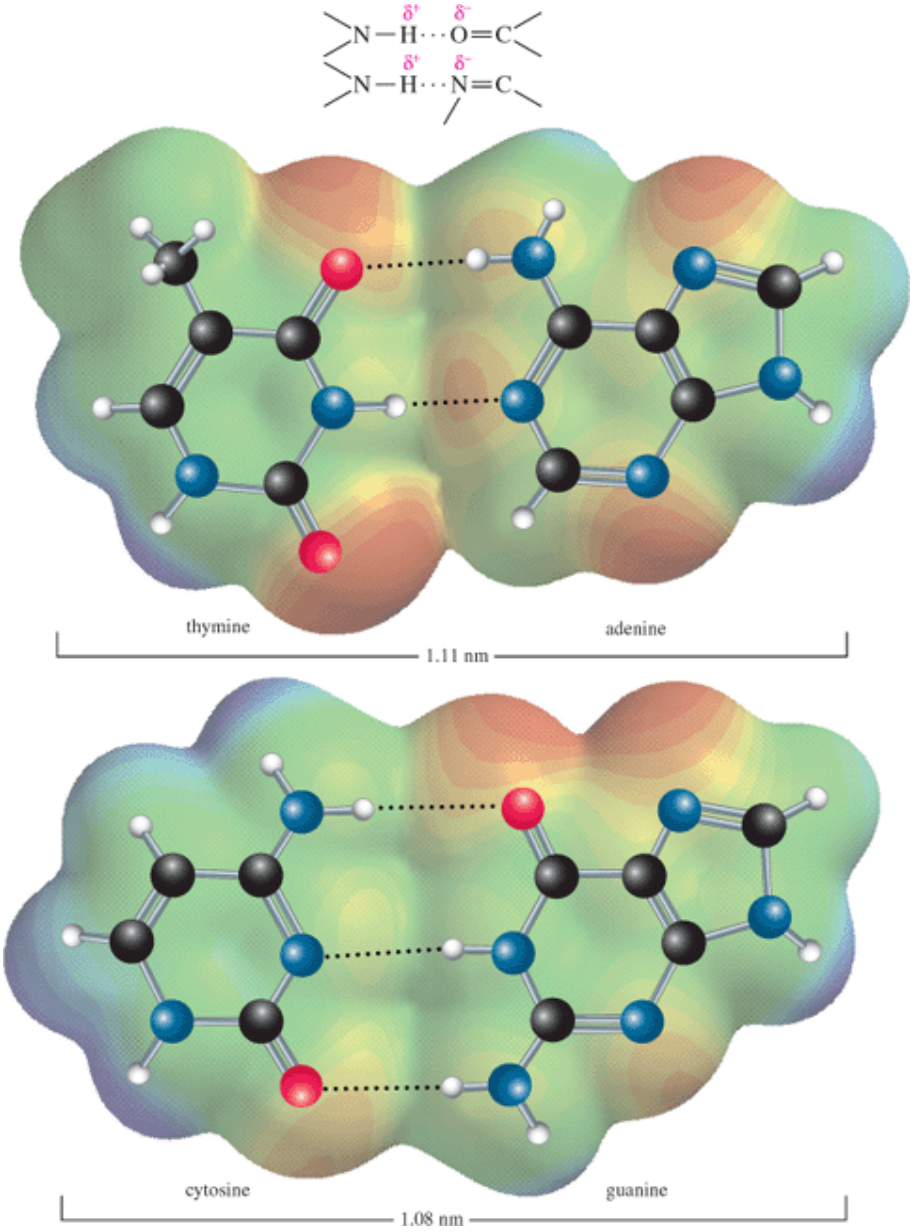


FIGURE 25.9 Base pairing between the complementary bases adenine and thymine (A–T) and between the complementary bases guanine and cytosine (G–C). An A–T base pair is held by two hydrogen bonds, whereas a G–C base pair is held by three hydrogen bonds.

A significant feature of Watson and Crick's model is that no other base pairing is consistent with the observed thickness of a DNA molecule. A pair of pyrimidine bases is too small to account for the observed thickness, whereas a pair of purine bases is too large. Thus, according to the Watson–Crick model, the repeating units in a double-stranded DNA molecule are not single bases of differing dimensions, but rather base pairs of almost identical dimensions.

To account for the periodicity observed from X-ray data, Watson and Crick postulated that base pairs are stacked one on top of the other, with a distance of 0.34 nm between base pairs and with 10 base pairs in one complete turn of the helix. Thus, there is one complete turn of the helix every 3.4 nm. Figure 25.10 shows a ribbon model of double-stranded **B-DNA**, the predominant form of DNA in dilute aqueous solution and thought to be the most common form in nature.

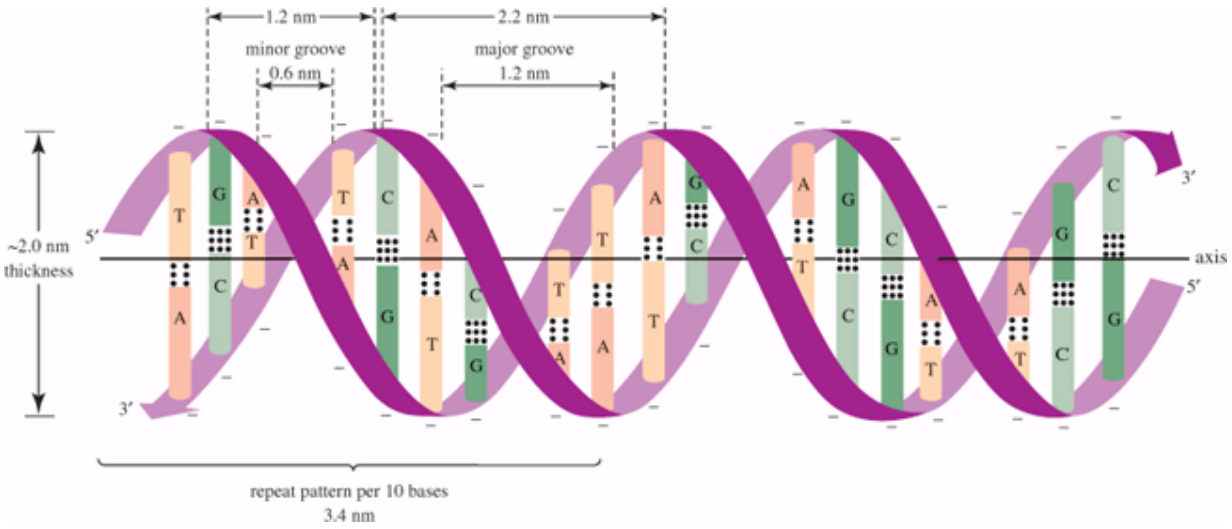


FIGURE 25.10 Ribbon model of double-stranded B-DNA. Each ribbon shows the 2′-deoxyribose-phosphodiester backbone of a single-stranded DNA molecule. The strands are antiparallel, one running to the left from the 5′ end to the 3′ end, the other running to the right from the 5′ end to the 3′ end. Hydrogen bonds are shown by three dotted lines between each G–C base pair and two dotted lines between each A–T base pair.

In the double helix, the bases in each base pair are not directly opposite each other across the diameter of the helix, but rather are slightly displaced. This displacement and the relative orientation of the glycosidic bonds linking each base to the sugar–phosphate backbone lead to two different sized grooves: a major groove and a minor groove (figure 25.10). Each groove runs along the length of the cylindrical column of the double helix. The major groove is approximately 1.2 nm wide and the minor groove approximately 0.6 nm wide with both having intermediate depth.

Figure 25.11b shows more detail of a B-DNA double helix, especially the major and minor grooves.

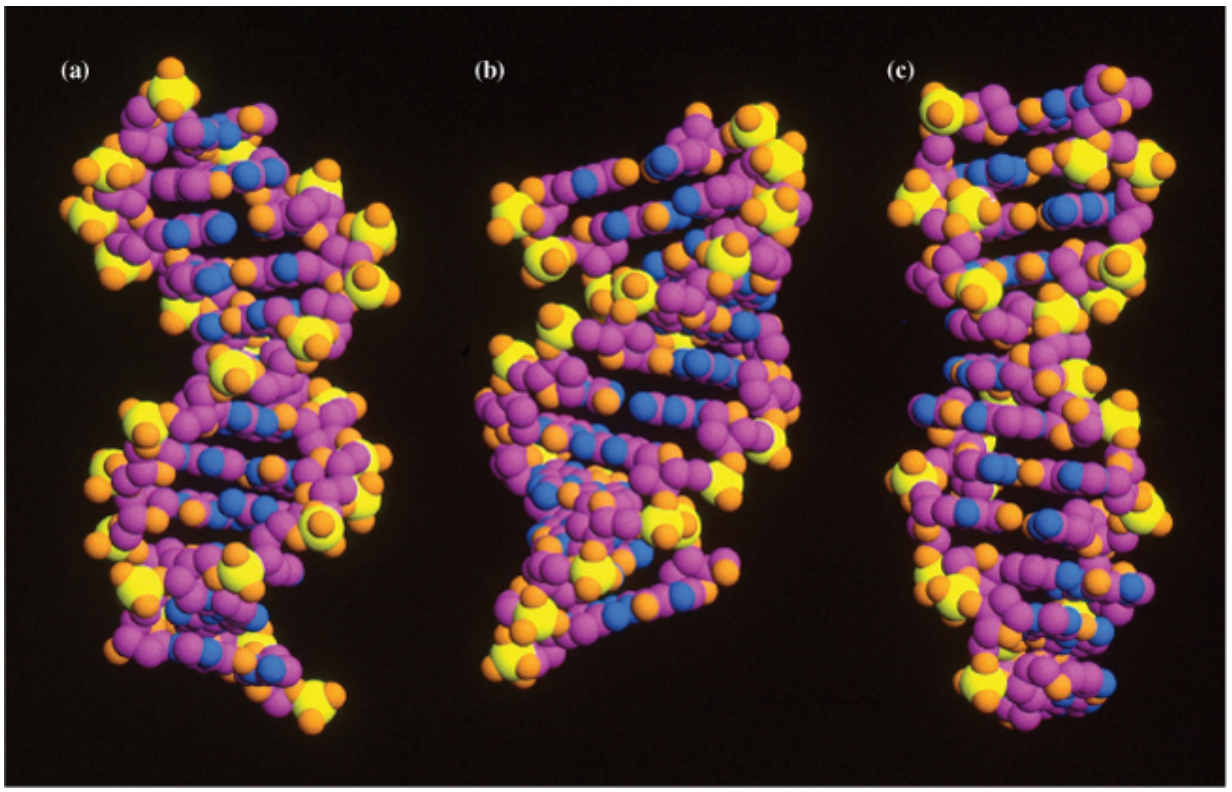


FIGURE 25.11 Computergenerated models of
(a) A-DNA,
(b) B-DNA and
(c) Z-DNA. All hydrogen atoms have been omitted for clarity.
Kenneth Eward

Other forms of secondary structure are known that differ in the distance between stacked base pairs and in the number of base pairs per turn of the helix.

WORKED EXAMPLE 25.3

Complementary DNA Base Sequence

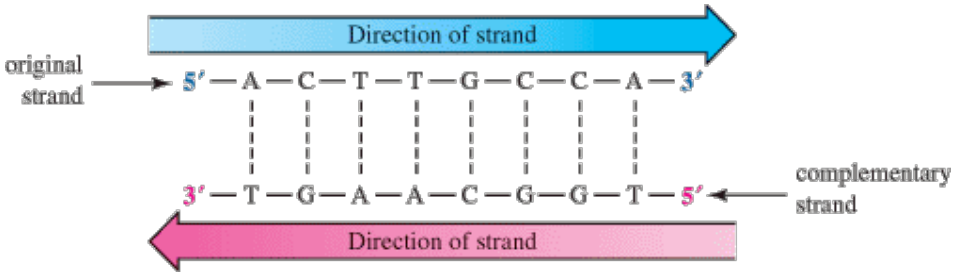
One strand of a DNA molecule contains the base sequence 5′-ACTTGCCA-3′. Write its complementary base sequence.

Analysis

Remember that a base sequence is always written from the 5′ end of the strand to the 3′ end, that A pairs with T, and that G pairs with C.

Solution

In double-stranded DNA, the two strands run in opposite (antiparallel) directions, so that the 5′ end of one strand is associated with the 3′ end of the other strand:



Written from the 5′ end, the complementary strand is 5′-TGGCAAGT-3′.

PRACTICE EXERCISE 25.3

Write the complementary DNA base sequence for 5′-CCGTACGA-3′.

Another of the most common secondary structures of DNA is **A-DNA** (figure 25.11a), which forms under conditions of high salt concentration and minimal water and is also a right-handed helix. A-DNA has a larger diameter than B-DNA (2.6 nm) and has 11 base pairs per turn, which is 2.5 nm long. The base pairs are displaced around the helix axis, unlike B-DNA where the base pairs are centred around the helix axis. The major groove in A-DNA is extremely narrow and very deep, whereas the minor groove is shallow and wide.

Z-DNA (figure 25.11c) is a conformation variation, which has a left-handed double helix. Compared with B-DNA, Z-DNA is smaller in diameter (1.8 nm) and longer (4.6 nm per turn and each turn has 12 base pairs). The major groove is flattened out on the helix surface, and the minor groove is very deep and narrow. Z-DNA has no definite biological significance. However, it is assumed that temporary formation of Z-DNA during DNA transcription could provide torsional strain relief.

Tertiary Structure: Supercoiled DNA

The length of a DNA molecule is considerably greater than its diameter, and the extended molecule is quite flexible. A DNA molecule is said to be relaxed if it has no twists other than those imposed by its secondary structure. Put another way, relaxed DNA does not have a clearly defined tertiary structure. However, DNA can exhibit two types of **tertiary structure**: one induced by perturbations in circular DNA, the other introduced by the coordination of linear DNA with nuclear proteins called histones. The formation of tertiary structure of nucleic acids, whatever the type, is called **supercoiling**.

Supercoiling of Circular DNA

Circular DNA is a type of double-stranded DNA in which the 5′ and 3′ ends of each strand are joined by phosphodiester bonds (figure 25.12a). This type of DNA, which is the most prominent form in bacteria and viruses, is also referred to as *circular duplex* (because it is double-stranded) *x* DNA. One strand of circular DNA may be opened, partially unwound and then rejoined. The unwound section introduces a strain into the molecule because the nonhelical gap is less stable than hydrogen-bonded, base-paired helical sections. The strain can be localised in the nonhelical gap. Alternatively, the strain may be spread uniformly over the entire circular DNA by the introduction of **superhelical twists**, one twist for each turn of a helix unwound (supercoiled circular DNA). The circular DNA shown in figure 25.12b has been unwound by four complete turns of the helix. The strain introduced by this unwinding is spread uniformly over the entire molecule by the introduction of four superhelical twists (figure 25.12c). Interconversion of relaxed and supercoiled DNA is catalysed by groups of enzymes called topoisomerases and gyrases.

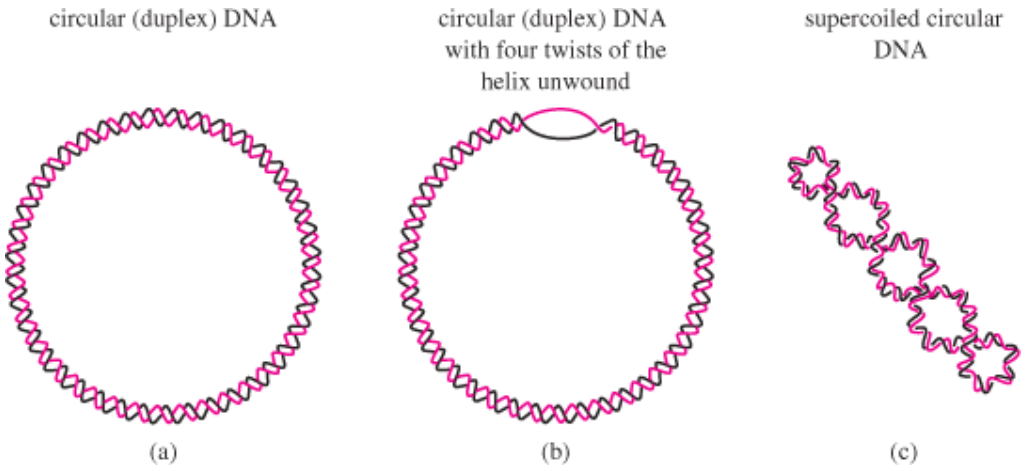


FIGURE 25.12 Relaxed and supercoiled DNA:

(a) Circular DNA is relaxed.

(b) One strand is broken, unwound by four turns and the ends then rejoined. The strain of unwinding is localised in the nonhelical gap.

(c) Supercoiling by four twists distributes the strain of unwinding uniformly over the entire molecule of circular DNA.

Supercoiling of Linear DNA

Chromatin is a combination of DNA and proteins that make up chromosomes. Chromatin contains all of the DNA of the nucleus in animal or plant cells and represents a type of supercoiling of linear DNA. The fundamental structural unit of chromatin is the **nucleosome**, an assembly consisting of a group of certain proteins, called **histones** (designated H1, H2A, H2B, H3 and H4, see figure 25.13a), wrapped in DNA (figure 25.13b). Histones are particularly rich in the basic amino acids lysine and arginine, and, at physiological pH, have an abundance of positively charged sites along their length. In a nucleosome, B-DNA is wound around the histone unit by about 1.8 coils (figure 25.13b,25.13c). This arrangement is held together through electrostatic forces between the negatively charged phosphate backbone of the DNA and the positive charges in the histone proteins. The nucleosomes are further folded to form a filament, with a diameter of ~30 nm, which has been proposed to have the structure shown in figure 25.13d.

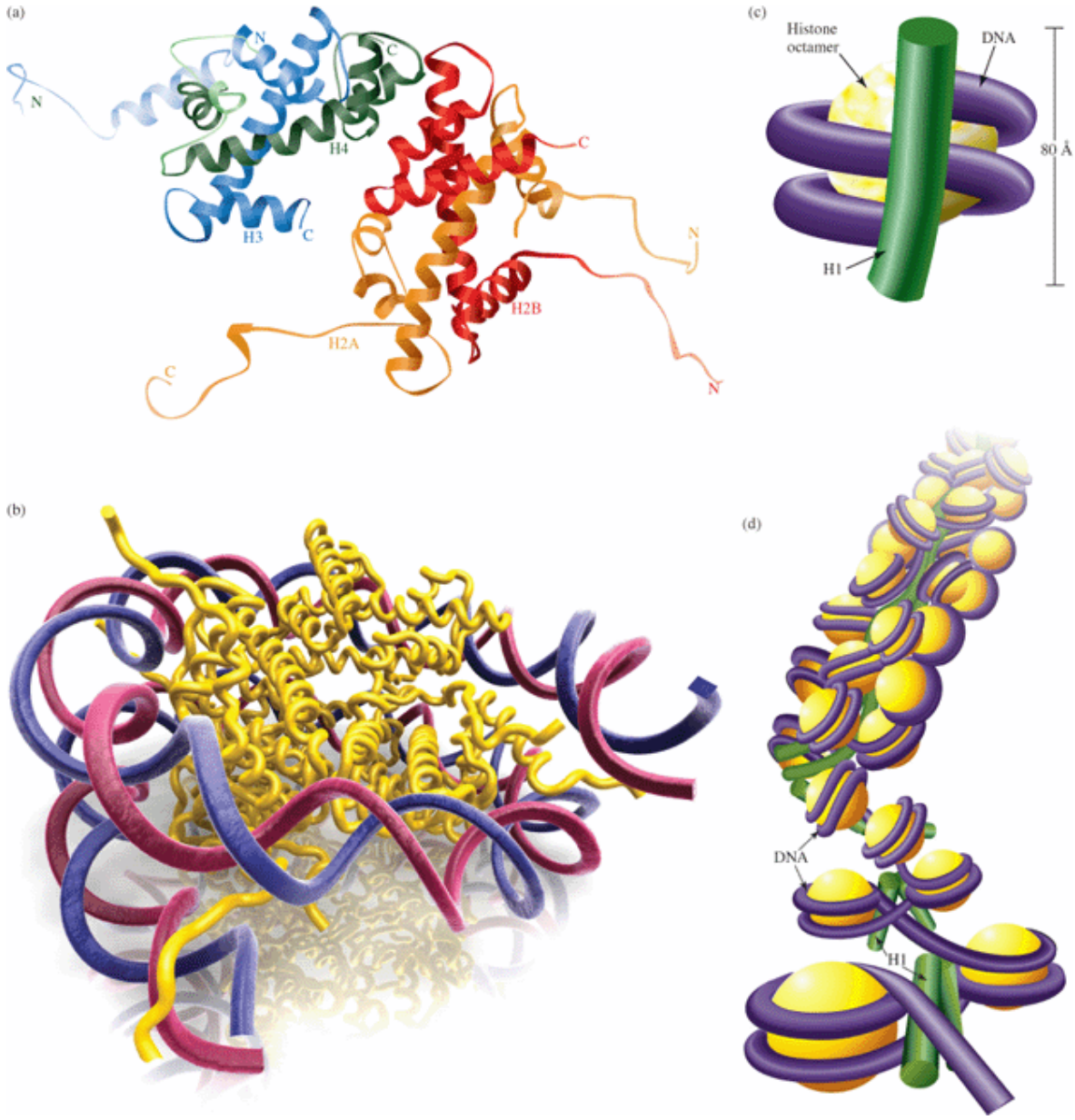
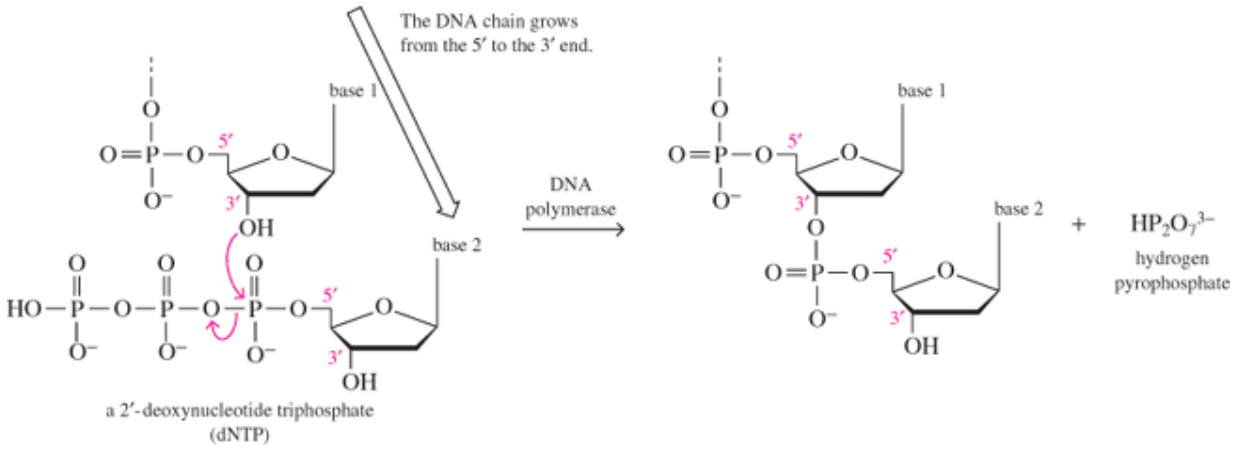


FIGURE 25.13 Chromatin fibres consist of
(a) histones
(b) wrapped in DNA to form
(c) nucleosomes, which are
(d) grouped to resemble beads on a thread (C = C-terminal and N = N-terminal end of the protein; H = histone).

DNA supercoiling is important for packaging DNA within cells. DNA is a very long molecule, and supercoiling reduces space.

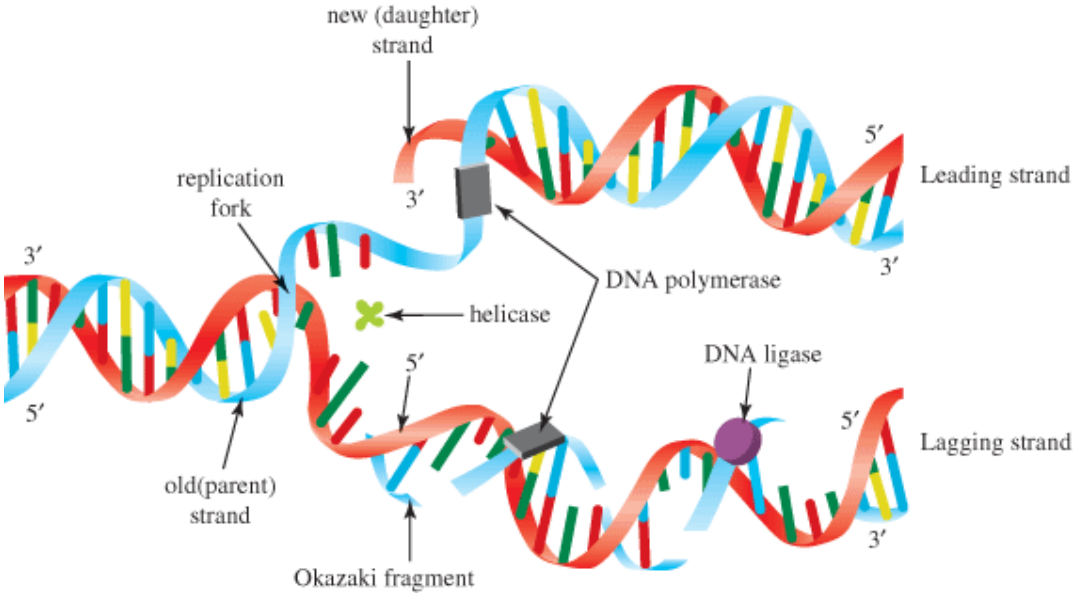
DNA Replication

Replication of DNA occurs when cells divide. The replication is catalysed by enzymes called **DNA polymerase**, which use single-stranded DNA as templates for the synthesis of the complementary strand from the appropriate 2′-deoxyribonucleoside triphosphate. Nearly all known DNA polymerases can add a nucleotide only at the free 3′-hydroxyl group, so DNA chains are extended in the 5′ → 3′ direction.



DNA replicates by the progressive separation of the duplex strands, which is accompanied by synthesis of the respective complimentary strands. Helicases are enzymes that break the hydrogen bonds to form a structure known as the **replication fork**. The two prongs are called the leading strand and the lagging strand. The leading strand is the template where the replication fork moves along in the 3′ → 5′ direction so that the complementary strand can be continuously synthesised by DNA polymerase in the 5′ → 3′ direction.

In contrast to this, the lagging strand is oriented in the 5′ → 3′ direction. Since this is opposite to the orientation of DNA polymerase, replication of the lagging strand is more complicated. It was found that the complementary strand is also synthesised in the 5′ → 3′ direction, but discontinuously in small fractions (the so-called **Okazaki fragments**), which are subsequently covalently joined by the enzyme **DNA ligase**. This synthesis is initiated by the enzyme **primase**, which reads the DNA and adds RNA in short segments. DNA polymerase uses this primer to synthesise the Okazaki fragments, from which the RNA moieties are subsequently removed and replaced by DNA nucleotides before ligation fuses the fragments together.



Chemistry Research

Protein Recognition

Associate Professor Jacqueline Anne Wilce, Monash University

Proteins are employed to carry out an enormous range of tasks in our cells. These include proteins on the surface of cells to receive extracellular signals, structural proteins that give our cells shape, enzymes that catalyse reactions and proteins that regulate the activities of oligonucleotides. As we saw in chapter 24, these proteins carry out their individual roles due to their unique three-dimensional structure. Their surface shape and its chemistry allow them to recognise a binding partner and bind through non-covalent interactions.

In order to understand how a protein structure recognises its binding partner, we can use a number of

spectroscopic tools, including X-ray crystallography (see chapter 7) and nuclear magnetic resonance (NMR) spectroscopy (see chapter 20). Associate Professor Jacqueline Wilce is interested in the molecular basis of protein interactions with binding partners. She is an NMR spectroscopist and Professor Matthew Wilce, with whom she runs her laboratory, is an expert in X-ray crystallography. These techniques complement one another to give highly detailed information about the chemistry of molecular recognition.

The replication terminator protein (RTP) of *Bacillus subtilis* plays an important role in coordinating the replication of the bacterial chromosome. It is a dimeric protein that binds with exceptionally high affinity to duplex DNA at specific nucleotide sequences forming a termination complex that prevents further DNA replication. Exactly how RTP recognises the DNA to form a termination complex has been studied using a combination of X-ray crystallography and NMR spectroscopy. After growing crystals of highly purified RTP combined with a short stretch of duplex DNA, the X-ray diffraction pattern can be used to obtain a detailed picture of the atoms involved in the RTP/DNA complex (figure 25.14).

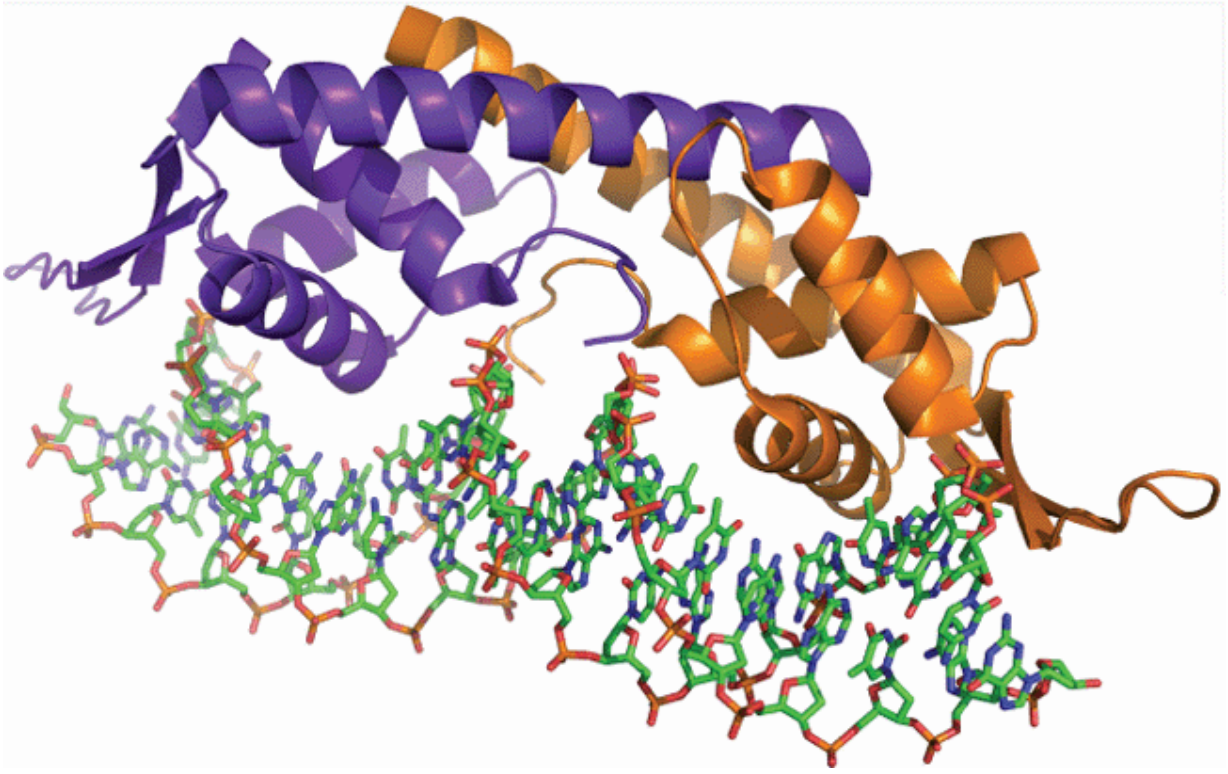


FIGURE 25.14 Structure of the replication terminator protein (RTP) bound to duplex DNA determined using X-ray crystallography. The RTP dimer is shown as a cartoon with one monomer coloured purple and the other monomer coloured orange. Reprinted from *Biochemical and Biophysical Research Communications*, Vol. 335(2), Hastings AF, Otting G, Folmer RH, Duggin IG, Wake RG, Wilce MC, Wilce JA

NMR spectroscopy is an alternative technique for deriving structural information for proteins. It uses the radio-frequency signals emitted from magnetically susceptible nuclei within the protein. The signals from ^{1}H are used to determine their distances from other ^{1}H nuclei. A model of the protein can be derived when enough of such distance constraints are determined. This method of structure determination is readily applied to smaller proteins but not to high-molecular-mass molecules from which signals are less readily measured.

However, NMR is also a highly sensitive technique for probing the interaction between a protein and its binding partner. Even interactions of quite large proteins, such as the 29 kDa RTP dimer, can be probed using NMR spectroscopy. A common NMR experiment is the heteronuclear single quantum coherence (HSQC) experiment that detects signals arising from ^{1}H nuclei that are covalently bound to ^{15}N nuclei. Since nearly every amino acid has an N—H group (except for proline), a signal can be obtained that represents the N—H of each amino acid. A two-dimensional HSQC NMR spectrum, which shows signals at the intersection of ^{1}H and ^{15}N frequency axes, acts as a very useful ‘molecular fingerprint’ for a protein (figure 25.15).

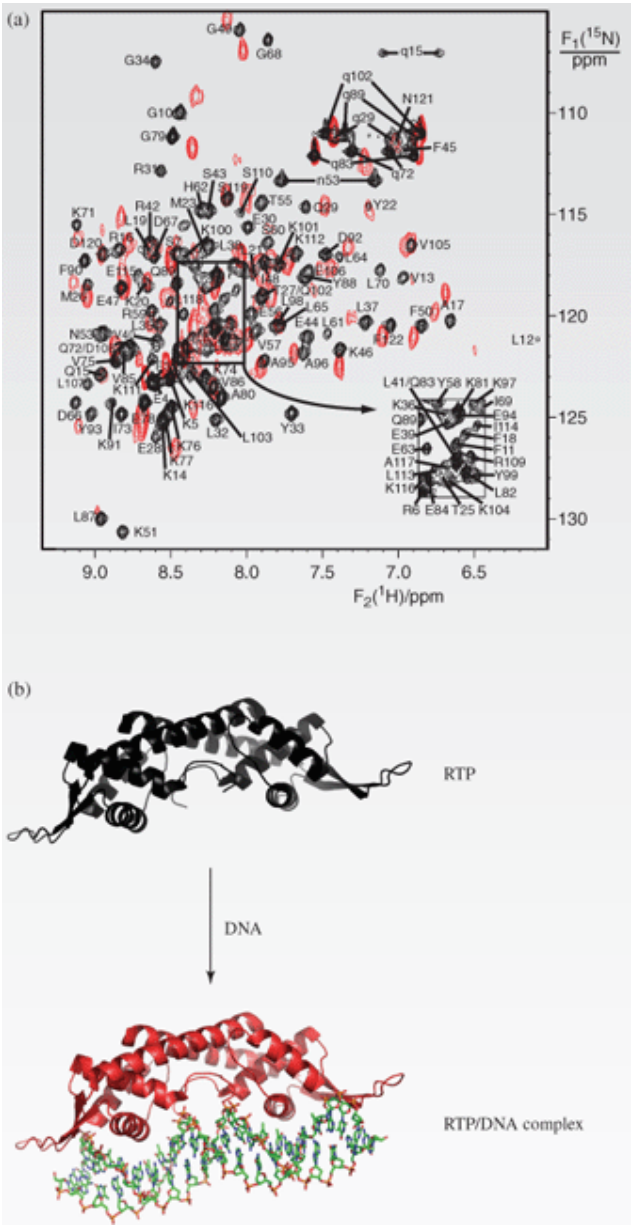


FIGURE 25.15 The HSQC NMR experiment.

(a) Overlayed HSQC spectra showing the signals arising from the N—H groups of each amino acid in RTP before DNA is added (black spots) and after DNA is added (red spots). Many signals stay in the same place, showing that the electronic environment of that N—H group is not perturbed by DNA binding. However, spots that move indicate that a particular N—H group has been perturbed by DNA binding.

(b) Depiction of uncomplexed RTP (black) and RTP in complex with DNA (red) corresponding to the two states observed in the HSQC experiment.

Reprinted from *Biochemical and Biophysical Research Communications*, Vol. 335(2), Hastings AF, Otting G, Folmer RH, Duggin IG, Wake RG, Wilce MC, Wilce JA

Since the radio-frequency signals of the 'fingerprint' are highly susceptible to their surrounding electronic environment, even a slight change to their local surroundings can be detected by a change in the frequency of the signal. Thus, if duplex DNA is added to the RTP protein, the HSQC spectrum that is obtained is visibly changed, revealing which individual amino acids are now experiencing a different electronic environment. Together with X-ray crystallography, NMR can be used to get a detailed understanding of how two molecular species interact.

Chemistry Research

Nanotechnology

Professor Max Lu and Dr Zhi Ping Xu, University of Queensland

Clean energy, environment and health care are all critical to our continued sustainable development. This poses a great challenge for science and technology, but nanostructured materials will make significant contributions to meet these challenges. Nanoscale science and engineering represent new paradigms in science and technology and are logical convergences of the basic sciences of chemistry, biology and physics. Nanotechnology offers tremendous potential to revolutionise materials and devices, the way they are made and perform, and indeed the way we live.

Nanotechnology will make things better, faster, smaller and cheaper, and will also create new classes of products and services, and consequently new markets. Nanoscience is a huge interdisciplinary field, but, with many challenges ahead, it is hard to predict where it will lead. Chemists, biologists, physicists and engineers will need to work together to meet these challenges.

Compared with bulk materials, nanomaterials probably possess improved physical and chemical properties. These properties change with particle size and can be controlled by manipulating the building blocks. In nanomaterial research, we often refer to functional nanomaterials; these have essential functional properties that are useful in processes such as adsorption, ion conduction, separation, catalysis, biosensing and biomolecular delivery.

One example of functional nanoparticles is nanometre-sized layered double hydroxides (LDHs), which have been successfully explored as cellular delivery vehicles for various drugs and bioactive molecules such as gene segments. Recent work, led by Professor Max Lu at the University of Queensland, reveals that the hexagonal LDH nanoparticles (figure 25.16) can deliver small molecular weight heparin (HP, a good blood anti-coagulant) to vascular smooth muscle cells (SMCs) more efficiently than heparin itself (figure 25.17). This efficient delivery of HP to SMCs, together with its sustainable release from LDH–HP nanohybrids (figure 25.18), enhances the prohibition effect of HP on SMC migration and proliferation, which is actively pursued in search of effective anti-restenosis treatment. Nonetheless, LDH nanoparticles have been proven to be less toxic than any commercial delivery agent and safe even in doses up to 100 μg mL^{-1}. Ongoing research in Professor Lu's laboratory includes the treatment of rats with an artificially injured artery by using LDH–HP nanohybrids that are modified with an antibody that can find the injured artery regions. Investigations are ongoing to evaluate the efficiency of this systemic delivery.

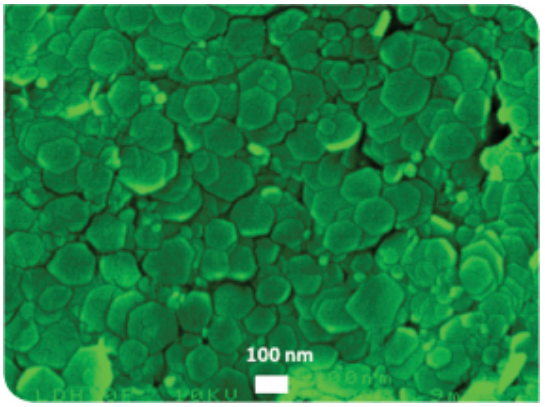


FIGURE 25.16 SEM of plateletlayered double hydroxide– heparin nanohybrids (LDH–HP).

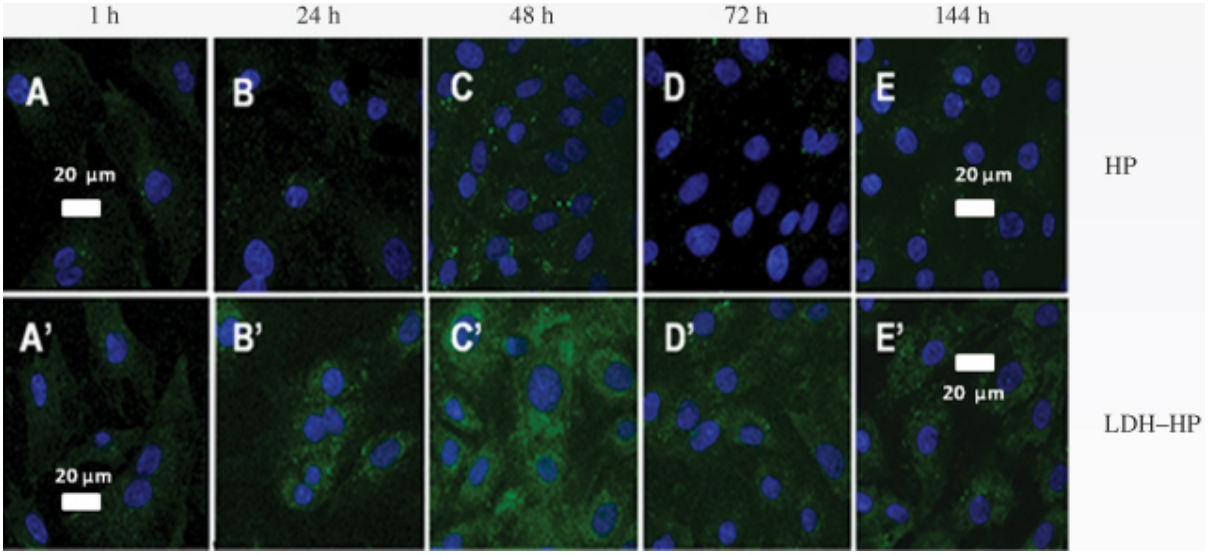


FIGURE 25.17 Confocal images of smooth muscle cells (blue) internalising **(A–E)** FITC-labelled heparin (HP, green) or **(A′–E′)** FITC-labelled LDH–HP (green) at different times.

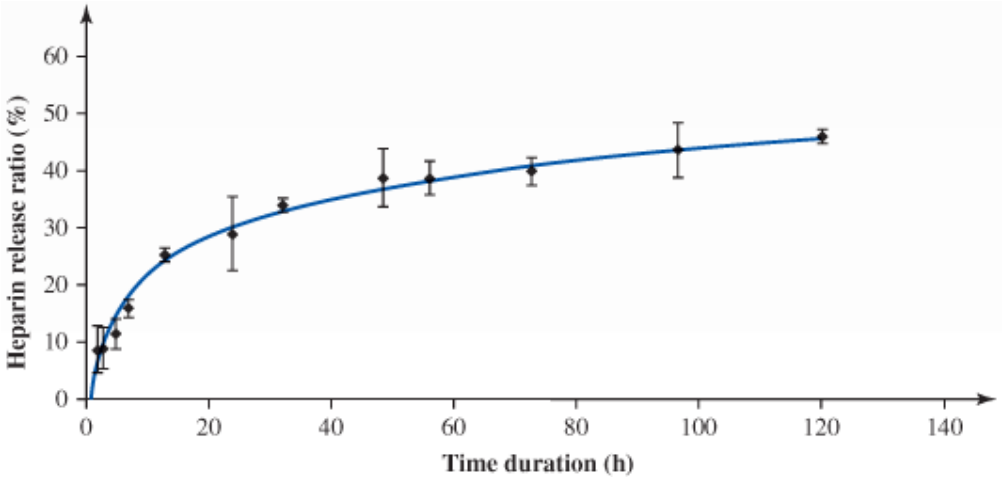


FIGURE 25.18 In vitro heparin release profile from LDH–HP in PBS solution at 37 °C. Reprinted from *Biochemical and Biophysical Research Communications*, Vol. 335(2). Hastings AF, Otting G, Folmer RH, Duggin IG, Wake RG, Wilce MC, Wilce JA, 'Interaction of the replication terminator protein of *Bacillus subtilis* with DNA probed by NMR spectroscopy', 361–6, September 23, 2005, with permission from Elsevier

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25.3 Ribonucleic Acid (RNA)

Ribonucleic acid (RNA) is involved in protein synthesis. The structure of RNA is principally similar to deoxyribonucleic acid (DNA) in that it, too, consists of long, unbranched chains of nucleotides joined by phosphodiester groups between the 3′ hydroxyl of one pentose and the 5′ hydroxyl of the next. There are, however, three major differences in structure between RNA and DNA:

1. The pentose unit in RNA is β-D-ribose rather than β-2-deoxy-D-ribose (see figure 25.2).
2. The pyrimidine bases in RNA are uracil and cytosine rather than thymine and cytosine (see figure 25.1).
3. RNA is single stranded rather than double stranded.

Cells contain up to eight times as much RNA as DNA, and, in contrast to DNA, RNA occurs in different forms and in multiple copies of each form. RNA molecules are classified according to their structure and function during protein synthesis into three major types: ribosomal RNA, transfer RNA and messenger RNA. Table 25.3 summarises the molar mass, number of nucleotides and percentage of cellular abundance of the three types of RNA in cells of *Escherichia coli*. This organism is one of the best studied bacteria and a workhorse for cellular studies. It is one of the main species of bacteria living in the lower intestines of mammals, and its presence in surface water is an indicator of faecal contamination. *E. coli* can cause several intestinal and extraintestinal infections, such as urinary tract infections, meningitis and gramnegative pneumonia.

TABLE 25.3 Types of RNA found in cells of *Escherichia coli*.

Type	Molar mass range (u)	Number of nucleotides	Percentage of cell RNA
mRNA	25 000–1 000 000	75–3000	2
tRNA	23 000–30 000	73–94	16
rRNA	35 000–1 100 000	120–2904	82

Ribosomal RNA

The bulk of **ribosomal RNA (rRNA)** is found in the cytoplasm in subcellular particles called **ribosomes**, which contain about 60% RNA and 40% protein. Ribosomes are the sites in cells at which protein synthesis takes place.

Ribosomes are major targets for the development of new antibiotics against various diseases. Antibiotics can block the function of bacterial ribosomes, killing the bacteria. Because of the importance of the ribosome's innermost workings in the development of new drugs, the 2009 Nobel Prize in chemistry was awarded to Venkatraman Ramakrishnan, Thomas A Steitz and Ada E Yonath for their work on understanding the binding interactions between antibiotics and ribosomes.

Transfer RNA

Transfer RNA (tRNA) molecules have the lowest molar mass of all nucleic acids. They consist of 73 to 94 nucleotides in a single strand. tRNA has the rough shape of a cloverleaf, which is formed by pairing of complementary bases within the strand (figure 25.19). The function of tRNA is to carry amino acids to the sites of protein synthesis on the ribosomes. Each amino acid has at least one tRNA dedicated specifically to this purpose; several amino acids have more than one.



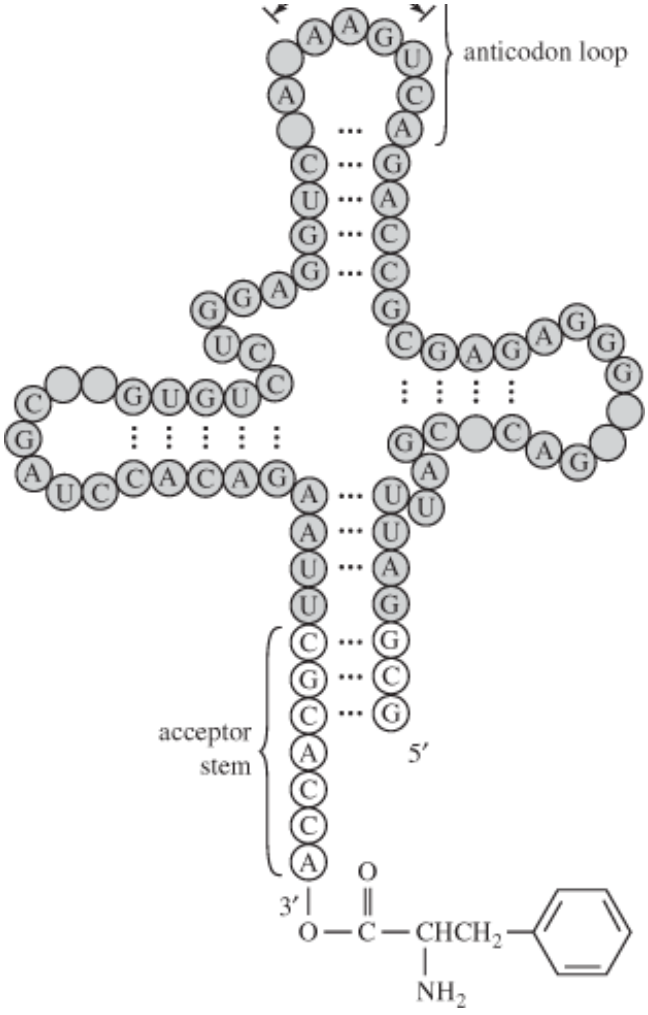


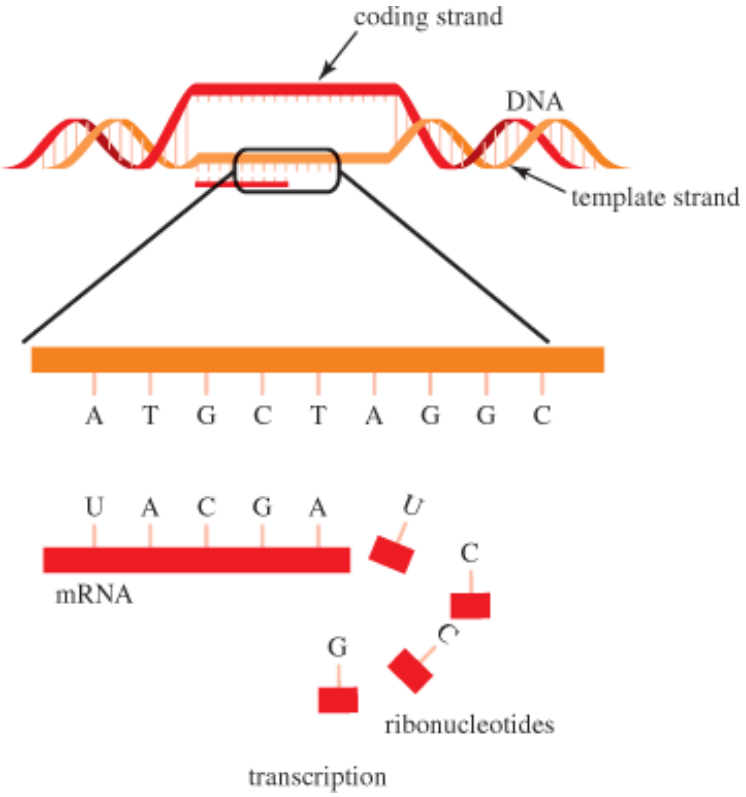
FIGURE 25.19 Secondary structure of a yeast tRNA that codes for phenylalanine.

Each amino acid is coded by a so-called **anticodon** triplet on one leaf of the tRNA (see figure 25.19). In the transfer process, the amino acid is joined to its specific tRNA by an ester bond between the α-carboxyl group of the amino acid and the 3′ hydroxyl group of the ribose unit at the 3′ end of the tRNA (**acceptor stem**). The example in figure 25.19 is a yeast tRNA that codes for phenylalanine.

Messenger RNA

Messenger RNA (mRNA) is present in cells in relatively small amounts and is very short lived. Messenger RNA molecules are single stranded, and their synthesis is directed by information encoded on DNA molecules. As illustrated at the bottom of the next page, double-stranded DNA is unwound, and a complementary strand of mRNA is synthesised along one strand of the DNA template, beginning at the 3′ end. The synthesis of mRNA from a DNA template is called **transcription** because genetic information in a sequence of bases of DNA is transcribed into a complementary sequence of bases on mRNA.

The name ‘messenger’ is derived from the function of this type of RNA, which is to carry coded genetic information (the blueprints for a special polypeptide) from DNA to the ribosomes for the synthesis of proteins.



With respect to the synthesis of mRNA from a DNA template, it is important to understand that only one of the two DNA strands is transcribed into mRNA. The strand containing the gene is called the **coding strand** (or **sense strand**), and the strand that is transcribed into mRNA is the **template strand** (or **antisense strand**). Since the template and the coding strands are complementary, and the template strand and the mRNA molecule are also complementary, the mRNA molecule produced during transcription is a copy of the coding strand. The only difference between the coding strand and mRNA (apart from the fact that RNA contains ribose and DNA contains 2-deoxyribose) is that the RNA molecule has U in every place that the DNA coding strand has a T.

WORKED EXAMPLE 25.4

Sequence of Bases of mRNA — 1

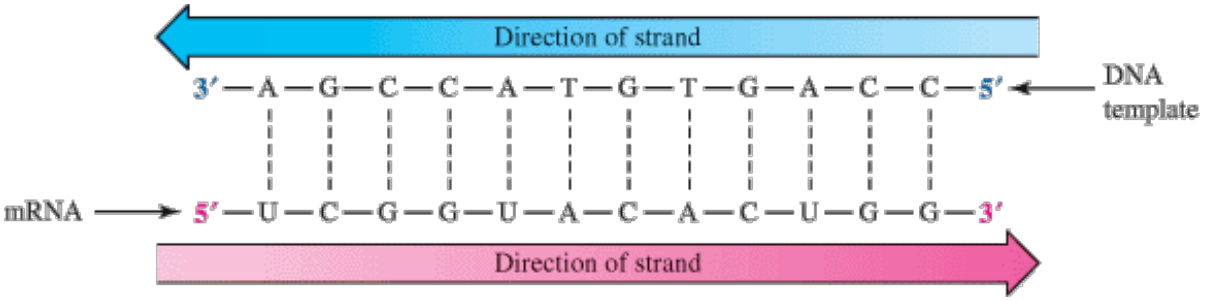
The following is a base sequence from a portion of DNA:

$$3'-A-G-C-C-A-T-G-T-G-A-C-C-5'$$

Write the sequence of bases of the mRNA synthesised with this section of DNA as a template.

Solution

RNA synthesis begins at the 3′ end of the DNA template and proceeds towards the 5′ end. The complementary mRNA strand is formed using the bases C, G, A and U. Uracil (U) is the complement of adenine (A) on the DNA template.



Reading from the 5′ end, we see that the sequence of mRNA is 5′-UCGGUACACUGG-3′.

PRACTICE EXERCISE 25.4

Here is a portion of the nucleotide sequence in phenylalanine tRNA:

$$3' - \text{ACCACCUGCUCAGGCCUU} - 5'$$

Write the nucleotide sequence of the DNA complement of this sequence.

WORKED EXAMPLE 25.5

Sequence of Bases of mRNA — 2

Write the mRNA produced from the following segment of a DNA coding strand.

$$5' - \text{CTAACTAGCGGGTCGCCG} - 3'$$

Solution

The mRNA produced during transcription is a copy of the DNA coding strand with each T replaced by a U. Therefore, the mRNA strand has the following sequence.

$$5' - \text{CUAACUAGCGGGUCGCCG} - 3'$$

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25.4 The Genetic Code

It was clear by the early 1950s that the sequence of bases in DNA molecules constitutes the store of genetic information and directs the synthesis of messenger RNA, which, in turn, directs the synthesis of proteins by ribosomal RNA with the assistance of transfer RNA. This correspondence between nucleic acid sequences and polypeptide sequences is called the **genetic code**.

Triplet Nature of the Code

The idea that the sequence of bases in DNA directs the synthesis of proteins presents the following problem: How can a molecule containing only four variable units (adenine, cytosine, guanine and thymine) direct the synthesis of molecules containing up to 20 variable units (the protein-derived amino acids)? How can an alphabet of only four letters code for the order of letters in the 20-letter alphabet that occurs in proteins?

An obvious answer is that a combination of bases, rather than a single base, codes for each amino acid. If the code consists of nucleotide pairs, there are $4^2 = 16$ combinations; this is a more extensive code, but it is still not extensive enough to code for 20 amino acids. If the code consists of nucleotides in groups of three, there are $4^3 = 64$ combinations, more than enough to code for the primary structure of a protein. This appears to be a very simple solution to the problem for a system that must have taken eons of evolutionary trial and error to develop. Yet proof now exists, from comparisons of gene (nucleic acid) and protein (amino acid) sequences, that nature does indeed use a simple three-letter or triplet code to store genetic information. Such a triplet of nucleotides is called a **codon**.

Deciphering the Genetic Code

The next question is: Which of the 64 triplets codes for which amino acid? In 1961, Marshall Nirenberg provided a simple experimental approach to the problem, based on the observation that synthetic polynucleotides direct polypeptide synthesis in much the same manner as do natural mRNAs. Nirenberg found that, when ribosomes, amino acids, tRNAs and appropriate protein-synthesising enzymes were incubated in vitro, no polypeptide synthesis occurred. However, when he added synthetic polyuridylic acid (poly-U), a polypeptide of high molar mass was synthesised. More importantly, the synthetic polypeptide contained only phenylalanine. With this discovery, the first element of the genetic code was deciphered: The triplet UUU codes for phenylalanine.

Similar experiments were carried out with different synthetic polyribonucleotides. It was found, for example, that polyadenylic acid (poly-A) leads to the synthesis of polylysine, and that polycytidylic acid (poly-C) leads to the synthesis of proline. By 1964, all 64 codons had been deciphered (table 25.4). Nirenberg, Robert Holley and Har Gobind Khorana shared the 1968 Nobel Prize in physiology or medicine for their groundbreaking work.

TABLE 25.4 The genetic code: mRNA codons and the amino acid that each codon directs

First position (5′ end)	Second position								Third position 3′ end)
	U		C		A		G		
U	UUU	Phe	UCU	Ser	UAU	Tyr	UGU	Cys	U
	UUC	Phe	UCC	Ser	UAC	Tyr	UGC	Cys	C
	UUA	Leu	UCA	Ser	UAA	Stop	UGA	Stop	A
	UUG	Leu	UCG	Ser	UAG	Stop	UGG	Trp	G
C	CUU	Leu	CCU	Pro	CAU	His	CGU	Arg	U
	CUC	Leu	CCC	Pro	CAC	His	CGC	Arg	C

C	CUA	Leu	CCA	Pro	CAA	Gln	CGA	Arg	A
	CUG	Leu	CCG	Pro	CAG	Gln	CGG	Arg	G
A	AUU	Ile	ACU	Thr	AAU	Asn	AGU	Ser	U
	AUC	Ile	ACC	Thr	AAC	Asn	AGC	Ser	C
	AUA	Ile	ACA	Thr	AAA	Lys	AGA	Arg	A
	AUG[(a)]	Met	ACG	Thr	AAG	Lys	AGG	Arg	G
G	GUU	Val	GCU	Ala	GAU	Asp	GGU	Gly	U
	GUC	Val	GCC	Ala	GAC	Asp	GGC	Gly	C
	GUA	Val	GCA	Ala	GAA	Glu	GGA	Gly	A
	GUG	Val	GCG	Ala	GAG	Glu	GGG	Gly	G

(a) AUG also serves as the principal initiation codon.

Properties of the Genetic Code

Several features of the genetic code are evident from a study of table 25.4.

1. Only 61 triplets code for amino acids. The remaining three (UAA, UAG and UGA) are signals for chain termination; they signal to the protein-synthesising machinery of the cell that the primary sequence of the protein is complete. The three chain termination triplets are indicated in the table by ‘Stop’.
2. The code is degenerate, which means that several amino acids are coded for by more than one triplet. Only methionine and tryptophan are coded for by just one triplet. Leucine, serine and arginine are coded for by six triplets, and the remaining amino acids are coded for by two, three or four triplets.
3. For the 15 amino acids coded for by two, three or four triplets, it is only the third letter of the code that varies. For example, glycine is coded for by the triplets GGA, GGG, GGC and GGU.
4. There is no ambiguity in the code, meaning that each triplet codes for only one amino acid.
5. AUG is the initiation signal, and it is also the codon for the amino acid methionine. In all protein sysnthesis, the first amino acid placed is always methionine.

WORKED EXAMPLE 25.6

Transcription

During transcription, a portion of mRNA is synthesised with the following base sequence:

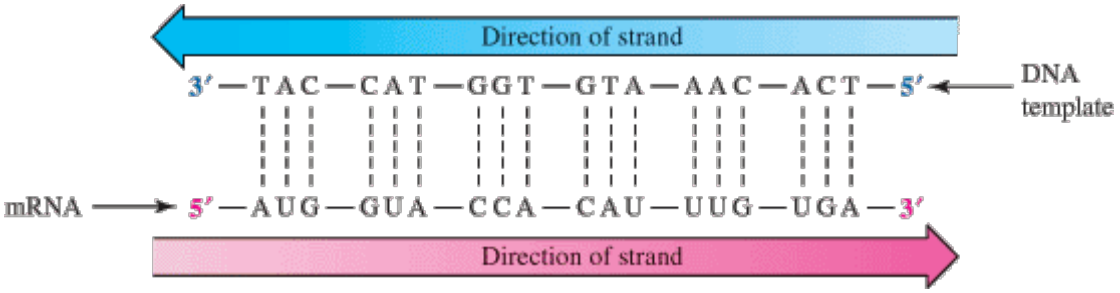
$$5' - AUG - GUA - CCA - CAU - UUG - UGA - 3'$$

(a) Write the nucleotide sequence of the DNA template strand from which this portion of mRNA was synthesised.

(b) Write the primary structure of the polypeptide coded for by this section of mRNA.

Solution

(a) During transcription, mRNA is synthesised from a DNA strand, beginning from the 3′ end of the DNA template. The DNA strand must be the complement of the newly synthesised mRNA strand:



Note that the codon UGA codes for termination of the growing polypeptide chain; therefore, the sequence given in this problem codes for a pentapeptide.

(b) The sequence of amino acids is shown in the following mRNA strand:

$$5' - \underset{\text{met}}{\text{AUG}} - \underset{\text{val}}{\text{GUA}} - \underset{\text{pro}}{\text{CCA}} - \underset{\text{his}}{\text{CAU}} - \underset{\text{leu}}{\text{UUG}} - \underset{\text{stop}}{\text{UGA}} - 3'$$

PRACTICE EXERCISE 25.5

The following section of a DNA template strand codes for oxytocin, a polypeptide mammalian hormone that is released during labour:

$$3' - \text{ACA} - \text{ATG} - \text{TAA} - \text{GTT} - \text{TTA} - \text{ACG} - \text{GGA} - \text{GAA} - \text{CCA} - \text{ACT} - 5'$$

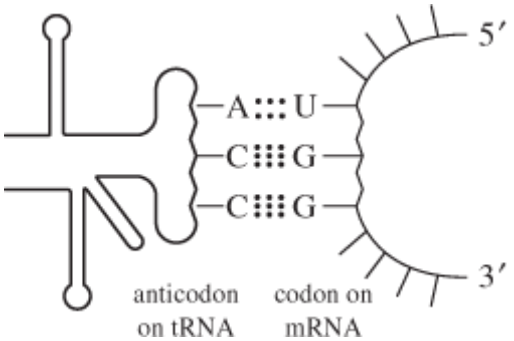
(a) Write the base sequence of the mRNA synthesised from this section of DNA.

(b) Use your sequence of bases in (a) to write the primary structure of oxytocin.

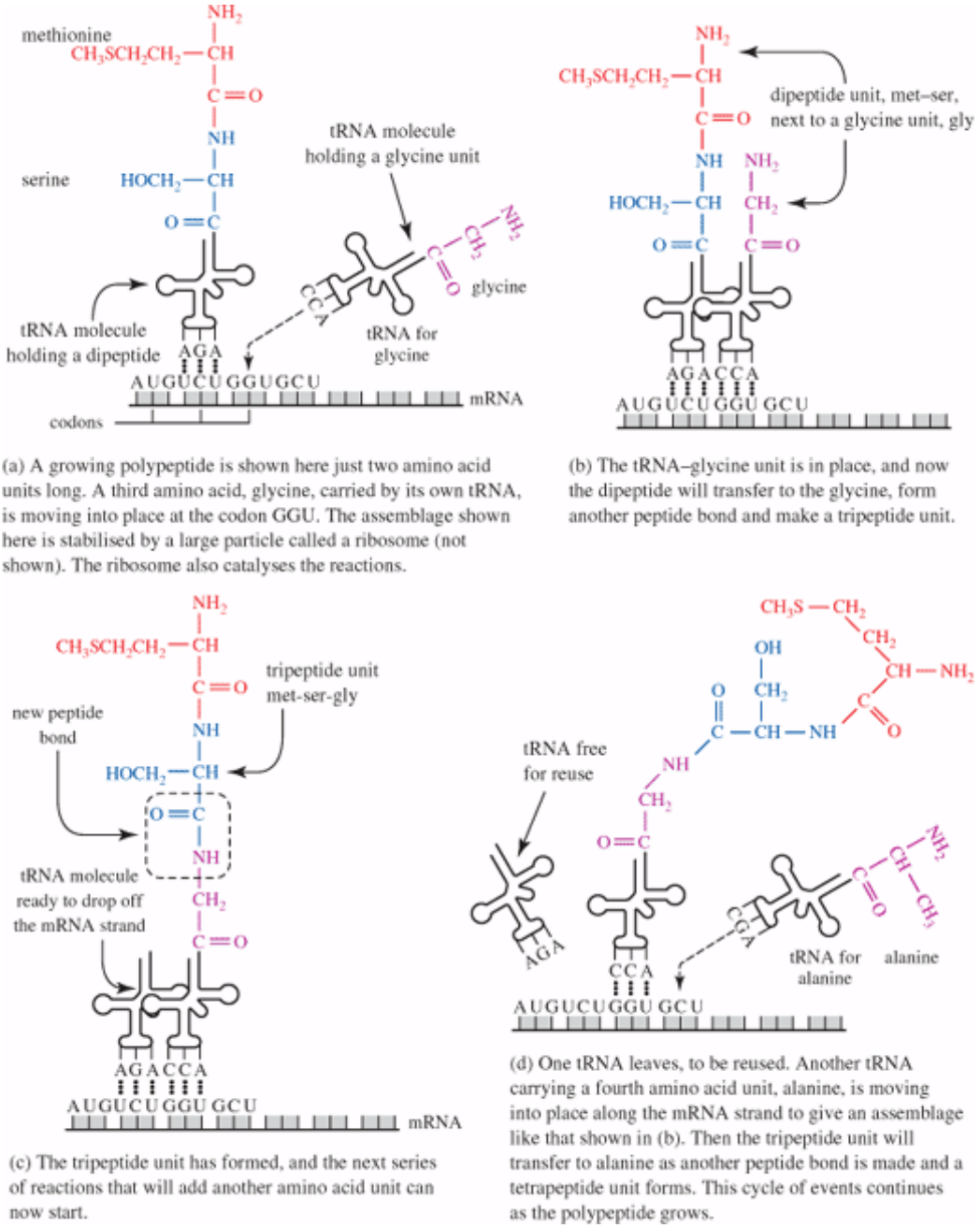
Polypeptide Synthesis

As we have just seen, each triplet of bases *as it occurs on mRNA* is called a codon, and each codon corresponds to a specific amino acid. The translation of codons to amino acids constitutes the genetic code. One of the most remarkable features of the code is that it is essentially universal. The codon specifying alanine in humans, for example, also specifies alanine in the genetic machinery of all known species of bacteria, aardvarks, camels, rabbits and stink bugs. Our chemical kinship with the entire living world is profound (even humbling).

A triplet of bases complementary to a codon occurs on tRNA and is called an anticodon (see figure 25.19). A tRNA molecule, bearing the amino acid corresponding to its anticodon, can line up at a position on a strand of mRNA only where the anticodon ‘fits’ by hydrogen bonding to the matching codon. For example, if the anticodon is ACC, the A on the anticodon must find a U on the mRNA at the same time that its neighbouring two C bases find neighbouring G bases on the mRNA strand. Thus the anticodon and codon line up as shown below, where the dotted lines indicate hydrogen bonds.



Codons on mRNA determine the sequence in which tRNA units line up, and this sets the sequence in which amino acid units become joined in a polypeptide. Figure 25.20 carries this description further, where we enter the process soon after special steps (not shown) have launched it.



(a) A growing polypeptide is shown here just two amino acid units long. A third amino acid, glycine, carried by its own tRNA, is moving into place at the codon GGU. The assemblage shown here is stabilised by a large particle called a ribosome (not shown). The ribosome also catalyses the reactions.

(b) The tRNA–glycine unit is in place, and now the dipeptide will transfer to the glycine, form another peptide bond and make a tripeptide unit.

(c) The tripeptide unit has formed, and the next series of reactions that will add another amino acid unit can now start.

(d) One tRNA leaves, to be reused. Another tRNA carrying a fourth amino acid unit, alanine, is moving into place along the mRNA strand to give an assemblage like that shown in (b). Then the tripeptide unit will transfer to alanine as another peptide bond is made and a tetrapeptide unit forms. This cycle of events continues as the polypeptide grows.

FIGURE 25.20 Polypeptide synthesis at an mRNA strand.

In figure 25.20a, a tRNA–glycine unit arrives at mRNA where it finds two situations, namely, a dipeptide already started and a codon to which the tRNA–glycine can fit. In figure 25.20b, the tRNA–glycine unit is in place. It is the only such unit that could fit here; base pairing between the two triplets — codon to anticodon — ensures this. It is important to understand that the binding of tRNA carrying a certain amino acid to the codons on mRNA is an equilibrium reaction. The reason that one and not another amino acid on a tRNA molecule binds is related to the relative magnitude of the hydrogen bonds that are created during this binding process.

In figure 25.20c, the whole dipeptide unit moves over and is joined to the glycine unit by a newly formed peptide bond. This leaves a tripeptide attached via a tRNA unit to the mRNA.

Because the next codon in figure 25.20d, GCU, codes for the amino acid alanine, only a tRNA–alanine unit can fit the next site. So alanine, with its methyl group as the side chain, is the only amino acid that can enter the polypeptide chain at this point. These elongation steps repeat until a special codon is reached that is designed

to stop the process. The polypeptide is now complete. It has a unique sequence of side chains that has been initially specified by the molecular structure of a gene.

As shown in figure 25.21, synthesis of the peptide takes place in ribosomes, which are made from complexes of RNA and proteins. Ribosomes consist of two subunits of different sizes. The smaller subunit binds to mRNA, while the larger subunit binds to tRNA and the amino acids. Once the ribosome has finished reading a sequence of mRNA, the subunits separate.

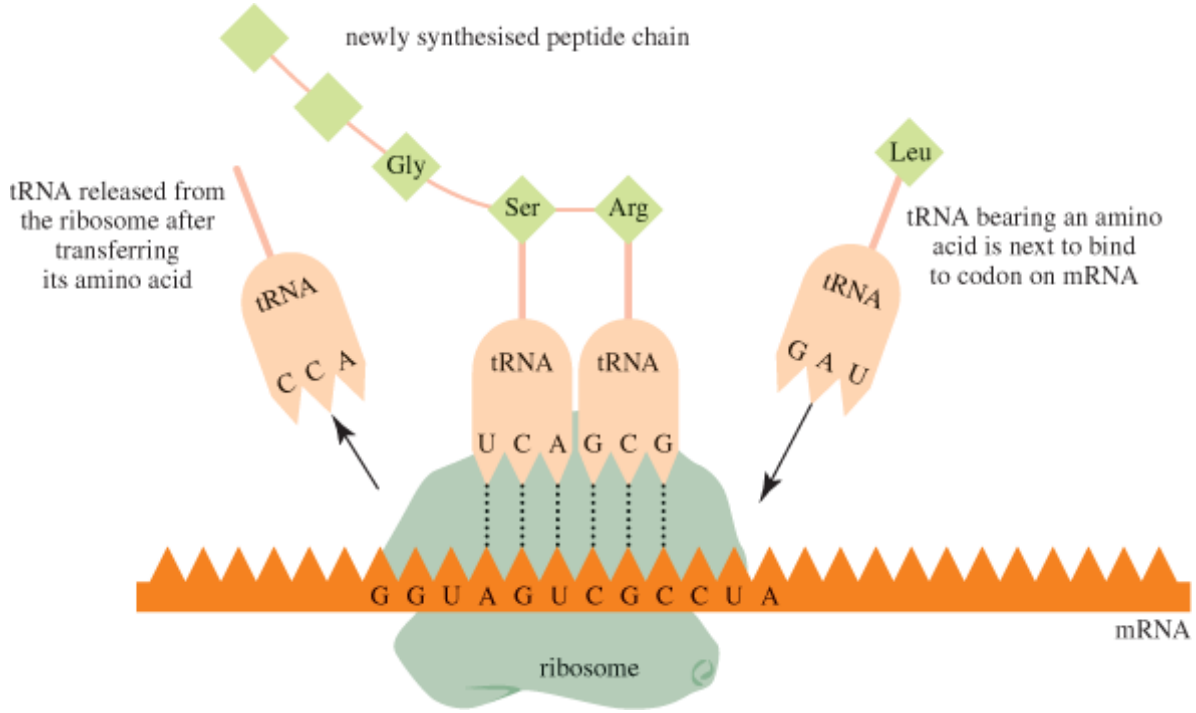


FIGURE 25.21 Representation of the translation of an mRNA sequence and synthesis of a peptide chain at a ribosome. An incoming tRNA molecule is shown ready to bind to the next codon and add a leucine amino acid to the growing chain.

Genetic Defects

About 2000 diseases are attributed to various kinds of defects in the genetic machinery of cells. With so many steps from gene to polypeptide, we should expect many opportunities for things to go wrong. Suppose, for example, that just one base in a gene was missing. This means that one base on an mRNA strand would be wrong (with respect to getting the polypeptide we want). This would change every remaining codon. For example, if the next codons on a strand of mRNA were -UCU-GGU-GCU-U…, and the first G was deleted, the sequence would become -UCU-GUG-CUU-. All remaining triplets change! You can imagine how this could lead to an entirely different polypeptide from the one we want.

Suppose, instead, that the second G was replaced by a C. This would mean that the GGU codon becomes a GCU codon so that -UCU-GGU-GCU- becomes -UCU-GCU-GCU-. One amino acid in the resulting polypeptide would be incorrect. Such a mutation makes the difference, for example, between the normal haemoglobin protein and the sickle-cell haemoglobin protein or can cause some forms of cystic fibrosis.

Viruses

Viruses are microscopic particles usually consisting of nucleic acids and proteins that can infect cells of biological organisms. They cannot reproduce on their own, but replicate through infection of a host cell. Thus, the nucleic acids of viruses can take over the genetic machinery of the cells of particular host tissues, manufacture more virus particles and multiply enough to burst the host cell. Because cancer cells divide irregularly, and usually more rapidly than normal cells, some viruses are thought to be among the agents that

can cause cancer.

There are extensive discussions about whether viruses are living organisms. Since they do not possess a cell membrane or metabolise on their own (the generally accepted definition of life), they are often considered nonliving species. Figure 25.22 on this page shows an electronmicrograph of the Ebola virus. This virus causes Ebola haemorrhagic fever, a disease with no vaccine or treatment and that has a mortality rate of between 50 and 90%. The symptoms of Ebola include vomiting, diarrhoea, internal and external bleeding and fever.



FIGURE 25.22 An electronmicrograph of the Ebola virus at 19 000 times magnification. SPL/Barry Dowsett

Reverse Transcriptase

As we have seen, normal transcription involves the synthesis of mRNA from DNA. In 1970, it was discovered that the reverse process is also possible, where single-stranded RNA is ultimately transcribed into double-stranded DNA (see figure 25.23). The RNA-dependent DNA polymerase enzyme (also called **reverse transcriptase**), which is responsible for this process, is central to the infectious nature of reverse-transcribing viruses (**retroviruses**), several of which cause disease in humans.

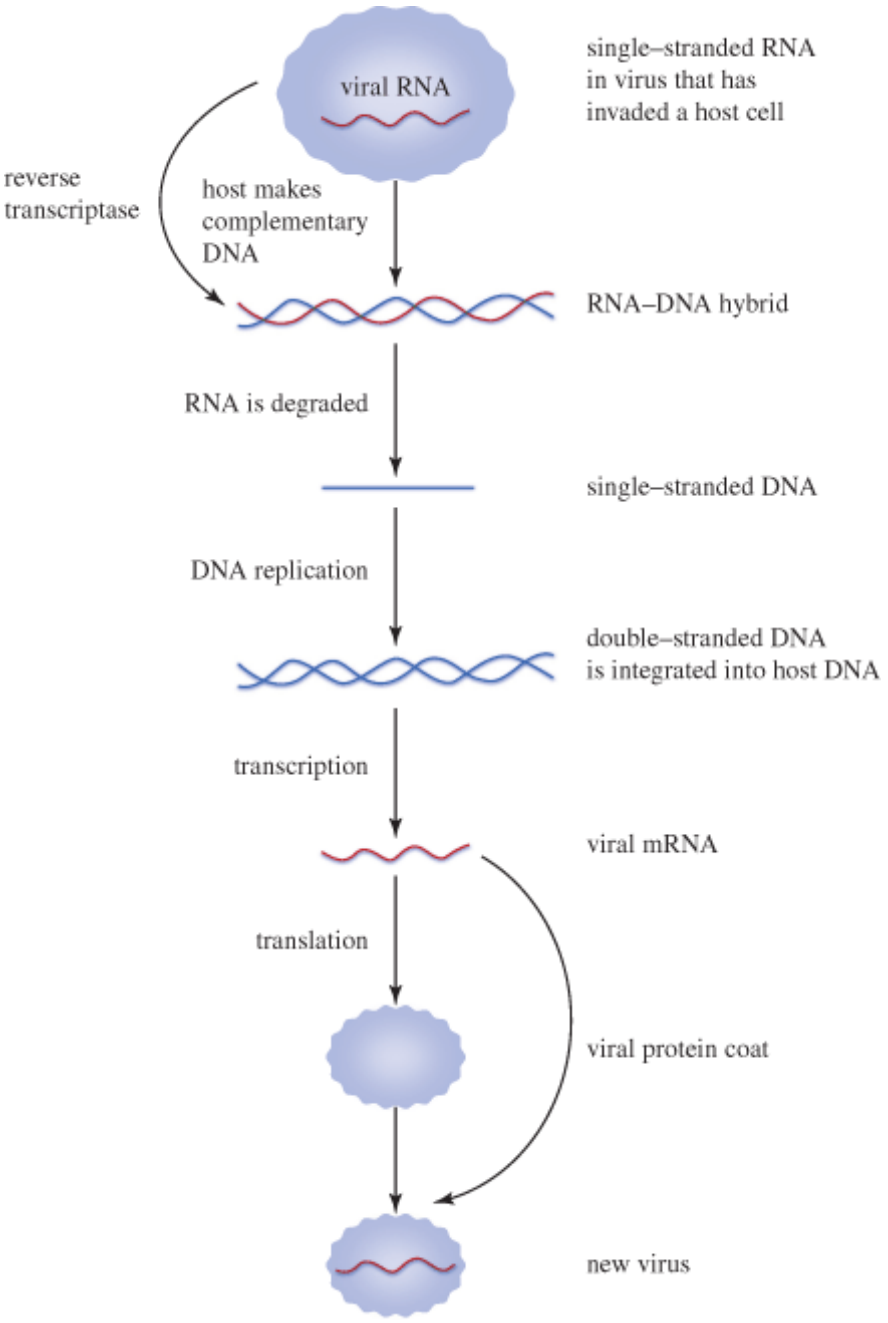


FIGURE 25.23 Replication of viral DNA requires the transcription of single-stranded RNA into double-stranded DNA. This process is the reverse of normal transcription of mRNA from DNA, and it requires the enzyme reverse transcriptase.

A prominent example is the human immunodeficiency virus type 1 (HIV-1). Once inside a cell, retroviruses reverse-transcribe their RNA genome into DNA, which is then integrated into the host genome and replicated along with the host's DNA. Without reverse transcriptase, the viral genome cannot be incorporated into the host cell, and this is essential for the virus to reproduce.

Since errors can occur during reverse transcriptase, not all viruses produced in a single infected cell are identical. This results in viruses with a variety of subtle molecular differences in their surface protein coats. Vaccines, which induce the production of antibodies that recognise and bind to very specific surface molecules on a virus, are an unlikely solution to fighting HIV infection; this is because, throughout the infection, HIV surface molecules are continually changing.

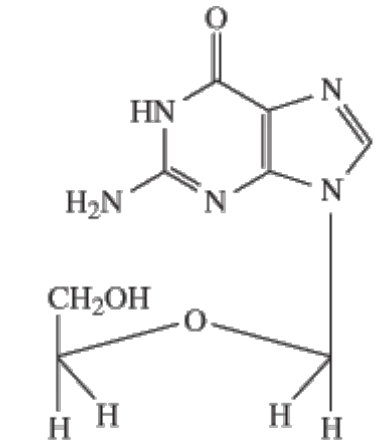
The first drugs that were successful in slowing down HIV infections act by blocking the recoding of viral RNA into DNA. One example of such a **reverse transcriptase inhibitor** is the compound AZT (see figure 25.22), which delays the progression from HIV infection to AIDS (acquired immune deficiency syndrome).

Chemical Connections

The Search for Antiviral Drugs

The search for antiviral drugs has been more difficult than the search for antibacterial drugs, primarily because viral replication depends on the metabolic processes of the invaded cell. Thus, antiviral drugs are also likely to cause harm to the cells that harbour the virus. The challenge in developing antiviral drugs is to understand the biochemistry of viruses and to develop drugs that target processes specific to them. Compared with the large number of antibacterial drugs available, there is only a handful of antiviral drugs, and they have nowhere near the effectiveness that antibiotics have against bacterial infections.

Acyclovir was one of the first of a new family of drugs for the treatment of infectious diseases caused by DNA viruses called herpes virus. Herpes infections in humans are of two kinds: herpes simplex type 1, which gives rise to mouth and eye sores, and herpes simplex type 2, which gives rise to serious genital infections. Acyclovir is highly effective against herpes virus-caused genital infections. The structural formula of acyclovir in figure 25.24 shows its structural relationship to 2-deoxyguanosine. The drug is activated in vivo by the conversion of the primary —OH (which corresponds to the 5′-OH of a riboside or a deoxyriboside) to a triphosphate. Because of its close resemblance to deoxyguanosine triphosphate, an essential precursor of DNA synthesis, acyclovir triphosphate is taken up by viral DNA polymerase to form an enzyme–substrate complex on which no 3′-OH exists for replication to continue. Thus, the enzyme–substrate complex is no longer active (it is a dead-end complex), viral replication is disrupted, and the virus is destroyed.



acyclovir
(drawn to show its structural relationship to 2-deoxyguanosine)

FIGURE 25.24 Acyclovir is an analogue of 2′-deoxyguanosine, which does not contain a carbohydrate moiety.

Perhaps the best known of the HIV-fighting viral antimetabolites is zidovudine (AZT), an analogue of deoxythymidine in which the 3′-OH has been replaced by an azido group, N_3 (figure 25.25). AZT is effective against HIV-1, a retrovirus that is the causative agent of AIDS. AZT is converted in vivo by cellular enzymes to the 5′-triphosphate, is then recognised as deoxythymidine 5′-triphosphate by viral RNA-dependent DNA polymerase (reverse transcriptase), and is added to a growing DNA chain. There, it stops chain elongation because there is no 3′-OH on which to add the next deoxynucleotide. AZT owes its effectiveness to the fact that it binds more strongly to viral reverse transcriptase than it does to human DNA polymerase.

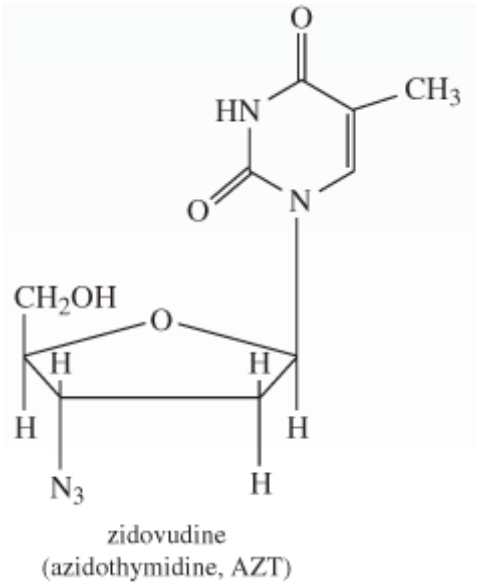


FIGURE 25.25 Zidovudine is an analogue of 2′-deoxythymidine in which the 3′ —OH group has been replaced by an azido group, N_3.

Chemical Connections

DNA Profiling

If the many crime dramas on television are to be taken as a guide, DNA holds the key to solving otherwise unsolvable crimes. In addition to helping convict criminals, it has also exonerated suspects (and people wrongly convicted), helped in the identification of disaster victims and established the paternity of children. Comparing DNA samples is known as DNA profiling or DNA fingerprinting.

Each human being has a genetic make-up consisting of approximately 3 billion pairs of nucleotides. Almost all of the DNA sequence is identical between different individuals. However, parts of DNA molecules differ from person to person or animal to animal (with the exception of identical twins and clones); highly variable repeated sequences of side-chain bases called short tandem repeats or minisatellites give each person a unique DNA ‘fingerprint’ that can be used quite reliably to identify an individual. Human DNA samples can be obtained from hair, blood, semen, saliva or skin left at a crime scene. In fact, every cell, except the sex cells (sperm and ova) and hair shafts, contains the entire set of DNA unique to the individual.

To produce a DNA fingerprint, a sample of DNA from a trace of blood, skin or other tissue is treated with specific enzymes that break the DNA into small fragments, which can be visualised by special techniques. The final result of DNA profiling looks much like a barcode: a series of parallel lines that differ from person to person in number, thickness and separation.

In the DNA fingerprint in figure 25.26, lanes 1, 5 and 9 represent internal standards, or control lanes. Lanes 2, 3 and 4 were used in a paternity suit. The DNA fingerprint of the mother in lane 4 contains

five bands that match five of the six bands in the DNA fingerprint of the child in lane 3. The DNA fingerprint of the alleged father in lane 2 contains six bands, three of which match bands in the DNA fingerprint of the child. Because the child inherits only half of its genes from the father, only about half of the child's and father's bands in the DNA fingerprints are expected to match. In this instance, we can say, on the basis of the DNA fingerprint matching, that the alleged father is, indeed, the child's father. The probability that he is not the father is extremely small — about 1 in 100 000.

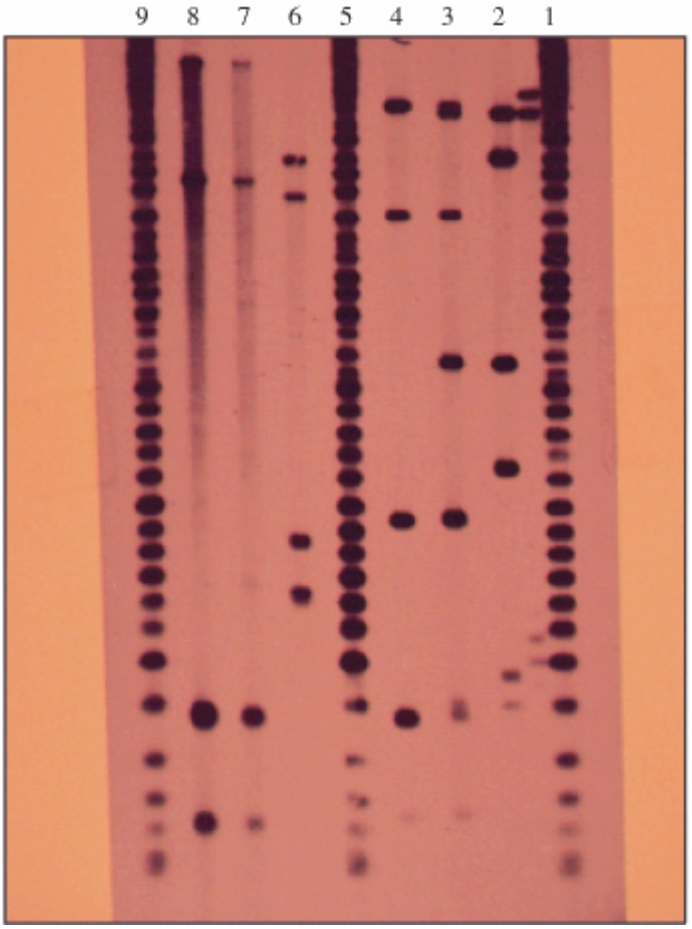


FIGURE 25.26 DNA fingerprint. Dr Lawrence Kobilinsky

Lanes 6, 7 and 8 contain DNA fingerprint patterns used as evidence in a criminal case. Lanes 6 and 7 are DNA fingerprints obtained from a crime scene. Lane 8 is the DNA fingerprint pattern of the

suspect. As can be seen, the DNA fingerprint patterns in lanes 7 and 8 are identical. The pattern in lane 6 must arise from a person other than the suspect. In cases where the sequence profiles from a known individual match the DNA obtained at the crime scene, the probability that the DNA is not from the same person (i.e. that another person committed the crime) is approximately 1 in 82 billion — extraordinarily low.

The fierce debate over the use of DNA evidence in criminal cases is not related to the reliability of DNA matching; rather it is related to the vagaries of the various laws and to the care or lack of care shown in gathering the samples from the crime scene. Identification can be complicated if a crime scene is contaminated with DNA from several people, who may include the perpetrator, victim, investigators and anyone else who had visited the location. Investigators eliminate the victim's DNA and that of others known to be innocent, leaving them with the DNA of potential suspects.

New Zealand was the second country in the world to create a national DNA database, using DNA from volunteers and convicted offenders. Australia lagged behind, with different state laws preventing the establishment of a national DNA database. At the end of 2006, the DNA forensic laboratories in the largest states in Australia had a backlog of several thousand cases. In 2007, the states agreed to align their legislation and so allow sharing of DNA profiles via the federal government's CrimTrac agency.

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SUMMARY

Nucleosides and Nucleotides

Nucleic acids are composed of three types of monomer units: heterocyclic aromatic amine bases derived from pyrimidine and purine, the monosaccharide D-ribose or 2-deoxy-D-ribose, and phosphate ions. A nucleoside is a compound containing D-ribose or 2-deoxy-D-ribose bonded to a heterocyclic aromatic amine base by a β-*N*-glycosidic bond. A nucleotide is a nucleoside in which a molecule of phosphoric acid is esterified with an — OH group of the monosaccharide, most commonly the 3′ or the 5′ — OH group. Nucleoside mono-, di- and triphosphates are strong polyprotic acids and are extensively ionised at pH 7.0. At that pH, adenosine triphosphate, for example, is a 50 : 50 mixture of ATP^{3-} and ATP^{4-}.

The Structure of Deoxyribonucleic Acid (DNA)

The primary structure of deoxyribonucleic acid (DNA) consists of nucleosides (possessing 2′-deoxyribose) linked by 3′,5′-phosphodiester bonds. The sequence of nucleotides is read from the 5′ end of the polynucleotide strand to the 3′ end.

The heart of the Watson–Crick model of the structure of DNA is the postulate that a molecule of DNA consists of two antiparallel polynucleotide strands coiled in a right-handed manner around the same axis to form a double helix. Purine and pyrimidine bases point inwards to the axis of the helix and are always paired G-C and A-T. In B-DNA, base pairs are stacked one on top of another, with a spacing of 0.34 nm and 10 base pairs per 3.4 nm helical repeat. In A-DNA, bases are arranged with 11 base pairs per 2.5 nm helical repeat. Z-DNA is a left-handed double helix, which is thinner and longer than B-DNA.

The formation of the tertiary structure of DNA is commonly called supercoiling. Bacterial circular DNA is a type of double-stranded DNA in which the 5′ and 3′ ends of the strands are joined by phosphodiester groups. The opening of one strand followed by the partial unwinding and rejoining of the ends introduces strain in the nonhelical gap. The strain can be spread over the entire molecule of circular DNA by the introduction of superhelical twists.

Histones are particularly rich in lysine and arginine and so have an abundance of positive charges. The association of DNA with histones produces a complex called chromatin.

Ribonucleic Acid (RNA)

There are two important differences between the primary structures of ribonucleic acid (RNA) and DNA:

(a) The monosaccharide unit in RNA is D-ribose.

(b) Both RNA and DNA contain the purine bases adenine (A) and guanine (G) and the pyrimidine base cytosine (C). As the fourth base, however, RNA contains uracil (U), whereas DNA contains thymine (T).

The Genetic Code

The genetic code consists of nucleosides in groups of three; that is, it is a triplet code. Only 61 triplets code for amino acids; the remaining three code for the termination of polypeptide synthesis.

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KEY CONCEPTS AND EQUATIONS

Nucleic acids *(section 25.1)*

These consist of pyrimidine and purine bases, ribose or 2-deoxyribose, and phosphate.

Base pairing *(section 25.2)*

In DNA and RNA, G (guanine) pairs with C (cytosine).

In DNA, A (adenine) pairs with T (thymine); in RNA, A pairs with U (uracil).

The genetic code *(section 25.4)*

This describes the correspondence between nucleic acid sequences and the resultant polypeptide sequences. DNA is transcribed to mRNA, which is then translated to protein via tRNA, which matches codons to amino acids.

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REVIEW QUESTIONS

Nucleosides and Nucleotides

25.1 Write the names and structural formulae of the five nitrogen bases found in nucleosides.

25.2 Write the names and structural formulae of the two sugars found in nucleosides.

25.3 Explain the difference in structure between a nucleoside and a nucleotide.

The Structure of Deoxyribonucleic Acid (DNA)

25.4 What are the principal structural differences between DNA and RNA?

25.5 List the compositions, abbreviations and structures of the various nucleotides in DNA.

25.6 Write a structural formula for a segment of a polynucleotide with four nucleotides.

25.7 List the postulates of the Watson–Crick model of DNA secondary structure.

25.8 What is meant by the term ‘complementary bases’?

25.9 Describe the differences between A-DNA, B-DNA and Z-DNA.

Ribonucleic Acid (RNA)

25.10 Describe the differences between mRNA, tRNA and rRNA.

25.11 List the compositions, abbreviations and structures of the various nucleotides in RNA.

25.12 Explain the difference between the coding strand and the template strand during mRNA synthesis.

The Genetic Code

25.13 What is the genetic code?

25.14 Describe and illustrate the replication process of DNA.

25.15 Why are at least three nucleotides needed for one unit of the genetic code?

25.16 Briefly outline the biosynthesis of proteins, starting from DNA.

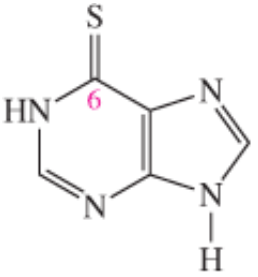
25.17 In protein synthesis, how does termination differ from elongation?

25.18 How does a codon differ from an anticodon?

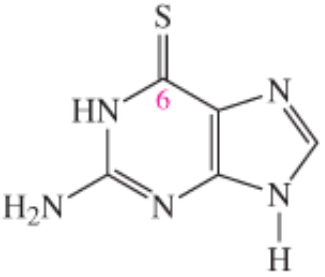
25.19 What is reverse transcription?

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25.20 Two drugs used in the treatment of acute leukaemia are 6-mercaptopurine and 6-thioguanine.



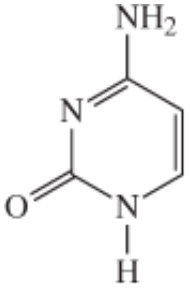
6-mercaptopurine



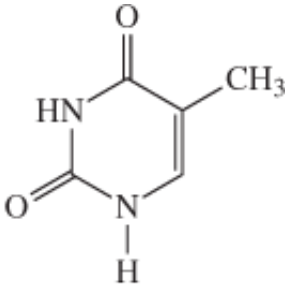
6-thioguanine

Note that, in each of these drugs, the oxygen atom at C(6) of the parent molecule is replaced by divalent sulfur. Draw structural formulae for the enethiol (the sulfur equivalent of an enol) forms of 6-mercaptopurine and 6-thioguanine. Show that they can form 10-electron aromatic systems.

25.21 The following are structural formulae for cytosine and thymine.



cytosine (C)



thymine (T)

Draw two additional tautomeric enol forms for cytosine and three for thymine. Show the 6-electron aromatic system.

25.22 Indicate whether each functional group of the five bases in nucleic acids can function as a hydrogen bond acceptor (A), hydrogen bond donor (D) or both (A/D).

25.23 Using the A, D and A/D designation from question 25.22, indicate how base pairing would be affected if the bases existed in the enol forms.

25.24 Draw structural formulae for nucleosides composed of:

(a) β-D-ribose and adenine

(b) β-2-deoxy-D-ribose and cytosine.

25.25 Nucleosides are stable in water and in dilute base. In dilute acid, however, the glycosidic bond of a nucleoside undergoes hydrolysis to give a pentose and a heterocyclic aromatic amine base. Propose a mechanism for this acid-catalysed hydrolysis.

25.26 Draw a structural formula for each of the following nucleotides and estimate its net charge at pH 7.4, the pH of blood plasma.

(a) 2′-deoxyadenosine 5′-triphosphate (dATP)

(b) guanosine 3′-monophosphate (GMP)

(c) 2′-deoxyguanosine 5′-diphosphate (dGDP)

25.27 Cyclic adenosine monophosphate (AMP), first isolated in 1959, is involved in many diverse biological processes as a regulator of metabolic and physiological activity. In this compound, a single phosphate group is esterified with both the 3′ and 5′ hydroxyls of adenosine. Draw the structural formula of cyclic-AMP.

25.28 Why are deoxyribonucleic acids called acids? What are the acidic groups in their structure?

25.29 Why are the pyrimidine and purine bases in nucleosides called bases? What are the basic groups in their structure?

25.30 Human DNA is approximately 30.4% A. Estimate the percentages of G, C and T and compare them with the values presented in table 25.2.

25.31 Explain why the ratio of thymine to adenine in DNA is 1 : 1, but the ratio of adenine to cytidine is not necessarily 1 : 1.

25.32 Which of the following pairs of nucleotides are present in DNA in equal amounts?

(a) TA and AT

(b) GT and CA

(c) AT and CG

(d) CA and TG

(e) GG and CC

(f) CG and GT

(g) AA and GG

(h) AC and TG

25.33 Draw a structural formula for the DNA tetranucleotide 5′-AGCT-3′. Estimate the net charge on this tetranucleotide at pH 7.0. What is the complementary tetranucleotide of this sequence?

25.34 Draw in detail the structure of a section of RNA four residues long that has the sequence 5′-GCUA-3′. Label the 5′ and 3′ ends.

25.35 The Watson–Crick model is based on certain experimental observations of base composition and molecular dimensions. Describe these observations and show how the model accounts for each.

25.36 Compare the α-helix of proteins and the double helix of DNA in terms of:

(a) the units that repeat in the backbone of the polymer chain

(b) the projection in space of substituents along the backbone (the R groups in the case of amino acids; purine and pyrimidine bases in the case of double-stranded DNA) relative to the axis of the helix.

25.37 Discuss the role of hydrophobic interactions in stabilising double-stranded DNA.

25.38 Name the type of covalent bond(s) joining monomers in each of the following biopolymers.

(a) polysaccharides

(b) polypeptides

(c) nucleic acids

25.39 At elevated temperatures, nucleic acids become denatured; that is, they unwind into single-stranded DNA. Account for the observation that shorter DNA strands generally undergo denaturation at lower temperature than longer strands.

25.40 The stability of a DNA double helix can be determined by its melting temperature, T_m, which is defined as the temperature at which 50% of the double helix is dissociated into individual strands.

(a) Why does the double helix formed between polydeoxyadenylic acid (poly-A) and polydeoxythymidylic acid (poly-T) have a T_m of only 68 °C, but the double helix formed between polydeoxyguanylic acid (poly-G) and polydeoxycytidylic acid (poly-C) has a T_m of 91 °C?

(b) Which of human adenovirus I (T_m = 58.5 °C) and fowl pox virus (T_m = 35 °C) has the higher ratio of (G + C) to (A + T)? Explain.

25.41 Write the DNA complement of 5′-ACCGTTAAT-3′. Label the 5′ and 3′ ends of the complement

strand.

25.42 Write the DNA complement of 5′-TCAACGAT-3′. Label the 5′ and 3′ ends of the complement strand.

25.43 Compare the degree of hydrogen bonding in the base pair A-T found in DNA with that in the base pair A-U found in RNA.

25.44 Compare DNA and RNA in terms of each of the following.

(a) monosaccharide units

(b) principal purine and pyrimidine bases

(c) primary structure

(d) location in the cell

(e) function in the cell

25.45 Which type of RNA has the shortest lifetime in cells?

25.46 Write the mRNA complement of 5′-ACCGTTAAT-3′. Label the 5′ and 3′ ends of the complement strand.

25.47 Write the mRNA complement of 5′-TCAACGAT-3′. Label the 5′ and 3′ ends of the complement strand.

25.48 The genetic code is degenerate. What does this mean?

25.49 Aspartic acid and glutamic acid have carboxyl groups on their side chains and are called acidic amino acids. Compare the codons for these two amino acids.

25.50 Compare the structural formulae of the aromatic amino acids phenylalanine and tyrosine. Compare their codons.

25.51 Glycine, alanine and valine are classified as nonpolar amino acids. Compare their codons. What similarities and differences do you find?

25.52 The codons CUU, CUC, CUA and CUG all code for the amino acid leucine. In this set, the first and second bases are identical, and the identity of the third base is irrelevant. For which other sets of codons is the third base irrelevant, and for which amino acid(s) does each set code?

25.53 Compare the amino acids coded for by the codons with a pyrimidine, either U or C, as the second base. Do the majority of the amino acids specified by these codons have hydrophobic or hydrophilic side chains?

25.54 Compare the amino acids coded for by the codons with a purine, either A or G, as the second base. Do the majority of the amino acids specified by these codons have hydrophilic or hydrophobic side chains?

25.55 What polypeptide is coded for by this mRNA sequence?

$$5' - GCU - GAA - GUC - GAG - GUG - UGG - 3'$$

25.56 The alpha chain of human haemoglobin has 141 amino acids in a single polypeptide chain. Calculate the minimum number of bases on DNA necessary to code for the alpha chain. Include in your calculation the bases necessary for specifying the termination of polypeptide synthesis.

25.57 There is evidence that alkylation of the oxygen atom at position 4 in thymine is a mutagenic event leading to cancer.

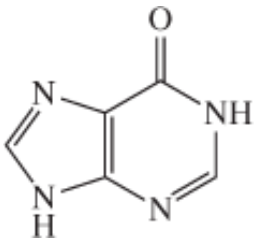
(a) Draw the structure of thymine after *O*-4 methylation.

(b) Explain why *O*-4 alkylation at thymine would disrupt Watson– Crick base pairing.

25.58 Spontaneous mutations can occur during the process of replication by improper base pairing, as shown in question 25.57. If tautomerisation of guanine (see p. 1088) occurs at a particular moment of replication, thymine instead of cytosine could be introduced to the complementary DNA strand. What error would this new DNA strand introduce into *its* complementary strand

during replication?

25.59 Genetic mutations can be caused by chemicals. Nitrous acid, HNO_2, is one of the most potent mutagens; it reacts with and ultimately removes amino groups in cytosine, adenine and guanine. Treatment of adenine with HNO_2 leads to the following modified base:



This modified base has been shown to pair with cytosine. Write a structural formula showing the hydrogen bonds in this base pair.

25.60 Sickle-cell anaemia is caused by replacement of the amino acid glutamic acid by valine in the 6 position of the β-chain in the human haemoglobin HbS.

(a) List the two codons for glutamic acid and the four codons for valine.

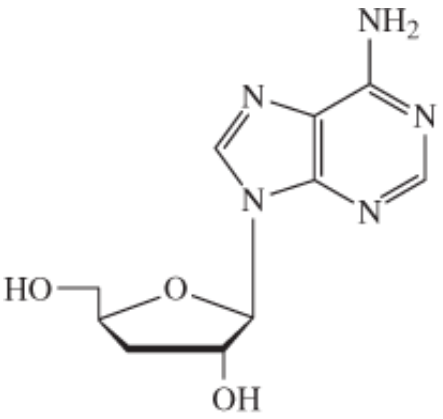
(b) Refer to questions 25.57 to 25.59 to explain how an error of a single base in each strand of DNA could bring about this amino acid error.

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25.61 The loss of three consecutive units of T from the gene that codes for CFTR, a transmembrane conductance regulator protein, results in the disease known as cystic fibrosis. Which amino acid is missing from CFTR to cause this disease?

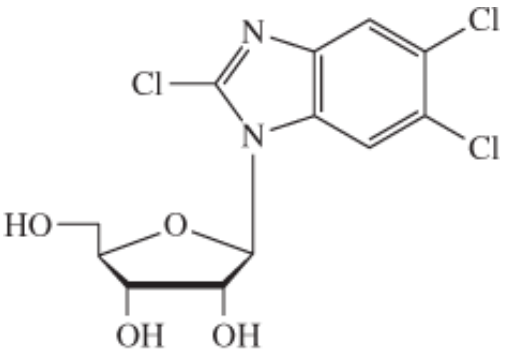
25.62 The following compounds have been studied as potential antiviral agents:

(a)



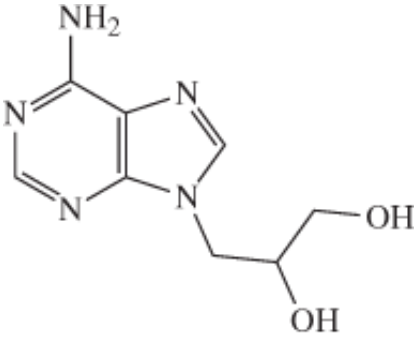
cordycepin (3′-deoxyadenosine)

(b)



2,5,6-trichloro-1-(β-D-ribofuranosyl) benzimidazole

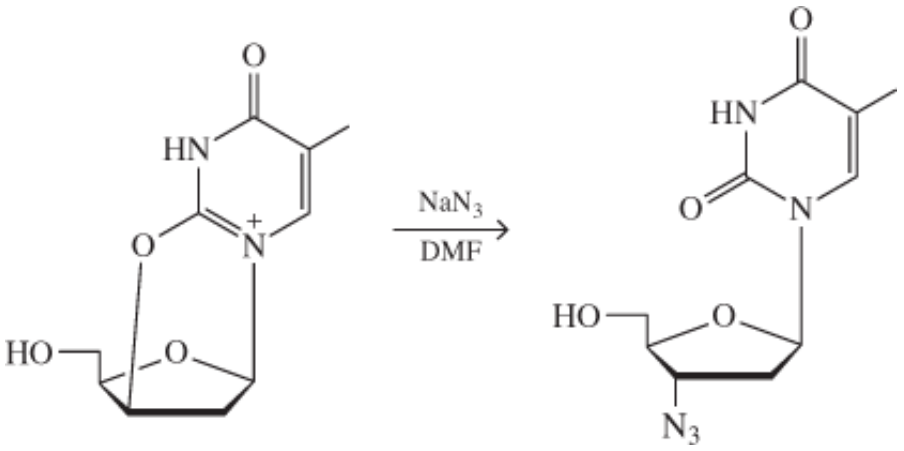
(c)



9-(2,3-dihydroxypropyl) adenine

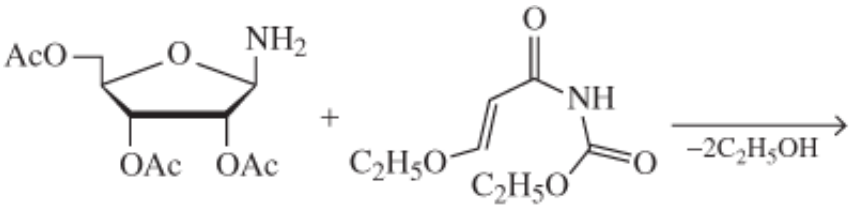
Suggest how each of these compounds might block the synthesis of RNA or DNA.

25.63 One synthesis of zidovudine (AZT) involves the following reaction (DMF is the solvent *N*, *N*-dimethylformamide):



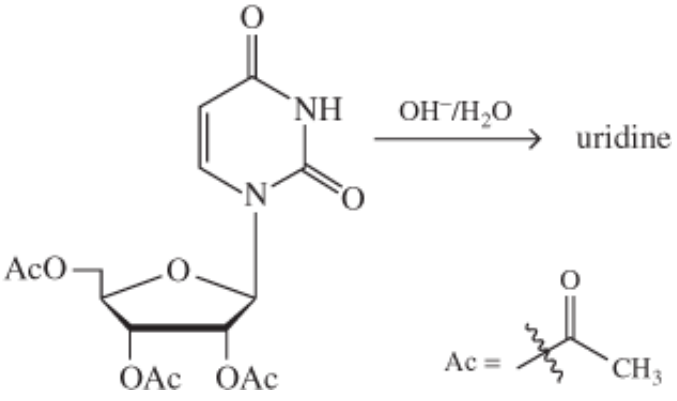
What type of reaction is this?

25.64 Many methods have been developed for the laboratory synthesis of nucleosides from the constituent sugars and bases or their respective precursors. One technique involves formation of the heterocyclic base through condensation on a ribosylamine derivative (in which the hydroxyl groups are protected with acetyl groups). Propose the mechanism for the first step in the uridine synthesis shown below.



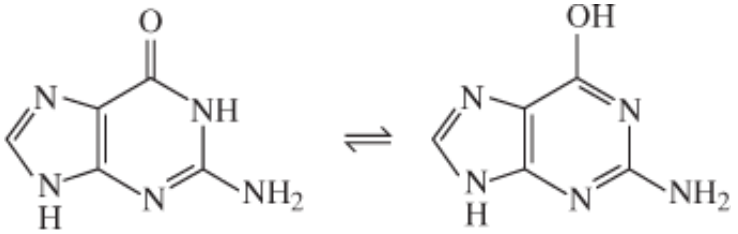
2,3,5-tri-*O*-acetyl-β-D-ribofuranosylamine

β-ethoxy-*N*-ethoxy carbonylacrylamide



25.65 Besides the normal Watson–Crick base pairing, which leads to the pairs C-G and A-T, several non-Watson–Crick pairs, such as U-G and U-A, are also possible. Write structural formulae showing the hydrogen bonds in the so-called *wobble pairs*, U-G and U-A.

25.66 As shown in section 25.1 (p. 1088), the most stable form of guanine is the lactam form. If guanine tautomerises to the abnormal lactim form, it pairs with thymine rather than cytosine. Write structural formulae showing the hydrogen bonds in this abnormal base pair.



lactam form lactim form

25.67 Show the errors that the conversion of adenine into the modified base shown in question 25.59 would generate in DNA through two replications.

25.68 Consider the following hexapeptide:

ala–val – trp – lys – gly – cys

(a) Using the first codon given for each amino acid in table 25.4, write the base sequence of mRNA that would translate into this hexapeptide.

(b) What base sequence in DNA would transcribe a synthesis of the mRNA in (a)?

(c) What anticodons would appear in the tRNAs involved in the synthesis of this hexapeptide?

25.69 The following base sequences are found in segments of DNA.

(a) 5′ -AUGCCCAGAACAAGC-3′

(b) 5′ -CTAAGCACTTCGGGGCCG-3′

(c) 5′ -TTTTATGGCGCTTAC-3′

i. Which bases would appear in the mRNA transcribed from these segments?

ii. If the first base is the beginning of a codon, write the primary structure of the polypeptides synthesised along these segments.

25.70 Consider an mRNA strand with the following sequence:

5′ – AAAAUGGAUCAAUAUUUUUGGGGG – 3′

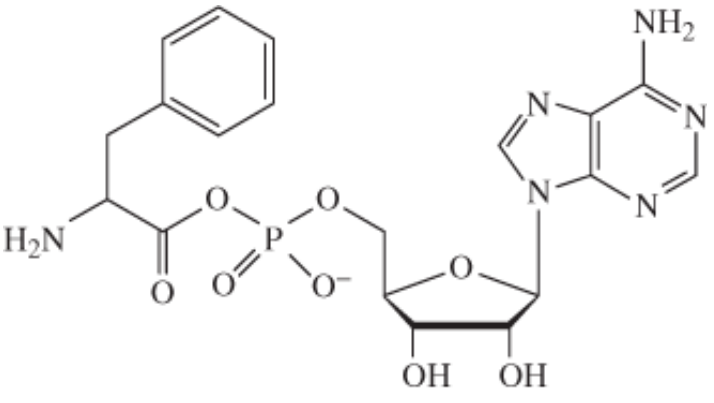
(a) What is the amino acid sequence of a peptide coded by this mRNA strand.

(b) Write the sequence of the DNA from which the mRNA is transcribed.

(c) What would be the translation product resulting from a single mutation that changes U to A at position 15 from the 5′ end?

25.71 Mutations in DNA can occur when one base is substituted by another or when an extra base is inserted into the DNA strand. Why is an insertion mechanism potentially more harmful than a substitution mutation?

25.72 In protein biosynthesis, amino acids are coupled to tRNAs to form aminoacyl–tRNA complexes using ATP. This is usually a two-step process; in the first step, an aminoacyl adenylate is formed.



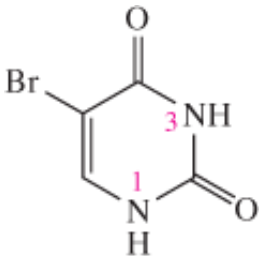
an aminoacyl adenylate

For this compound, identify the ribose sugar, the nucleic acid base, the amino acid and the phosphate group. By which functional group is the amino acid linked to the rest of the molecule?

25.73 If a peptide is synthesised from the following codons, how many carboxylate groups would be present?

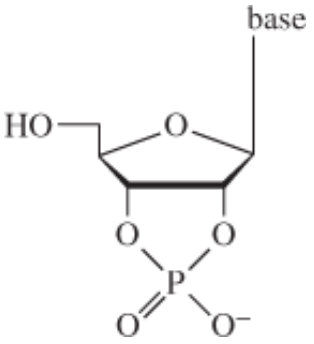
5′ – UAAGAGGCACAGGAUAUC – 3′

25.74 The highly mutagenic compound 5-bromouracil is used in cancer chemotherapy. After administration, it is ultimately incorporated into DNA in place of thymine. Why does it cause mutations? (*Hint:* The bromo- substituent increases the stability of the lactim tautomer.)



5-bromouracil

25.75 Hydrolysis of RNA gives the 2′,3′-cyclic phosphodiester shown below. When this cyclic phosphodiester reacts with water, a mixture of 2′- and 3′-phosphates is obtained. Propose a mechanism for this reaction.



25.76 Using the single-letter abbreviations for the amino acids in table 24.1 on p. 1057, write the sequence of amino acids in a pentapeptide represented by the first five different letters (which are assigned to amino acids) in your name or town. Don't use any letter more than once. Write a sequence of bases in mRNA that would result in the synthesis of that polypeptide. Write the base sequence on the sense strand of DNA that would result in formation of that fragment of mRNA.

25.77 Consider the following piece of mRNA:

$$5' - \text{GUUCACACGGACAUCCUAAAAACC} - 3'$$

(a) What octapeptide is coded for by this piece?

(b) What would the *N*-terminal amino acid be if the codon at the 5′ end underwent the following mutations: (i) the first base is changed to A, (ii) the second base is changed to A, (iii) the third base is changed to A, (iv) the third base is changed to C?

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KEY TERMS

3′ end
5′ end
A-DNA
acceptor stem
anticodon
antisense strand
B-DNA
chromatin
circular DNA
coding strand
codon
DNA
DNA ligase
DNA polymerase
double helix
genetic code
histone
messenger RNA (mRNA)
nucleic acid
nucleoside
nucleosome
nucleotide
Okazaki fragments
primary (1°) structure
primase
replication fork
retrovirus
reverse transcriptase
reverse transcriptase inhibitor
ribosomal RNA (rRNA)
ribosome
RNA
secondary (2°) structure
sense strand
supercoiling
superhelical twist
template strand
tertiary (3°) structure
transcription
transfer RNA (tRNA)
Z-DNA

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CHAPTER

26 Polymers

Australia has one of the harshest climates in the world. In summer, the temperature on the roofs of houses can reach 95 °C, which puts a lot of stress on the roofing material, especially the coatings present on a metal roof. This challenges scientists to develop paint materials that can withstand high temperatures and intense UV radiation without any measurable degradation or discolouration over many decades.

As part of the search for new materials, scientists have made increasing use of organic chemistry to prepare synthetic materials known as polymers. The versatility afforded by these polymers allows the creation and fabrication of materials with ranges of properties unattainable in materials such as wood, metals and ceramics. Deceptively simple changes in the chemical structure of a polymer can change its mechanical properties, for example, from those of something to wrap your lunch in to those of a bulletproof vest. Furthermore, structural changes can introduce properties never before imagined. For example, using well-defined organic reactions, chemists can turn one type of polymer into an insulator, such as that used to make the sheath that surrounds electrical cords; if treated differently, the same polymer becomes an electrical conductor with conductivity nearly equal to that of metallic copper.

Polymer technology has created the water-based (latex) paints that have revolutionised the coatings industry, and plastic films and foams have done the same for the packaging industry. The list could go on and on as we think of the manufactured items everywhere around us in our daily lives.





Corbis

KEY TOPICS

26.1 The architecture of polymers
26.2 Polymer notation and nomenclature
26.3 Formation of polymers
26.4 Silicon polymers
26.5 Recycling plastics

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26.1 The Architecture of Polymers

Nearly all of the compounds that we have encountered so far have relatively low molar masses. However, many molecules in nature and in the synthetic world are made from hundreds or even thousands of atoms. Molecules with such a large molar mass (over 1000 g mol^{-1}) are called **macromolecules**. In previous chapters, we have seen examples of the three major classes of biological macromolecules; DNA (which stores genetic information, see chapter 25), RNA and proteins (which induce biochemical transformations, see chapter 24), and polysaccharides (which store energy and are used as structural materials, see chapter 22) are called **biopolymer**, since they are synthesised by organisms. The structure and properties of these biopolymers have been discussed in previous chapters. In this chapter, we will focus on synthetic macromolecules.

Synthetic compounds made of macromolecules are examples of the chemical conversion of ordinary feedstocks, such as coal, oil, water and air, into new materials with new properties and useful applications. For example, surfboards, parachutes, backpacking gear and all sorts of other recreational equipment derive their strength from macromolecules. Many materials made into thread and cloth consist of macromolecules, as do contact and artificial lenses, and fillings for teeth.

Some macromolecular substances have more structural order than others. A **polymer** is a macro molecular substance consisting of large amounts of small identical units, called **monomers**, which are linked. The process of linking monomers to form a polymer is called **polymerisation** (figure 26.1). Polymerisation of the smallest alkene, ethene (common name ethylene), gives the polymer polyethylene. It should be noted that, although the common name ‘ethylene’ is no longer used for ethene, the common name is retained in the polymer name. The same is the case for propene and butene (common names propylene and butylene) and their polymers polypropylene and polybutylene, respectively.

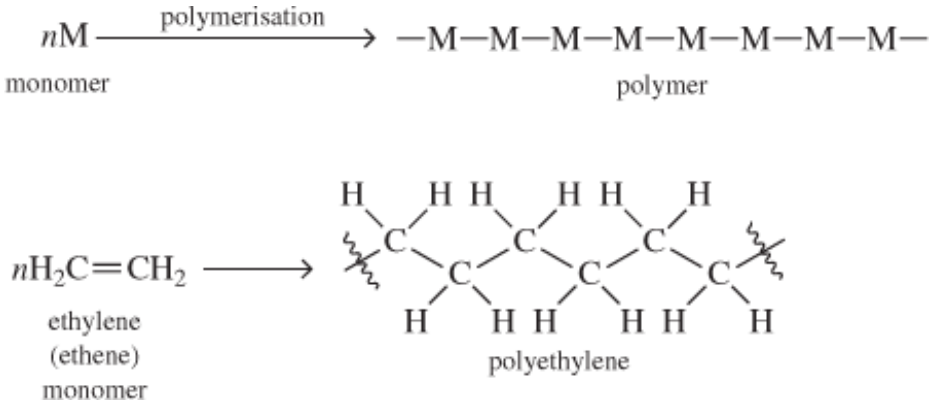


FIGURE 26.1 Polymerisation links monomers to form a polymer.

Because of their large size, the addition or removal of a few atoms or atom groups does not affect the properties of macromolecules. Polymers generally consist of many individual chains (see figure 26.5) of different lengths, and therefore different molecular masses, and so it is difficult to specify the molar mass of a polymer. With the exception of some biological molecules, macromolecules of a particular substance contain a distribution of molecular masses, usually forming a bell curve (figure 26.2). This means that some of the polymer chains are large, with high molecular masses, and appear on the right-hand side of the curve. Other polymer chains are much smaller with lower molecular masses, and are found on the left-hand side of the curve. Usually, most chain lengths are clumped around a central point, the highest point on the curve. This mass distribution, and hence the molar mass, depends on how the macromolecules are manufactured.

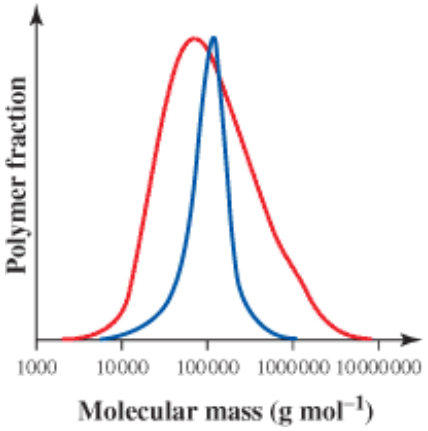


FIGURE 26.2 Comparison of the bell curves for two polymers with different molecular mass distributions. The red curve shows a polymer with a wide molecular mass distribution. The blue curve shows a polymer with a narrow molecular mass distribution.

It is quite remarkable that the existence of macromolecules was not demonstrated until the 1920s. Hermann Staudinger (1881–1965, figure 26.3), a German chemist who was awarded the Nobel Prize in chemistry in 1953, insisted that macromolecules are held together by covalent bonds, which are found in small molecules. It might sound strange today but, at that time, scientists thought that macromolecules could not be formed through normal chemical bonds but must be held together by other forces. We will come back to this in section 26.3.



FIGURE 26.3 Hermann Staudinger. SPL

The molar masses of polymers are generally higher than those of common organic compounds and typically range from 10 000 g mol^{-1} to more than 1 000 000 g mol^{-1}. The architectures of these macromolecules can be quite diverse; molecules can be linear or branched or have a comb, ladder or star structure (figure 26.4). Additional structural variations can be achieved by introducing covalent cross-links between individual polymer chains.

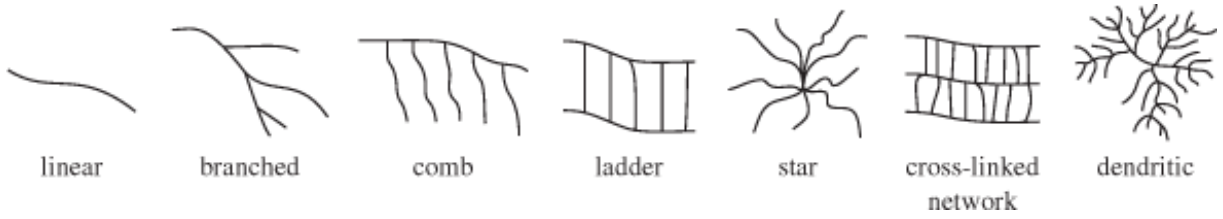


FIGURE 26.4 Various polymer architectures.

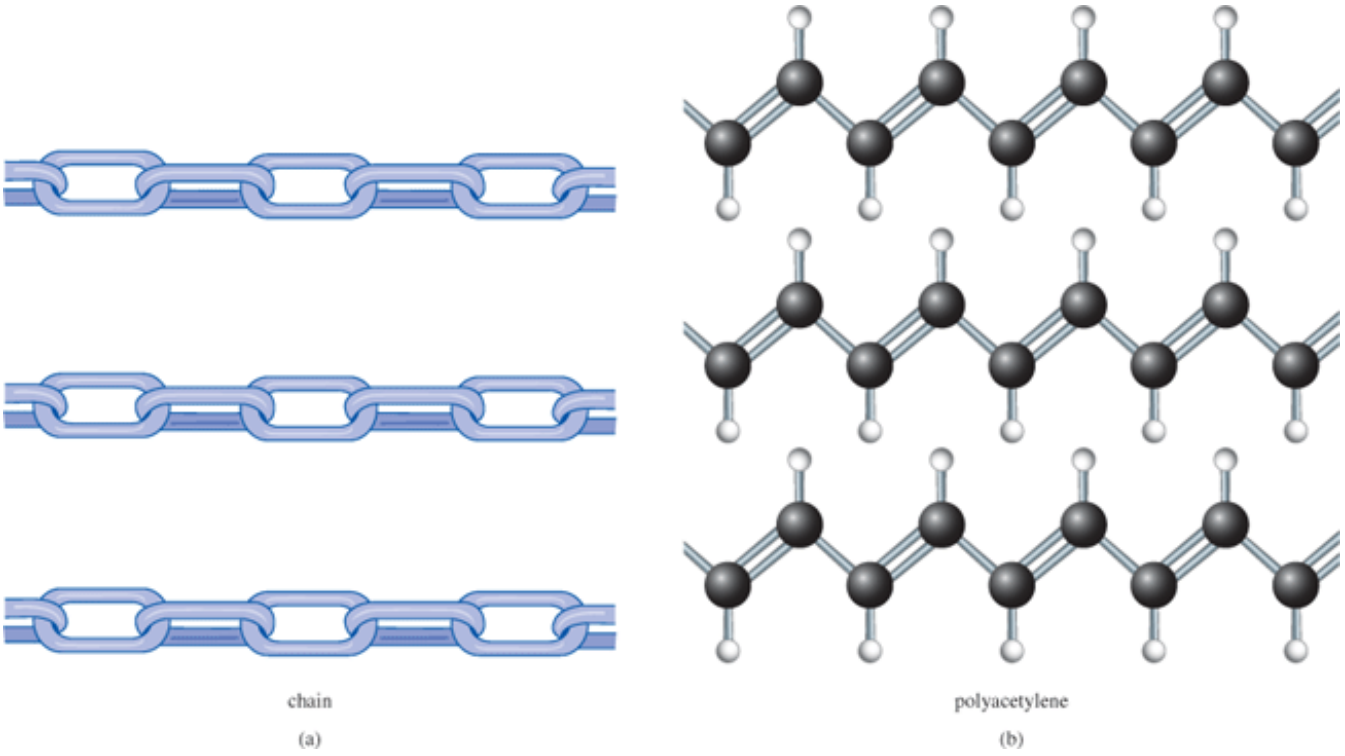


FIGURE 26.5 (a) A chain is a good model of a polymer, such as
(b) polyacetylene, which results from the polymerisation of ethyne (acetylene) monomers.

Linear and branched polymers made from hydrophobic monomers are often soluble in solvents such as chloroform, benzene, toluene, dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF). In addition, many linear and branched polymers can be melted to form highly viscous liquids. In polymer chemistry, the general term **plastic** describes any polymer that can be moulded, extruded or cast into various shapes. Plastics can be subdivided into thermoplastics and thermosetting plastics. **Thermoplastics** are polymers that, when melted, become sufficiently fluid that they can be moulded into shapes that are retained when they are cooled. Most thermoplastic materials are high-molar-mass polymers with chains that are associated by weak van der Waals forces (e.g. polyethylene), stronger dipole–dipole interactions and hydrogen bonding (e.g. nylons), or stacking of aromatic rings (so-called π stacking, e.g. polystyrene).

Thermosetting plastics (or thermosets) are polymers that cure by the addition of energy (as provided by heat, light or a chemical reaction) to a stronger form. This means that these materials can be moulded when they are first prepared but, once cooled, harden irreversibly and cannot be remelted. Examples of thermosets are epoxy resins (used as adhesives) and bakelite, a phenol–formaldehyde resin, the first plastic made from synthetic components, which is a non-conductive and heat-resistant material used in early telephone casings, electrical insulators, kitchenware, costume jewellery and toys. Because of their very different physical characteristics, thermoplastics and thermosets must be processed differently and are used in very different applications.

The most important properties of polymers at the molecular level are the size and shape of their chains. A good example of the importance of size is a comparison between paraffin wax, a natural polymer, and polyethylene, a synthetic polymer, both made from ethene (figure 26.1). These two distinct materials have identical **repeating units**, namely —CH_2—, but differ greatly in the size of their chains. Paraffin wax has between 25 and 50 carbon atoms per chain, whereas polyethylene has between 1000 and 3000 carbon atoms per chain. Paraffin wax, such as that used in birthday candles, is soft and brittle, but polyethylene,

used to make plastic beverage bottles, for example, is strong, flexible and tough. These vastly different properties arise directly from the difference in size of the individual polymer chains.

Polymers, like small organic molecules, tend to crystallise upon precipitation or as they are cooled from a molten state. However, their large size often hampers diffusion, and their sometimes complicated or irregular structures can prevent efficient packing of the chains. The result is that polymers in the solid state tend to be composed of both ordered **crystalline domains** (crystallites) and disordered **amorphous domain** (see figure 26.6). The relative amounts of crystalline and amorphous domains differ from polymer to polymer and frequently depend on how the material is processed. We often find high degrees of crystallinity in polymers with regular, compact structures and strong intermolecular forces, such as hydrogen bonding. The temperature at which crystallites melt is the **melt transition temperature (T_m)** of the polymer. As the degree of crystallinity of a polymer increases, its T_m increases. With an increase in crystallinity comes a corresponding increase in strength and stiffness. Examples of these polymers will be given later in this chapter.

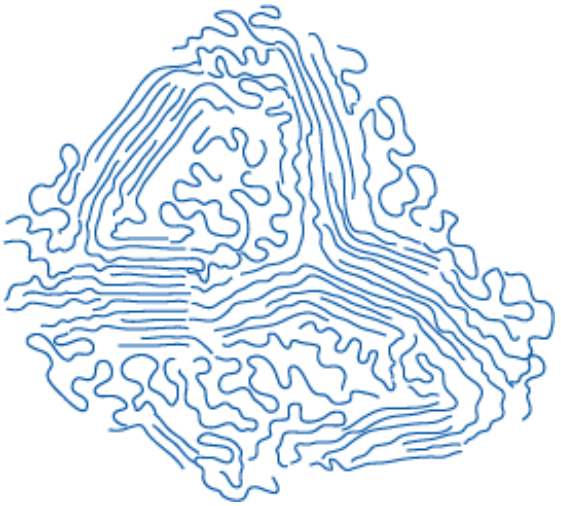


FIGURE 26.6 Representation of amorphous (irregular) and crystalline (regular) domains in a polymer.

Rubber materials, such as that used in rubber balls, are elastic and bounce at room temperature. Such polymers are called **elastomers** (elastic polymers). If such a rubber ball is cooled by placing it into liquid nitrogen (bp = -196 °C), the material is converted to a rigid, brittle (glassy) solid and all elastomeric properties are lost (figure 26.7). A poor understanding of this behaviour of elastomers contributed to the *Challenger* space shuttle disaster in 1986. The elas- *r* tomeric O-rings used to seal the solid booster rockets became brittle at around 0 °C. When the temperature dropped to an unanticipated low on the morning of the launch of the craft, the O-ring seals changed from elastomers to rigid glass, losing any sealing capabilities. The rest is tragic history. The physicist Richard Feynman demonstrated this dramatically in a famous televised hearing in which he put a *Challenger*-type O-ring in ice water and showed that its elasticity was lost.

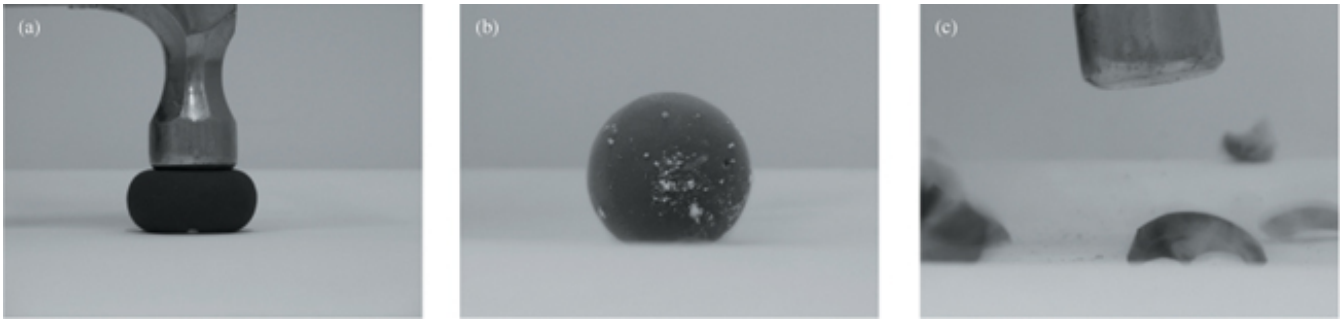


FIGURE 26.7 (a) A rubber ball is elastic at room temperature, as demonstrated by the deformation when the ball is struck with a hammer.

(b) If the rubber ball is cooled by placing it into liquid nitrogen, the material is converted to a rigid brittle (glassy) solid and

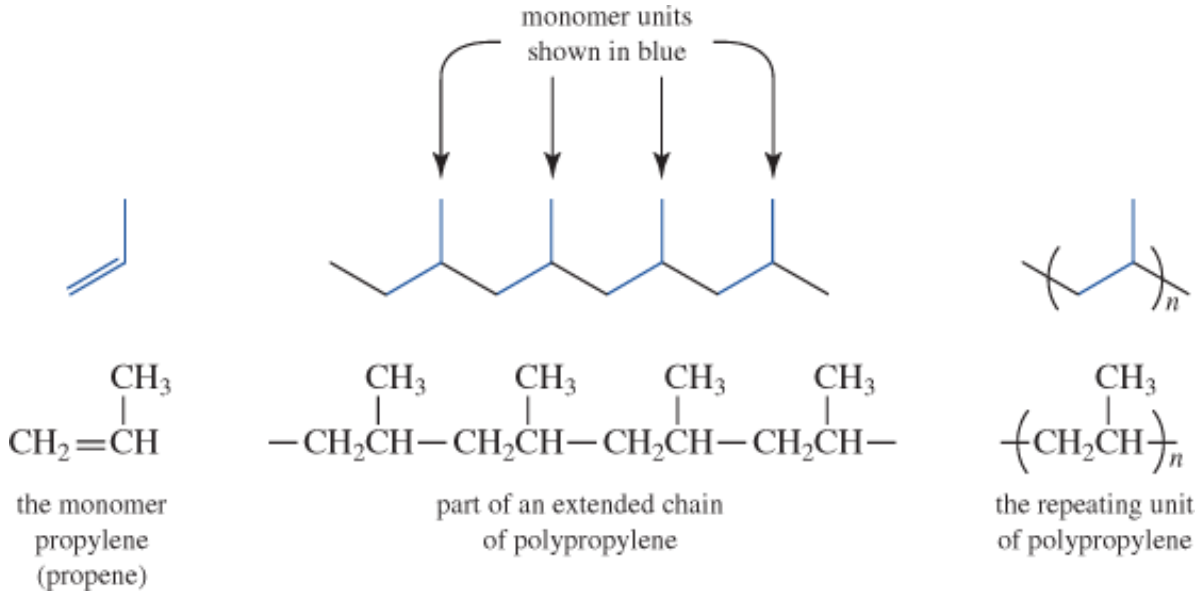
(c) all elastomeric properties are lost.

Allan Blackman

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26.2 Polymer Notation and Nomenclature

We typically show the structure of a polymer by placing parentheses around the repeating unit, which is the smallest molecular fragment that contains all the structural features of the monomer. A subscript *n* placed outside the parentheses indicates that the unit repeats *n* times. Thus, we can reproduce the structure of an entire polymer chain by repeating the enclosed structure in both directions. An example is polypropylene, which is derived by the polymerisation of propene. Polypropylene is a polymer with many uses, including dishwasher-safe food containers, indoor– outdoor carpeting and artificial turf.



Chemistry Research

Multi-functional Materials

Professor Craig Hawker, Director, Materials Research Laboratory, University of California, Santa Barbara

While nature has used molecular engineering on the nanoscale for billions of years, only recently have chemists been able to crudely mimic nature's perfection. Even with these tentative steps, significant progress and new discoveries have had an impact on our daily lives. By varying the three-dimensional structures and positions of functional groups, synthetic chemists have developed the ability to accurately control the physical properties of both small molecules and macromolecules, as well as to control their interactions with biological systems. Classical examples of the use of nanotechnology include the design of volatile esters in the fragrance industry, with aromas directly related to molecular shape/size, and the discovery of numerous synthetic drugs. This general theme of property control through molecular design has found increasing attention and application in polymer science in recent years and is the prime focus of the research group led by Craig Hawker, a University of Queensland graduate.

Traditionally, small changes in structure have been shown to have dramatic effects on the properties of polymers and one needs to look no further than poly(ethylene) and poly(propylene) to observe these effects, with poly(propylene) having a lower impact strength but superior working temperature and tensile strength than poly(ethylene). This allows polyethylene and polypropylene to be used in dramatically different applications. A major driving force behind this work is the realisation that many of the promising applications of

nanotechnology rely on extending synthetic organic chemistry into the nanometre-length scale, especially as nanodevices are designed with increasing sophistication. Therefore, the principle of controlling structure and functionality on the nanometre scale is applicable to these very different fields. As a result, creative approaches using synthetic chemistry are required to control every facet of macromolecular structure and to enable functional groups to be introduced at defined locations.

The Hawker research group designs multi-functional nanoscale materials for applications as diverse as the synthesis of nanoparticles for disease diagnosis and therapeutic treatment and the development of novel strategies for patterning silicon wafers at sub-20 nm dimensions for advanced microelectronic devices. The three-dimensional nanoparticles used for diagnostics and therapeutics have very specific and controlled surfaces, internal layers and cores (see figure 26.8). The surface of a ca. 50 nm nanoparticle is adorned with peptide ligands for specifically targeting the nanoparticles to the tissue of choice. The surface of the nanoparticles is also composed of poly(ethylene glycol) units to allow long circulation and residence times in the body without toxic or immunogenic responses. The internal layers have diagnostic units for imaging agents, such as Gd ions for magnetic resonance imaging (MRI) and ^{64}Cu for positron emission tomography (PET) imaging, while drug molecules can be attached or adsorbed to the internal layers or core. By precisely controlling all of these nanoscopic features, high-performance materials can be constructed that mimic many of the unique features of natural systems.

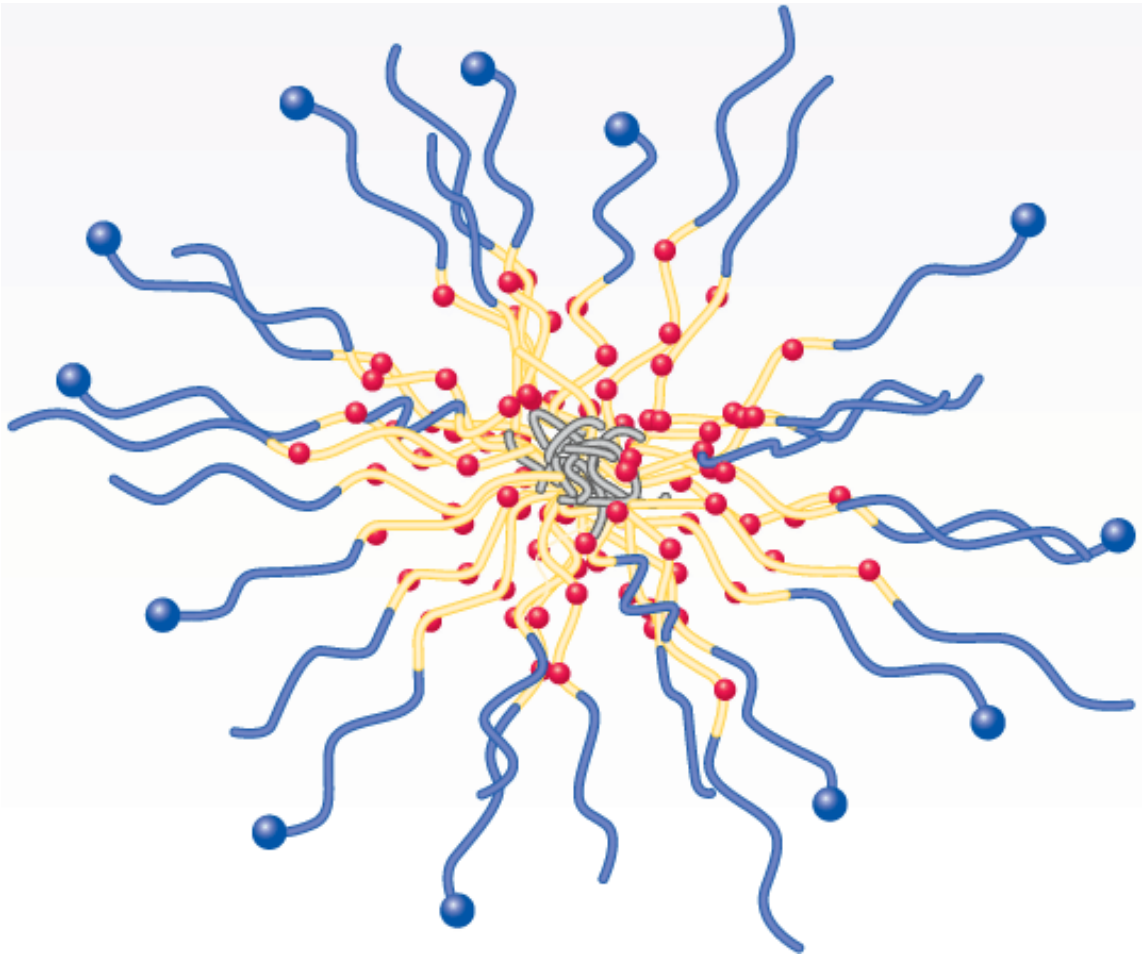


FIGURE 26.8 A schematic view of a functional nanoparticle. The core (grey), internal layers (yellow) and surface (blue) each performs a specific function within the nanosized molecular assembly. For example, the blue outer layers could be peptide-targeting groups, directing the nanostructure to specific cells where the internal (yellow) layers deliver a therapeutic drug.

The most common method of naming a polymer is to add the prefix *poly-* to the name of the monomer from which the polymer is synthesised. Examples are polyethylene and polystyrene. For more complex monomers or when the name of the monomer is more than one word (e.g. vinyl chloride), parentheses are used to enclose the name of the monomer:

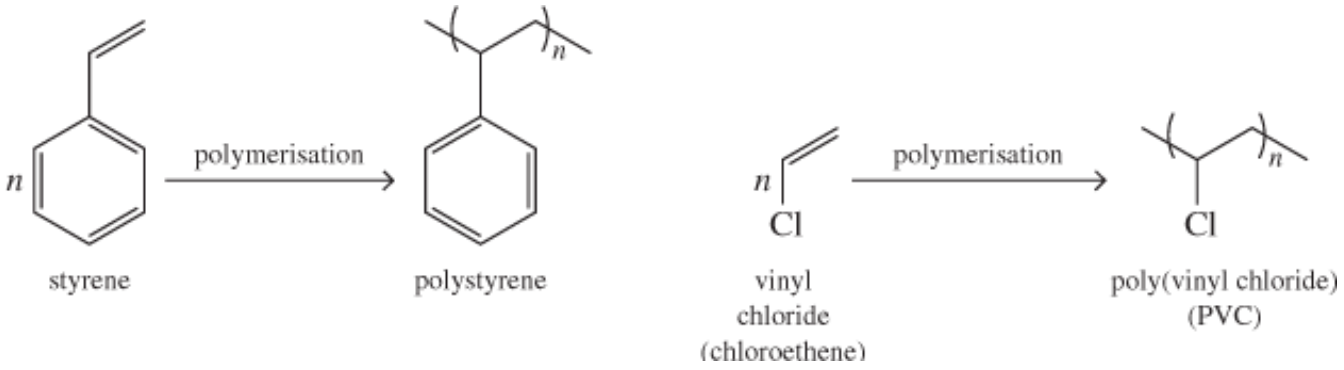


Table 26.1 gives some examples of polymers formed from compounds related to ethene, along with their common names and most important uses. Note that, while IUPAC generally encourages the use of systematic names, it retains some common names in polymer chemistry because of their establishment by usage. It is hoped, however, that common names for polymers are kept to a minimum for scientific communication.

TABLE 26.1 Polymers derived from ethene and substituted ethenes

Monomer formula	Common name (IUPAC name)	Polymer name(s); type; common uses
$CH_2{=}CH_2$	ethylene (ethene)	polyethylene, polythene (PE); thermoplastic polymer; break-resistant containers and packaging materials
$CH_2{=}CHCH_3$	propylene (propene)	polypropylene, Herculon (PP); thermoplastic polymer; textile and carpet fibres
$CH_2{=}CHCl$	vinyl chloride (chloroethene)	poly(vinyl chloride), PVC; thermoplastic polymer; construction and health care sector
$CH_2{=}CCl_2$	1,1-dichloroethylene (1,1-dichloroethene)	poly(1,1-dichloroethylene); thermoplastic polymer; cling film is a copolymer with vinyl chloride
$CH_2{=}CHCN$	acrylonitrile (propenenitrile)	polyacrylonitrile, Orolon®; acrylics and acrylates; nitrile rubber (Nipol®, Krynac® and Europrene®) is a copolymer with butan-1,3-diene
$CH_2{=}CF_2$	1,1-difluoroethylene (1,1-difluoroethene)	poly(1,1-difluoroethylene); thermoplastic polymer; piezo-electric material, headphone membranes
$CF_2{=}CF_2$	tetrafluoroethylene (tetrafluoroethene)	poly(tetrafluoroethylene), PTFE; thermoplastic polymer; Teflon®, nonstick coatings
$CH_2{=}CHC_6H_5$	styrene	polystyrene, Styrofoam®; thermoplastic polymer; insulating materials
	ethyl acrylate	poly(ethyl acrylate); moderately thermoplastic

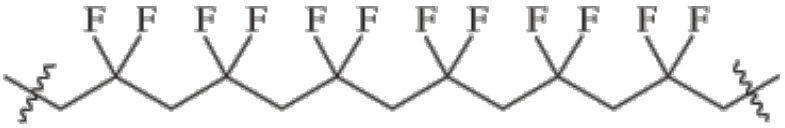
$CH_2{=}CHCOCH_2CH_3$	(ethyl propenoate)	polymer; latex paints
$CH_2{=}C(CH_3)COCH_3$	methyl methacrylate (methyl 2-methylpropenoate)	poly(methyl methacrylate), Lucite®, Plexiglas®; thermoplastic polymer; glass substituent

Polymers can be derived by polymerisation of only one monomer (these are often called homopolymers) or by polymerisation of two or more different monomers (copolymers). For example, a copolymer consisting of the monomer units A and B can have an **alternating** arrangement (—A—B—A—B—A—B—) or a **statistical** arrangement (—A—A—A—B—A— B—B—A—B—A—A—). **block** copolymers consists of two or more homopolymer subunits (—A—A—A—B—B—B—B—A—A—A—B—B—B—).

WORKED EXAMPLE 26.1

Writing the Formula for a Polymer

Given the following structure, determine the polymer's repeating unit:



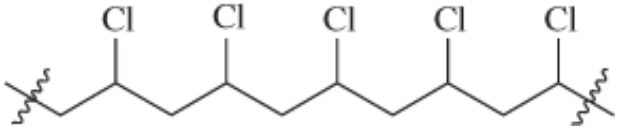
Redraw the structure using the simplified parenthetical notation and name the polymer.

Analysis and solution

The repeating unit is —(CH_2CF_2)— and the polymer is written —(CH_2CF_2)$_n$—. The repeating unit is derived from 1,1-difluoroethylene and the polymer is named poly(1,1-difluoroethylene).

PRACTICE EXERCISE 26.1

Given the following structure, determine the polymer's repeating unit:



Redraw the structure using the simplified parenthetical notation and name the polymer.

The discovery of Teflon (PTFE) can be dated back to 6 April 1938. DuPont chemist Dr Roy J Plunkett,

as DuPont's Jackson Laboratory in New Jersey, was checking a frozen, compressed sample of tetrafluoroethylene, when he and his associates discovered that the sample had polymerised spontaneously into a white, waxy solid, which was polytetrafluoroethylene (PTFE).

This discovery was an example of serendipity and is considered as one of science's top 10 accidental inventions. PTFE has revolutionised the plastics industry. Industrial coatings of PTFE can be used on carbon steel, aluminium, stainless steel, steel alloys, brass and magnesium, as well as nonmetals such as glass, fibreglass and some rubber and plastics. The versatility of these coatings allows application to an almost unlimited variety of sizes and configurations. One of the most widespread examples of this is possibly the nonstick frypan.

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26.3 Formation of Polymers

There are two main ways that monomers are joined to form polymers. One process is called **condensation** or **step-growth polymerisation**, in which a small molecule is usually eliminated when the two monomer units are joined. The other process is called **addition** or **chain-growth polymerisation**, in which monomer units are joined without the loss of atoms.

Condensation or Step-growth Polymers

Step-growth polymers are formed by the reaction between difunctional molecules (which have two functional groups of the same or different types) with each new bond created in a separate step. During polymerisation, monomers react to form dimers, dimers react with monomers to form trimers, dimers react with dimers to form tetramers, and so on. Although a small molecule is usually eliminated when the various units are joined together, this does not happen in all polymerisations of this type. However, because of their usually similar mechanism, they are all called condensations.

There are two common types of step-growth processes: (1) reaction between A—M—A and B—N—B type monomers to give — (A—M—A—B—N—B)$_n$— polymers and (2) the self-condensation of A—M—B monomers to give — (A—M—B)$_n$— polymers. In this notation, 'M' and 'N' indicate the monomer, and 'A' and 'B' the reactive functional groups on the monomer. In each type of step-growth polymerisation, an A functional group reacts exclusively with a B functional group, and a B functional group reacts exclusively with an A functional group. New covalent bonds in step-growth polymerisations are generally formed by reactions between A and B functional groups: for example, nucleophilic substitution at an acyl group (see chapter 23). After polymensation, the ends of the chain remain active. In this section, we discuss five types of step-growth polymers: polyamides, polyesters, polycarbonates, polyurethanes and epoxy resins. The molecular mass of the polymer is usually controlled by the reaction time, i.e. the longer the reaction, the higher is the molecular mass.

Polyamides

In the early 1930s, Wallace H Carothers (figure 26.9) and his co-workers at E.I. DuPont de Nemours & Company in the USA began fundamental research into the reactions between dicarboxylic acids and diamines to form **polyamides**. To put their research into historical context, as mentioned earlier, at that time the chemical reactions used to synthesise polymers such as polystyrene and poly(vinyl chloride) were not well understood by organic chemists. There was an ongoing scientific argument about the question: Which forces hold the monomer units together in the polymer? It was believed until the first few decades of the twentieth century that large mol ecules could not be bound by normal chemical bonds as in small molecules. Therefore, researchers at DuPont wanted to synthesise polymers using widely understood chemical reactions, such as those between acids and amines to give amides, or between acids and alcohols to give esters. Thus, in 1934, they synthesised the first fully synthetic commercial fibre, nylon 6,6, a polyamide, so named because it is produced from two different monomers, each containing six carbon atoms.

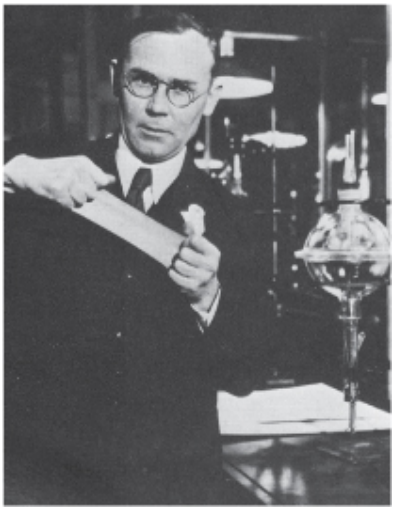


FIGURE 26.9 Wallace H Carothers.
Photo Researchers

In the synthesis of nylon 6,6, adipic acid (1,6-hexanedioic acid) and hexane-1,6-diamine are dissolved in aqueous ethanol, in which they react in an acid–base reaction to form a one-to-one salt called *nylon salt* (figure 26.10). This salt is then heated in an autoclave to 250 °C and an internal pressure of 15×10^5 Pa. Under these conditions, $—COO^-$ groups from the diacid and $—NH_3^+$ groups from the diamine react with the loss of H_2O to form an amide bond. Because water is released, this type of reaction is called a condensation. As you can see, the amide bond that holds the monomer units together is the same bond that holds the amino acids together in simple amides and peptides (see section 24.3). Nylon 6,6 formed under these conditions melts at 250 to 260 °C and has a molar mass ranging from 10 000 to 20 000 g mol^{-1}. The difference between peptides and polyamides is that the amide bonds in peptides are separated by only one carbon atom, whereas, in polyamides, the amide bonds are separated by more than one carbon atom.

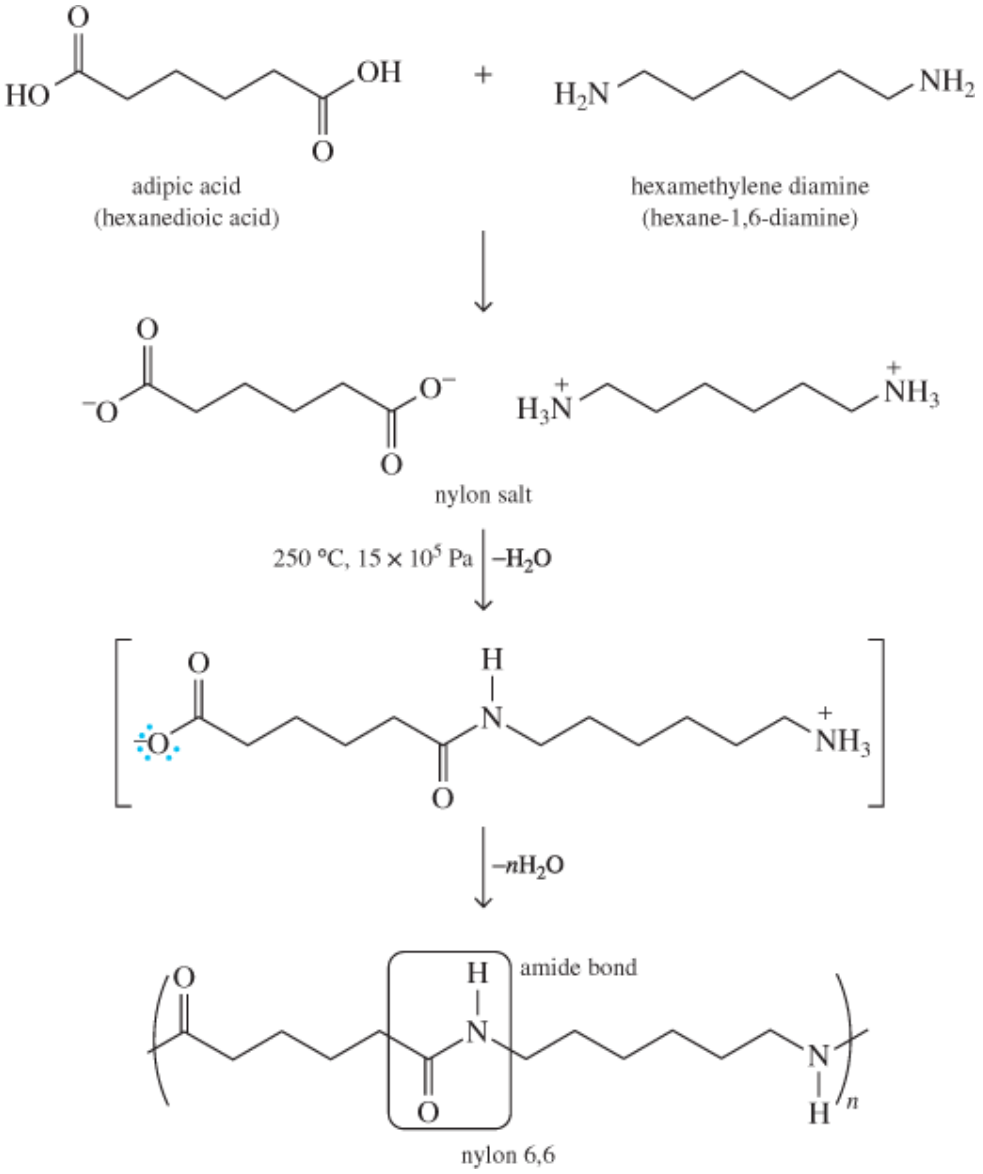
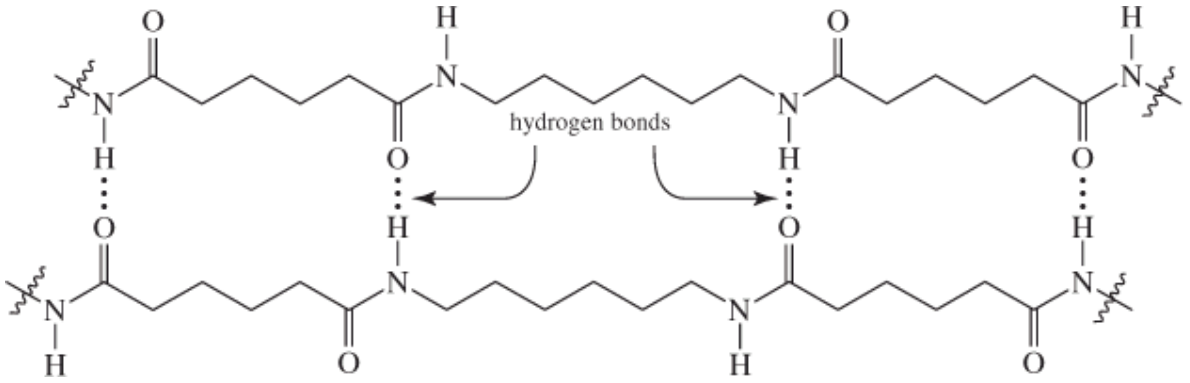


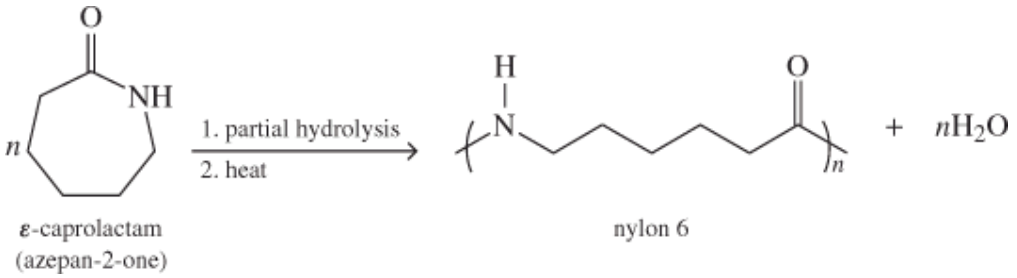
FIGURE 26.10 The formation of nylon 6,6.

In the first stage of fibre production, crude nylon 6,6 is melted, spun into fibres and cooled. Next, the melt-spun fibres are *cold drawn* (drawn at room temperature) to about four times their original length to increase their degree of crystallinity. How does this work? In the molten stage, the nylon 6,6 molecules are in disarray, tangled with one other. When the nylon is drawn, the individual polymer molecules are lined up and become oriented in the direction of the fibre axis, enabling hydrogen bonds to form between carbonyl oxygen atoms of one chain and amide hydrogen atoms of another chain (see section 6.8):



The regular arrangement of the chains enforced by hydrogen bonding between the many amide groups along the aligned chains (which are similar to the hydrogen bonds in peptides) encourages crystallisation to take place. This gives strength and stiffness to the nylon fibre and makes it an exceptionally strong material. Attempts to pull the fibres apart, either parallel or perpendicular to the stretch direction, must overcome the hydrogen bonds and the crystallisation forces, which both arise from the cold-drawing process of the melted polymer. Cold drawing has become an essential step in the production of most synthetic fibres.

The nylons are a family of polymers, the members of which have subtly different properties that make them suited to one use or another (figure 26.11). The two most widely used members of the family are nylon 6,6 and nylon 6. Nylon 6 is so named because it is synthesised from ε-caprolactam (azepan-2-one), a six-carbon monomer. In the synthesis of nylon 6, ε-caprolactam is partially hydrolysed to 6-aminohexanoic acid and then heated to 250 °C to bring about polymerisation:



ε-caprolactam
(azepan-2-one)

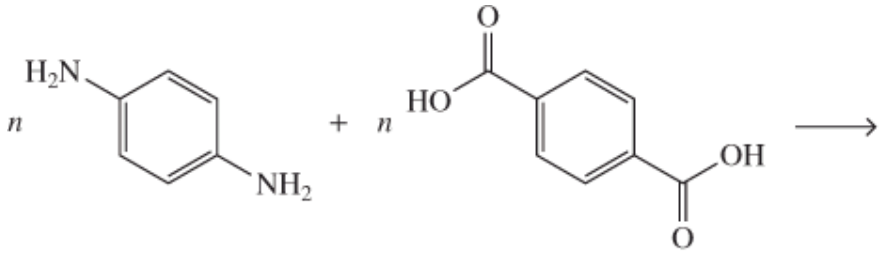
nylon 6

Nylon 6 is fabricated into fibres, bristles, rope, high-impact mouldings and tyre cords.



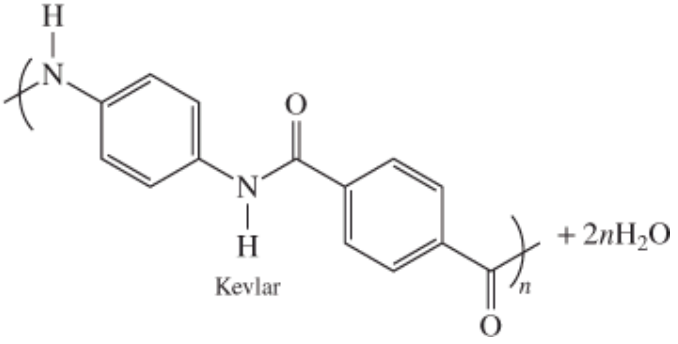
FIGURE 26.11 The first nylon product (a toothbrush with nylon bristles) was made in 1938. Women's preference for shorter skirts and dresses in the 1920s resulted in an increasing demand for stockings. Silk was the fibre of choice at that time, but it was expensive and had to be imported from east Asia. Nylon turned out to be the perfect synthetic replacement, and nylon stockings first became available in 1939.
Kari-Ann Tapp

Based on extensive research into the relationships between molecular structure and bulk physical properties, scientists at DuPont reasoned that a polyamide containing aromatic rings would be stiffer and stronger than either nylon 6,6 or nylon 6. In early 1960, DuPont introduced Kevlar, a polyaromatic amide (**aramid**) fibre synthesised from terephthalic acid (benzene-1,4-dicarboxylic acid) and benzene-1,4-diamine.



benzene-1,4-diamine

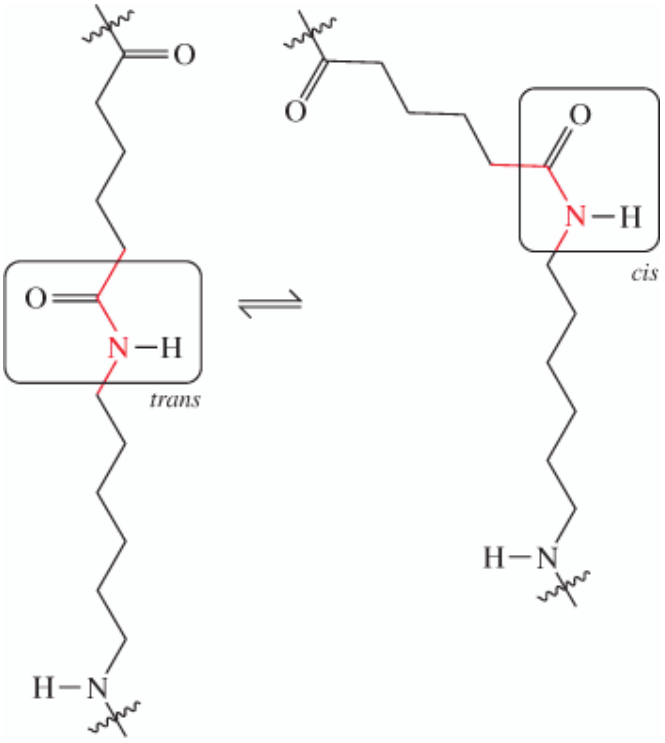
terephthalic acid
(benzene-1,4-dicarboxylic acid)



Kevlar

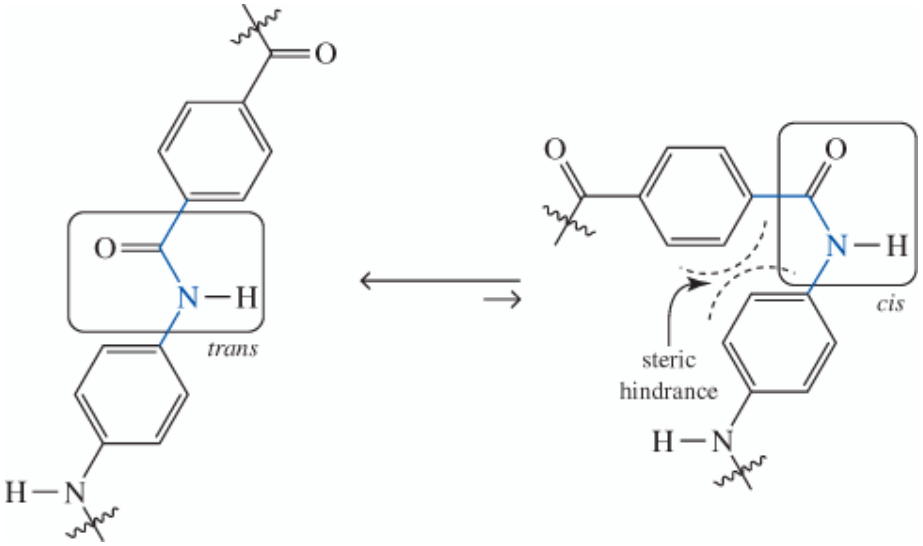
What makes Kevlar fibres so much stronger than nylon, even though the linking unit is the same in both? The

structural flexibility in nylon means that the amide linkage in a nylon fibre can assume two different conformations, which are in equilibrium (as shown on the left): the more stable *trans* arrangement and the less stable *cis* arrangement (this is similar to the conformation in peptides, which was described in chapter 24, p. 1069).

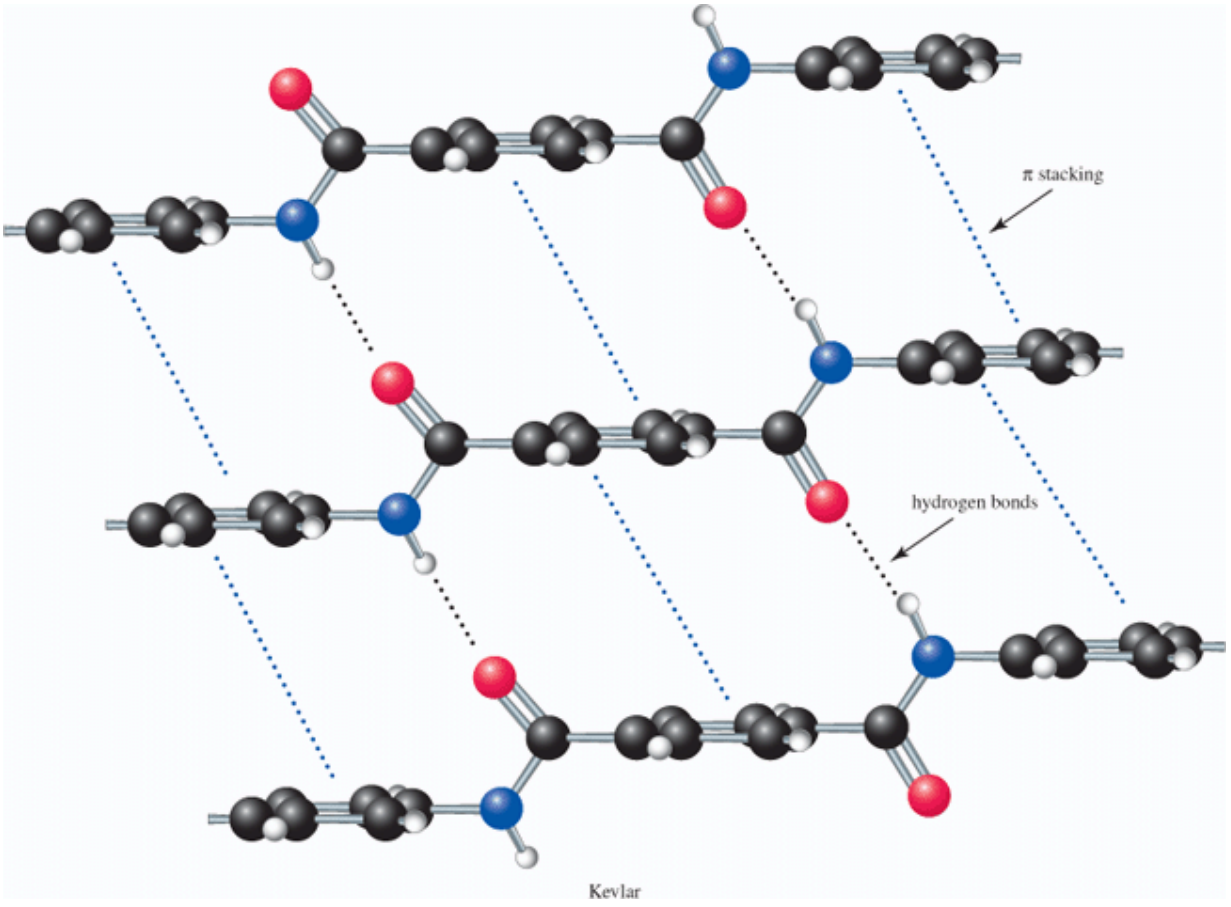


The fibre with *trans* conformation at the amide bond has a linear shape, which can easily line up into more ordered structures leading to crystallisation. However, increasing concentrations of *cis* amide bonds in the polymer break up this order, preventing a higher degree of crystallisation.

In Kevlar, because of the *para* arrangement (see section 16.7) of the amide bonds at the aromatic rings, the polymer chain is inflexible and stiff and cannot interloop. In contrast to nylons, aramids cannot assume the *cis* conformation at the amide bond because this would cause significant steric hindrance between the protons in the *ortho* position at the aromatic rings:



Therefore, Kevlar polymer strands can line up alongside each other to produce a high degree of order and therefore crystallinity. The extraordinary strength of Kevlar fibres is due not only to the hydrogen bonds between two amide moieties but also to stacking of the aromatic rings; this is called π stacking or π–π interactions.



One of the remarkable features of Kevlar is its light weight compared with that of other materials of similar strength. For example, a 7.6 cm cable woven of Kevlar has a strength equal to that of a similarly woven 7.6 cm steel cable. However, whereas the steel cable weighs about 30 kg m^{-1}, the Kevlar cable weighs only 6 kg m^{-1}. Kevlar now finds use in such articles as anchor cables for offshore drilling rigs, reinforcing fibres for car tyres, asbestos replacement, flame-resistant clothing and sail cloth. Kevlar is also woven into a fabric that is so tough that it can be used for bulletproof vests (figure 26.12).



FIGURE 26.12 Bulletproof vests have a thick layer of Kevlar.
AFP Photo/Candido Alves

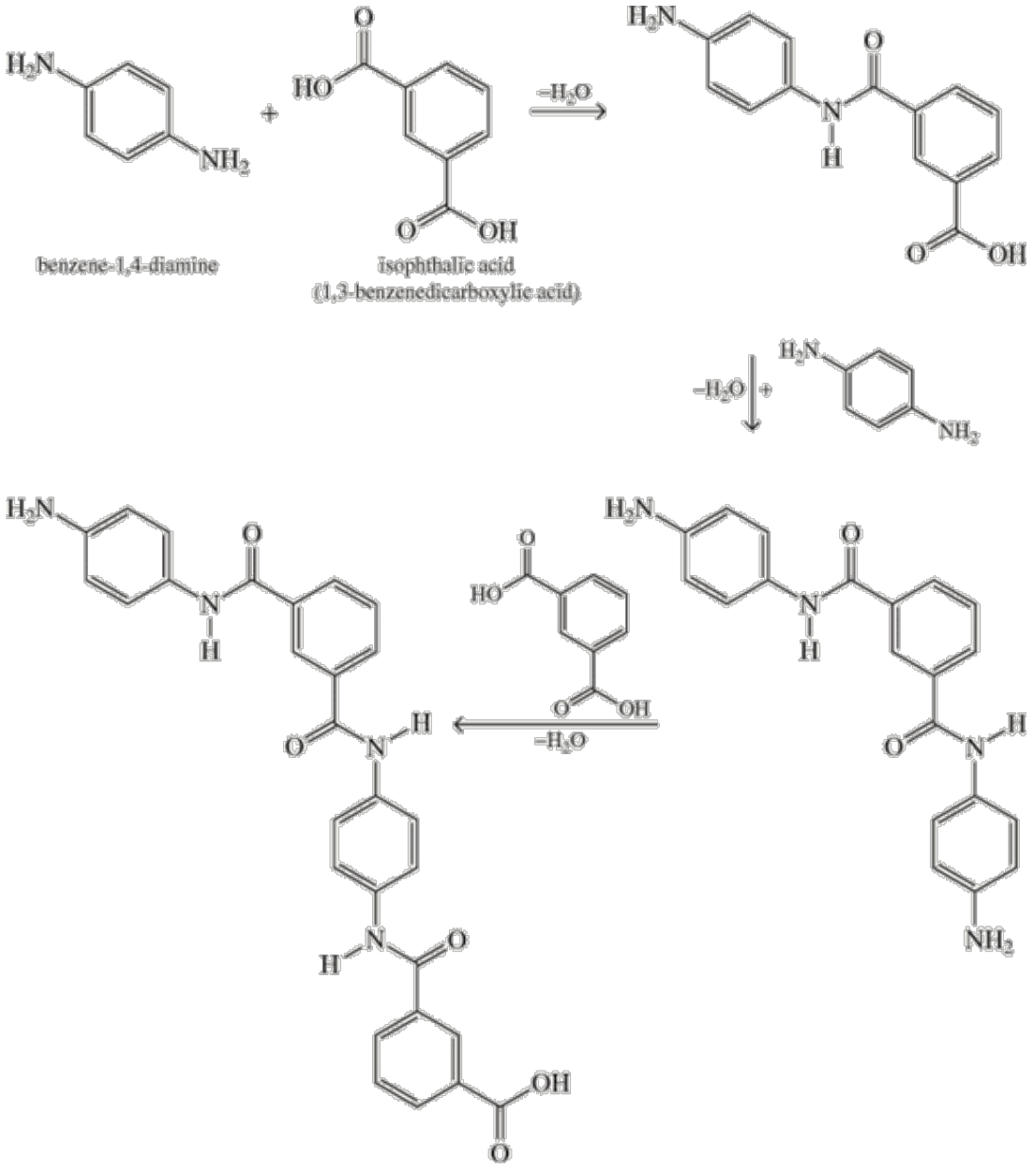
WORKED EXAMPLE 26.2

Synthesising an Aramid

How does the chemical structure of an aramid change if a *meta*-substituted aromatic dicarboxylic acid is used instead of the *para*-substituted aromatic dicarboxylic acid in Kevlar? Draw a polymer chain consisting of four monomer units.

Analysis and solution

The *meta*-substituted aromatic dicarboxylic acid is isophthalic acid (1,3-benzenedicarb oxylic acid) and the diamino compound is benzene-1,4-diamine. Reaction of an amino group with a carboxylic acid gives an amide bond. The polymer consisting of four monomers has a free amino group on one end and a free carboxylic acid moiety on the other end.

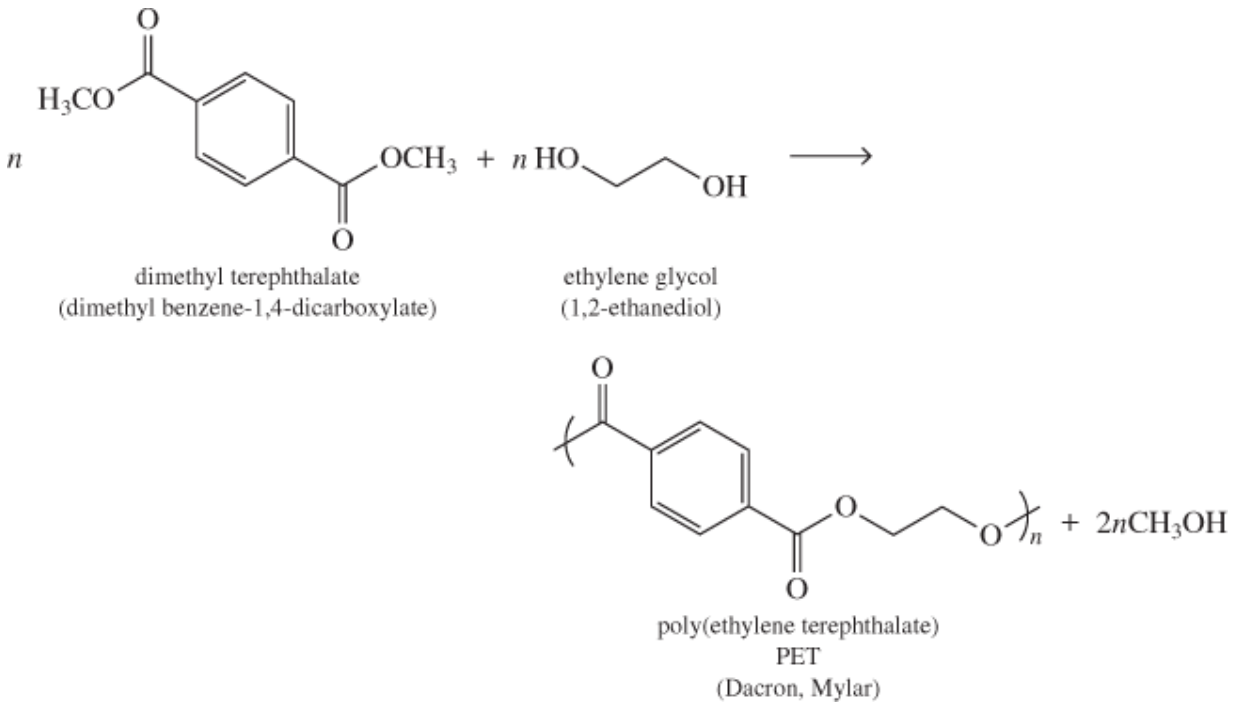


PRACTICE EXERCISE 26.2

Draw a chain of four monomer units of a polymer made from phthalic acid (1,2-benzenedicarboxylic acid) and benzene-1,3-diamine.

Polyesters

Polyesters are polymers in which each monomer unit is joined to the next by an ester bond. The first polyester, developed in the 1940s, was formed by polymerisation of terephthalic acid (benzene 1,4-dicarboxylic acid) with ethylene glycol (1,2-ethanediol) to give poly(ethylene terephthalate), abbreviated PET. Virtually all PET is now made from the dimethyl ester of terephthalic acid by the following transesterification reaction (p. 1022):



The crude polyester can be melted, extruded and then cold drawn to form the textile fibre Dacron® polyester, the outstanding features of which are its stiffness (about four times that of nylon 6,6), very high strength and remarkable resistance to creasing and wrinkling. Early Dacron polyester fibres were harsh to touch, due to their stiffness, so they were usually blended with cotton or wool to make acceptable textile fibres. Newly developed fabrication techniques now produce softer Dacron polyester textile fibres. PET is also fabricated into Mylar® films and recyclable plastic beverage containers (figure 26.13).



FIGURE 26.13 PET softdrink bottles.

Polymers in Medicine

Polymers are important materials for heavy-duty industrial and household purposes, and they have also found a role in medical applications. As the technological capabilities of medicine have grown, so has the demand for synthetic materials that can be used inside the body. Polymers have many of the characteristics of an ideal biomaterial; they are lightweight and strong, are inert or biodegradable (depending on their chemical structure) and have physical properties (softness, rigidity and elasticity) that are easily tailored to match those of natural tissues. Carbon–carbon backbone

polymers are resistant to degradation and are used widely in permanent organ and tissue replacements.

Artificial hearts, heart–lung machines and artificial kidneys are examples of artificial organs that consist, to a major extent, of synthetic polymers. Also, modern artificial joints are made from synthetic polymers; for example, artificial hips often contain a polymeric acetabular cup (figure 26.14).

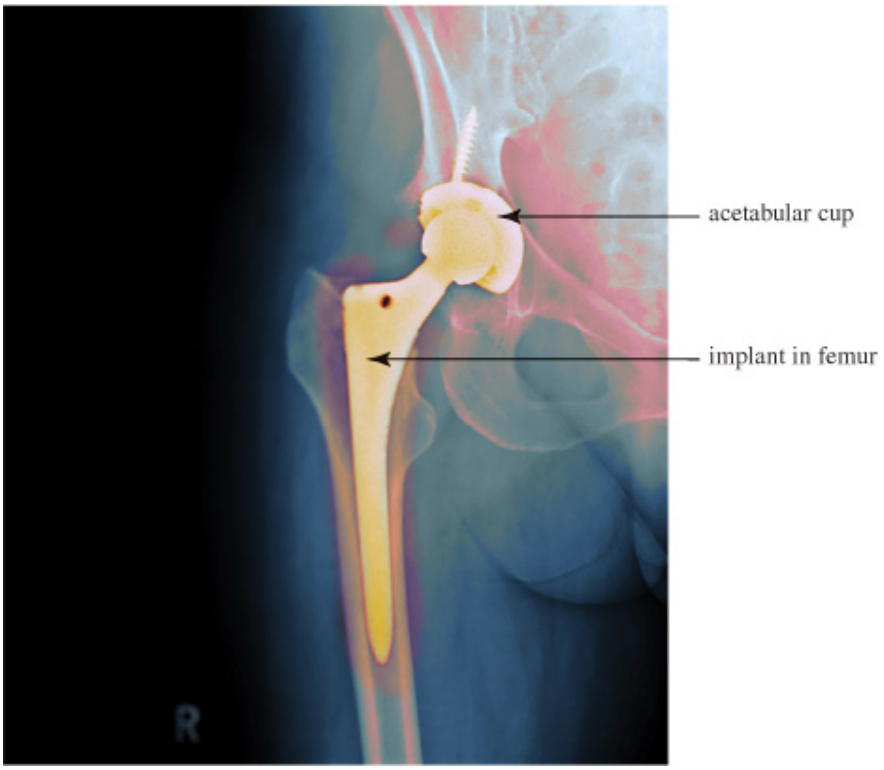
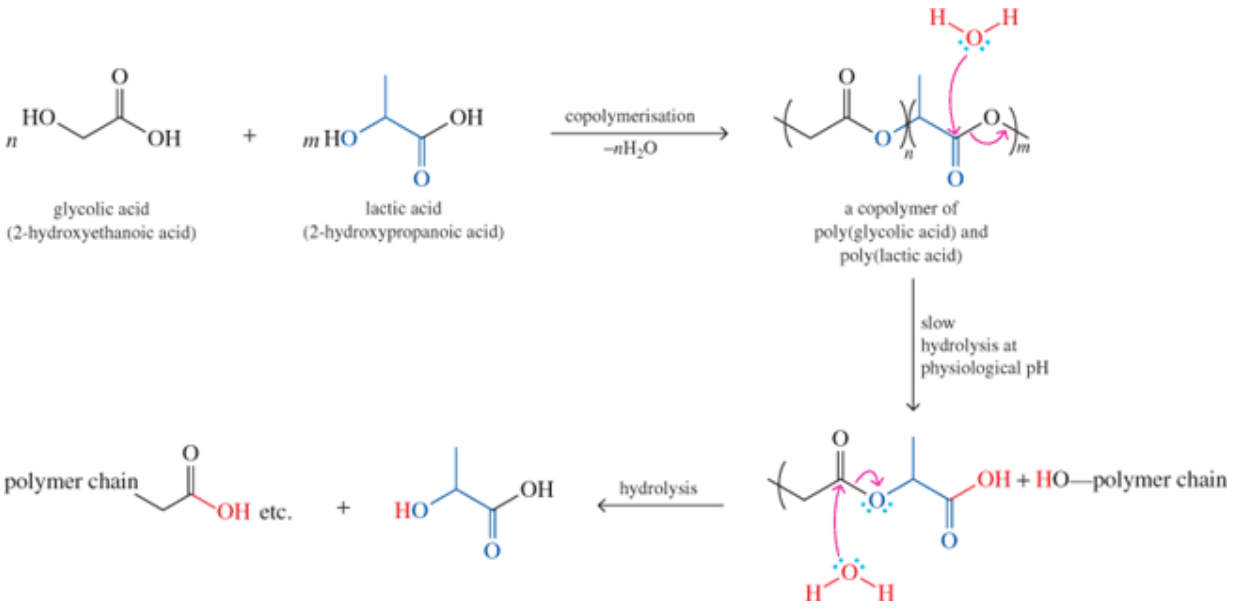


FIGURE 26.14 X-ray image of an artificial hip showing the polymer cup socket for the metallic ball joint. SPL/GustoImages

Polymeric drugs and polymer delivery systems have been developed with the aim of altering the pharmokinetics and pharmodynamics of therapeutic agents. These systems can be used to introduce new and efficient methods of drug administration and to decrease drug toxicity and ensure safety. For example, polymer-bound chemotherapeutic drugs for the treatment of cancer are constructs where the drug is covalently bound to a polymer. This ensures more efficient delivery of the drug to the affected organ in the body, and it also reduces the toxicity of the drug itself.

Even though most medical uses of polymeric materials require biostability, applications have been developed that use

the biodegradable nature of some macromolecules. An example is the use of glycolic acid (2-hydroxyethanoic acid) and lactic acid (2-hydroxypropanoic acid) to produce copolymers that act as absorbable sutures (dissolving stitches):



Traditional suture materials such as catgut must be removed by a health care specialist after they have served their purpose. Stitches of these hydroxyester polymers, however, are slowly hydrolysed at physiological pH over 2–3 weeks; by the time the tissues have healed, the stitches are fully degraded and need not be removed. The suture material degrades by nucleophilic attack of water at the carbon atom of one of the ester groups, which cleaves the ester into an acid and an alcohol. In the example above, this ruptures the polymer strand. Further step-by-step hydrolysis of the remaining ester groups leads ultimately to the complete breakdown of the polymer to the monomers, glycolic and lactic acid, which are excreted by existing biochemical pathways.

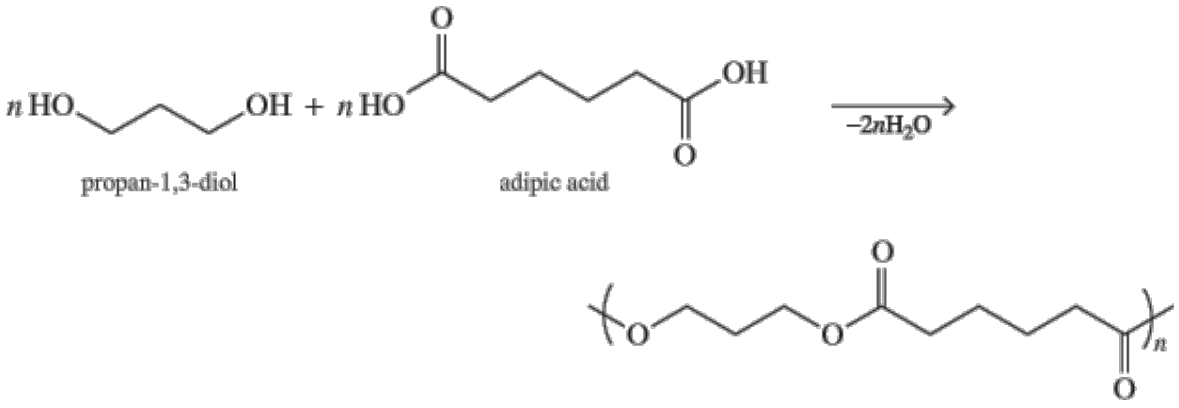
WORKED EXAMPLE 26.3

Synthesising a Polyester

Describe the structure of the polymer that would be formed from propan-1,3-diol and adipic acid. Draw the repeating unit.

Analysis and solution

These two compounds react to form an ester bond:

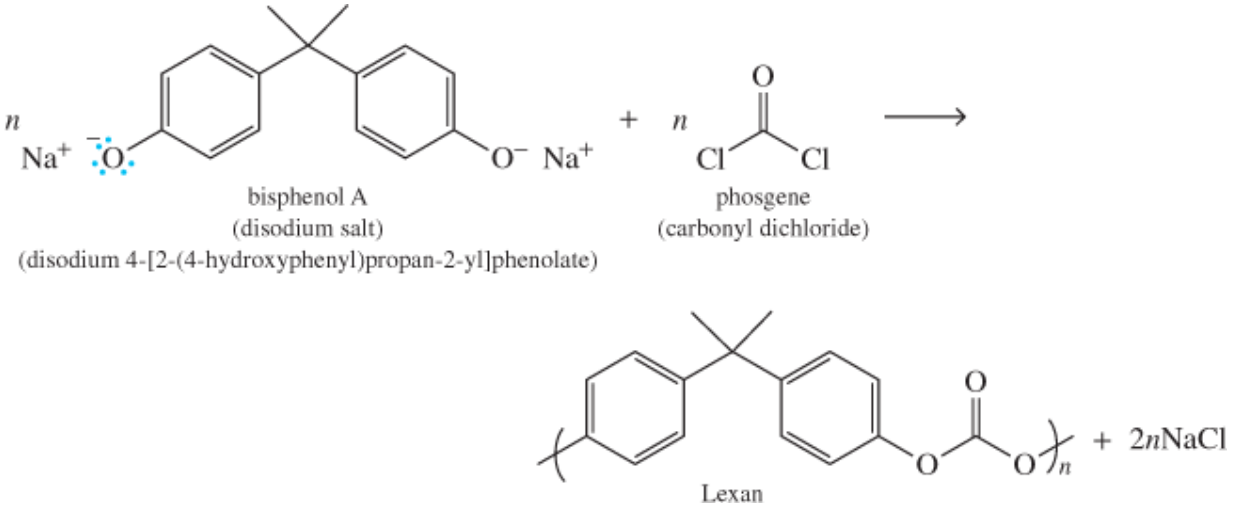


PRACTICE EXERCISE 26.3

Describe the structure of a polyester formed from adipic acid and glycerol (propane-1,2,3-triol). Draw the repeating unit.

Polycarbonates

Polycarbonates are polyesters in which the carboxyl groups are derived from carbonic acid. The most familiar is Lexan®, a commercially important class of engineering polyesters. Lexan forms by the reaction between phosgene (carbonyl dichloride) and the disodium salt of bisphenol A (4-[2-(4-hydroxyphenyl)propan-2-yl]phenol):



Note that phosgene is the dichloride of carbonic acid, which is unstable; hydrolysis of phosgene gives carbonic acid, H_2CO_3, and 2HCl.

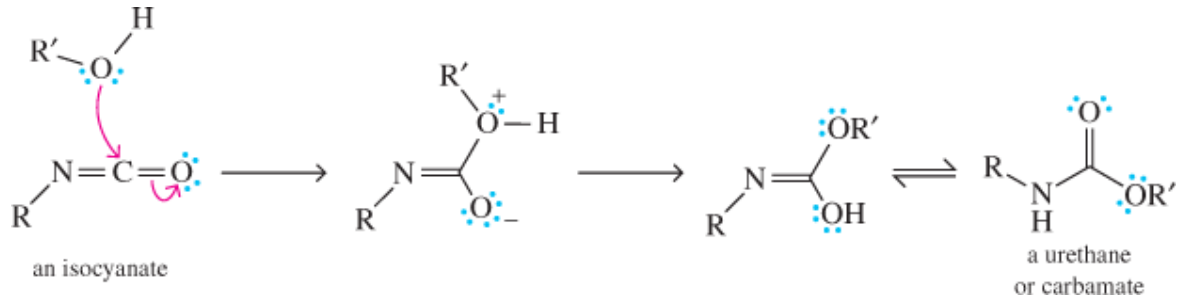
Lexan is a tough, transparent polymer with high impact and tensile strengths that retains its properties over a wide temperature range. It is used in sporting equipment (such as helmets and face masks, figure 26.15), to make light, impact-resistant housings for household appliances and in the manufacture of safety glass and unbreakable windows.



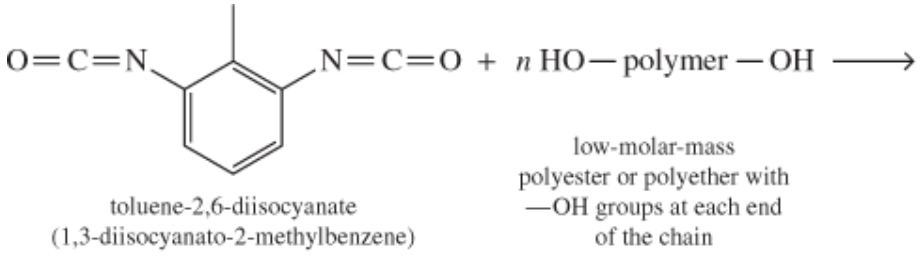
FIGURE 26.15 Many modern helmets incorporate a lightweight, impact-resistant, polycarbonate shell. AFP/Punit Paranjpe/Stringer

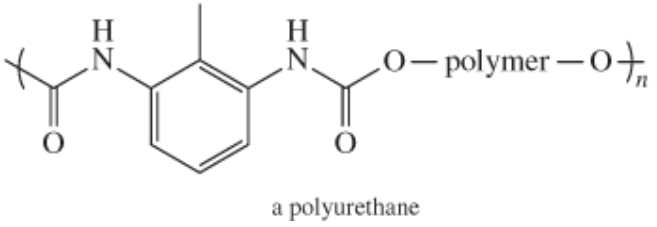
Polyurethanes

A urethane, or carbamate, is an ester of carbamic acid, H_2NCOOH; thus, a urethane or carbamate functional group consists of both an ester and an amide linkage. Carbamates are most commonly prepared by treating an isocyanate with an alcohol. In this reaction, the H and OR′ of the alcohol add to the C═N bond in a reaction comparable to the addition of an alcohol to a C═O bond:



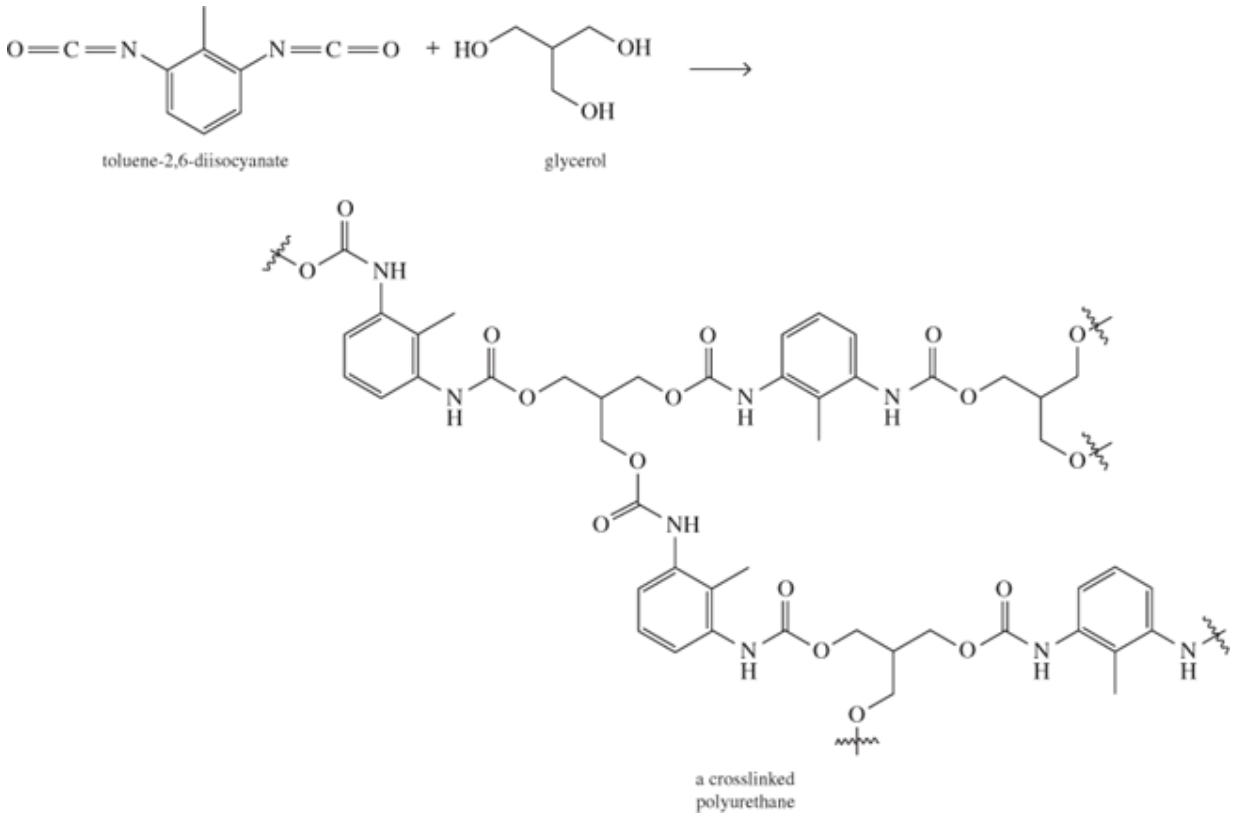
Polyurethanes consist of flexible low-molar-mass polyester or polyether units (blocks) alternating with rigid urethane blocks derived from a diisocyanate, commonly a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate (2,4-diisocyanato-1-methylbenzene and 1,3-diisocyanato-2-methylbenzene):





Note that formation of polyurethane is the only example of step-growth polymerisation that does not generate a small molecule as a by-product.

If the polymerisation of toluene-2,6-diisocyanate is performed with a molecule containing more than two hydroxyl groups, such as glycerol, crosslinking between the polymer chains occurs to form a three-dimensional network.



Generally, polymers with cross-linked chains lose the ability of the individual polymer chains to move independently. The more crosslinking there is, the less flexible is the resulting polymer; this is usually accompanied by a higher melting point of the polymer. Thermoset polymers have a rigid three-dimensional structure and usually cannot be heated to their melting point without decomposition.

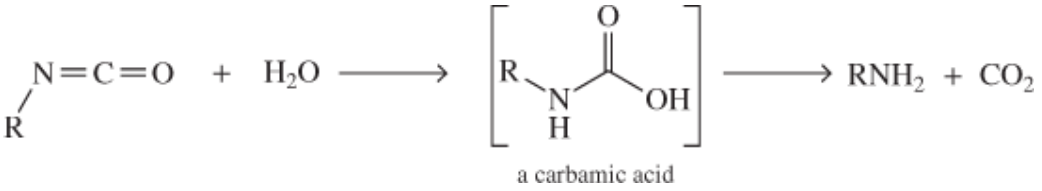
We can obtain softer, more elastic and more flexible polyurethanes by using linear difunctional polyethylene glycol segments (often called polyether polyols) to create the urethane links. Such fibres have found use as Spandex® and Lycra® (figure 26.16), the 'stretch' fabrics used in bathing suits, leotards, sports compression clothing and undergarments. More rigid products result if polyfunctional polyols are used, which create a three-dimensional cross-linked structure.



FIGURE 26.16 Many stretch fabrics incorporate flexible polyurethanes such as Spandex and Lycra.
Hamish Blair

Polyurethane foams for upholstery and insulating materials (figure 26.17) are made by adding small amounts of water during polymerisation. Water reacts with isocyanate groups to form a carbamic acid. Carbamic acids are unstable compounds that undergo spontaneous decarboxylation to produce gaseous carbon dioxide, which then acts as a

foaming agent:



a carbamic acid

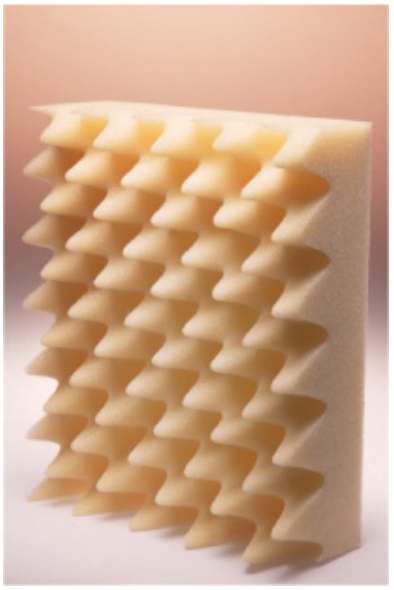
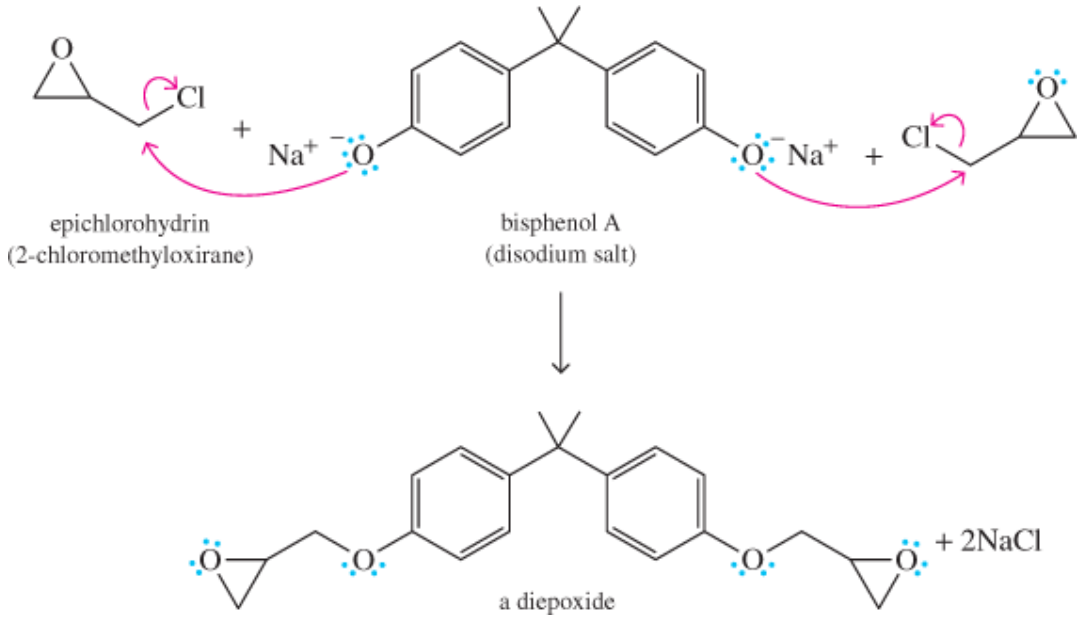


FIGURE 26.17 Polyurethane foam is often used for cushioning in furniture, insulation panels, carpet padding and packaging materials.
Photo Researchers/Charles D Winters

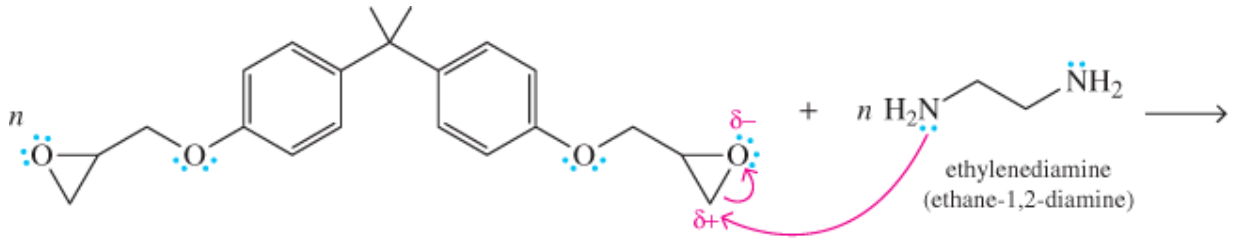
Epoxy Resins

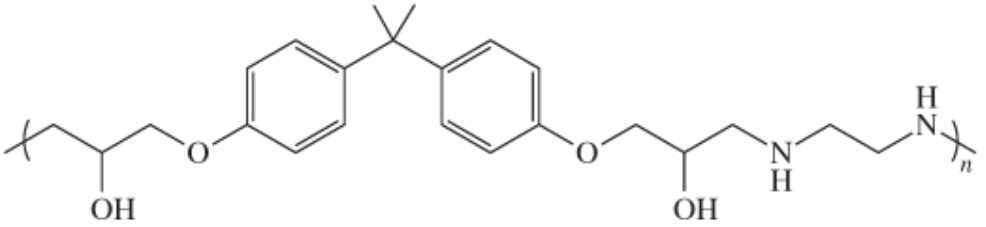
In contrast to the previously discussed highly ordered synthetic fibres, such as polyamides and polyesters, a resin is an amorphous, viscous or solid, mostly transparent polymer of natural or synthetic origin with a high molar mass and no definite melting point. **Epoxy resins** are synthetic materials prepared by polymerisation in which one monomer contains at least two epoxy groups (or ethylene oxide groups, see section 19.4). Within this range, a large number of polymeric materials are possible, and epoxy resins are produced in forms ranging from low-viscosity liquids to high-melting solids. The most widely used epoxide monomer is a diepoxide prepared by treating 1 mole of bisphenol A with 2 moles of epichlorohydrin (2-chloromethyloxirane):



a diepoxide

To prepare the following epoxy resin, the diepoxide monomer is treated with ethylenediamine (ethane-1,2-diamine):





an epoxy resin

The preceding reaction corresponds to nucleophilic opening of the highly strained three-membered epoxide ring at the less substituted carbon atom.

WORKED EXAMPLE 26.4

Mechanism of Diepoxide Formation

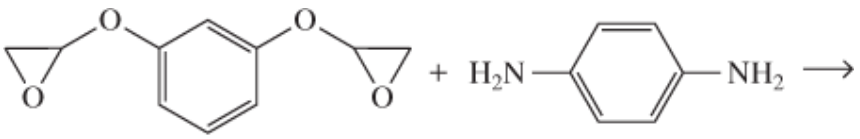
By what type of mechanism does the reaction on the previous page between the disodium salt of bisphenol A and epichlorohydrin take place?

Solution

The reaction occurs by the S_N2 mechanism. The phenoxide ion of bisphenol A is a good nucleo phile, and chlorine on the primary carbon atom of epichlorohydrin is the leaving group.

PRACTICE EXERCISE 26.4

Draw the repeating unit of the epoxy resin formed from the following reaction.
(*Hint:* Draw the mechanism of the epoxide ring opening reaction.)



a diepoxide a diamine

Ethylenediamine is usually one component in the two-component epoxy resin kits (figure 26.18) that you can buy in

hardware or craft stores (it is often wrongly called ‘catalyst’ on the packaging); it is also the reagent with the acrid smell.



FIGURE 26.18 An epoxy resin kit. Kari-Ann Tapp

Epoxy resins are widely used as adhesives and insulating surface coatings. They have good electrical insulating properties and so are used to encapsulate electrical components ranging from integrated circuit boards to switch coils, and insulators for power transmission systems. Epoxy resins are also used as composites with other materials, such as glass fibre, paper, metal foils and other synthetic fibres, to create structural components for jet aircraft, rocket motor casings and so on.

Addition or Chain-growth Polymers

Addition or chain-growth polymerisation is a type of polymerisation that involves sequential addition reactions, either to unsaturated monomers or to monomers with other reactive functional groups. In contrast to condensation polymerisation, all atoms of the monomer are found in polymers formed by addition polymerisation; no atom is lost or gained in the conversion of the monomer to the polymer. Addition polymerisation is fundamental to the chemical industry. An example is the formation of polyethylene from ethene:

$$n\ H_2C{=}CH_2 \xrightarrow{\text{initiator}} \left(\text{polyethylene}\right)_n$$

ethene

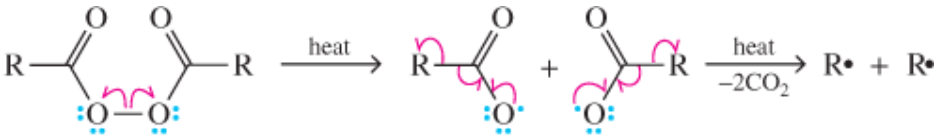
The mechanism of chain-growth polymerisation differs greatly from the mechanism of step-growth polymerisation. In the latter, all monomers plus the polymer end-groups possess equally reactive functional groups, allowing for all possible combinations of reactions to occur, including monomer with monomer, dimer with dimer, monomer with tetramer and so on. In contrast, chain-growth polymerisations involve end-groups with reactive centres that react only with a monomer. The overall process involves conversion of π bonds in the monomer into σ bonds that hold the repeating units in the polymer together. Since σ bonds are stronger than the π bonds of the monomer units, much energy is released during polymerisation. The reactive intermediates used in chain-growth polymerisation include radicals, carbanions, carbocations and certain metal compounds known as organometallic complexes.

Many monomers undergo chain-growth polymerisation, including alkenes, alkynes, allenes, isocyanates and cyclic

compounds such as lactones, lactams, ethers and epoxides. We will concentrate on the chain-growth polymerisation of ethene and substituted ethenes and show how these compounds can be polymerised by radical, cationic and organometal-mediated mechanisms.

Radical Chain-growth Polymerisation

The first commercial polymerisations of ethene were initiated by **radicals** formed by thermal decomposition of organic peroxides. A radical is any molecule that contains one or more unpaired electrons, and we have seen some examples of these in chapter 15. They can be formed by the cleavage of a bond in such a way that each atom or fragment participating in the bond retains one electron (*homolytic* cleavage). For example, when diacyl peroxides are heated (the most prominent are benzoyl peroxide and acetyl peroxide), the peroxidic O—O bond is cleaved to give two acyloxyl radicals, which both have an unpaired electron on the oxygen. Acyloxyl radicals can undergo further homolytic bond breakage, by which a radical R• is formed and carbon dioxide is released.



a diacyl peroxide

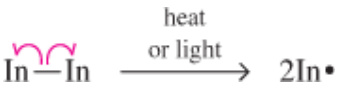
benzoyl peroxide: R = Ph
acetyl peroxide: R = Me

acyloxyl radicals

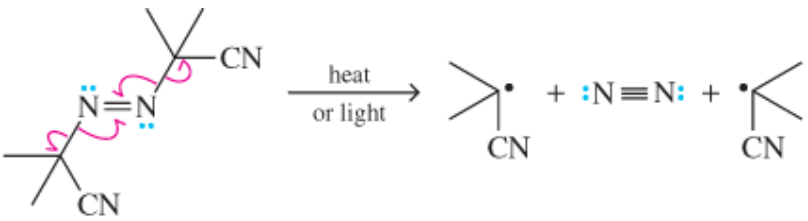
As a convention, **fishhook (single-headed) arrows** are used to show the change in position of single electrons.

radical chain-growth polymerisation of ethene and substituted ethenes involves three steps: (1) chain initiation, (2) chain propagation and (3) chain termination. Although radical polymerisations can be performed with all types of π systems (double bonds or triple bonds), we will discuss only polymerisations of alkenes since they are the most important addition polymerisations.

Step 1: **chain initiation** — formation of radicals from a molecule that has only paired electrons and that possesses a weak bond:



In the general equation above, In—In represents an initiator, which cleaves to give two radicals (In•). The energy required to break this bond homolytically can be provided by heat or by light of a suitable wavelength. There are many methods of producing radicals from many different types of initiators In—In. One class of radical initiators are diacyl peroxides, which have a very labile (reactive) O—O bond. In the reaction at the top of this page, both the acyloxyl radicals and the radicals, R•, that result through loss of CO_2 are actually acting as initiator radicals. Other common radical-chain initiator molecules are the azoalkanes, such as azobisisobutyronitrile (AIBN), which when heated or irradiated give two initiator radicals with the release of one molecule of N_2:



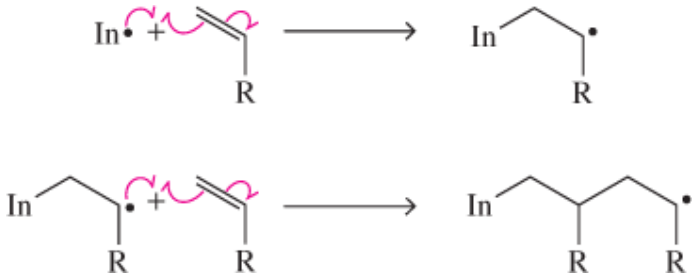
azobisisobutyronitrile (AIBN)

In•

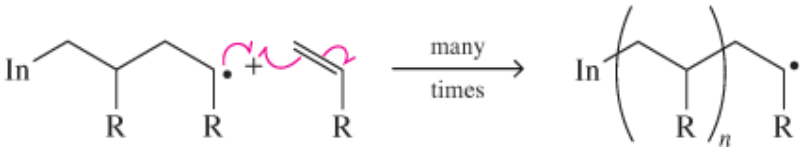
In•

The initiator radical In• undergoes addition to the π bond in an alkene. One of the electrons of the π bond forms a

new electron pair with the incoming radical, while the remaining electron of the former π bond remains unpaired:

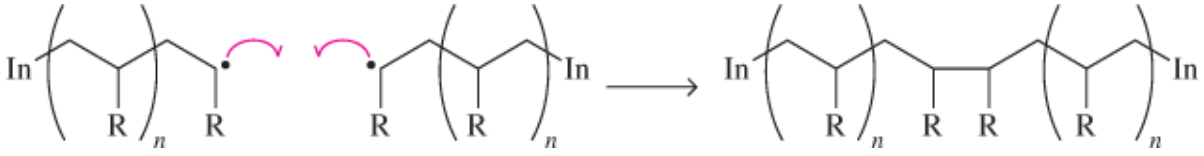


Step 2: **chain propagation** — The resulting radical subsequently adds to another alkane in a self-perpetuating reaction that builds a growing polymer chain.

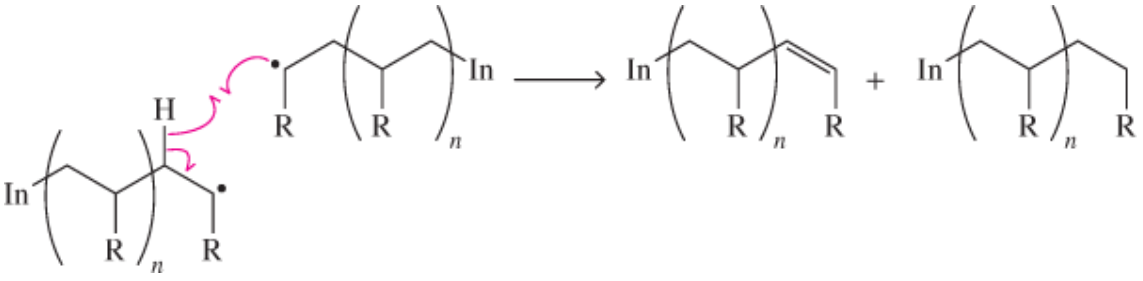


Step 3: **chain termination** — combination of radicals. Even if not all reactant molecules are consumed, reactions can occur that terminate the species carrying the radical chain. One termination process is the simple combination of two chains by forming a σ bond between free ends of the radical chain. Another pathway is a disproportionation between two radical chains, by which one radical species is oxidised to an alkene (through loss of a hydrogen atom) and the other is reduced to an alkane (through uptake of a hydrogen atom). In both cases, the radicals are transformed into nonradical species.

a. Coupling



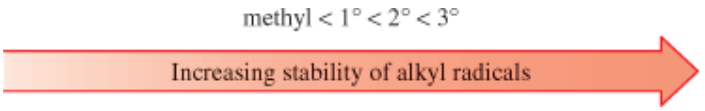
b. Disproportionation



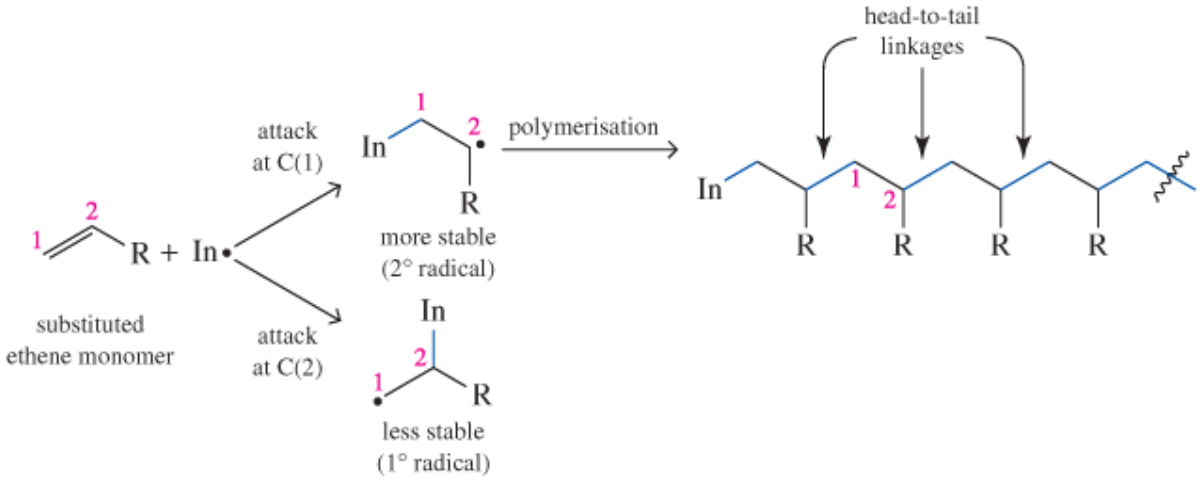
You may ask why the chain termination processes above occur at all, or why they do not occur all the time. The answer lies in the kinetics of radical-chain reactions (see chapter 15). The reason for the success of radical-chain processes is the very low concentration of reactive radical species. Only very few radicals are produced in the initiation process, and they react extremely fast with the excess alkene to produce new radicals, again in very low concentration, and so on. Because of the large concentration of alkene, there is only a very low probability of two radicals meeting to terminate the chain — however, this does happen and is the reason why chain propagation can stop before all starting materials are consumed.

The characteristic feature of the chain-propagation step is the reaction of a radical and a molecule to give a new radical. Propagation steps repeat over and over, with the radical formed in one step reacting with a monomer to produce a new radical and so on. The number of times a cycle of chain-propagation steps repeats is called the **chain length** and is given the symbol *n*. In the polymerisation of ethene, chain-lengthening reactions occur at a very high rate, often as fast as thousands of additions per second, depending on the experimental conditions.

The relative stabilities of alkyl radicals are similar to those of alkyl carbocations:



Thus, radical polymerisations of substituted ethenes almost always give the more stable (more substituted) radical. Because additions are biased in this fashion, polymerisations of substituted ethene monomers tend to yield polymers with monomer units joined by the head, C(1), of one unit to the tail, C(2), of the next unit:



The molecular mass of an addition of chain-growth polymer is usually controlled by the ratio of initiator and monomer. If more initiator is used, more polymer chains will grow simultaneously, which will consume monomers, resulting in polymers with a low molar mass. On the other hand, if very few initiator molecules are present, each polymer chain will grow longer so that the molar mass increases.

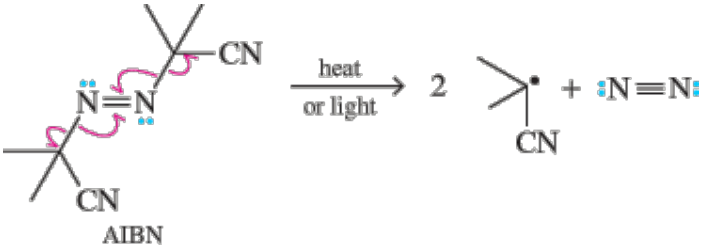
WORKED EXAMPLE 26.5

Synthesising a Chain-growth Polymer

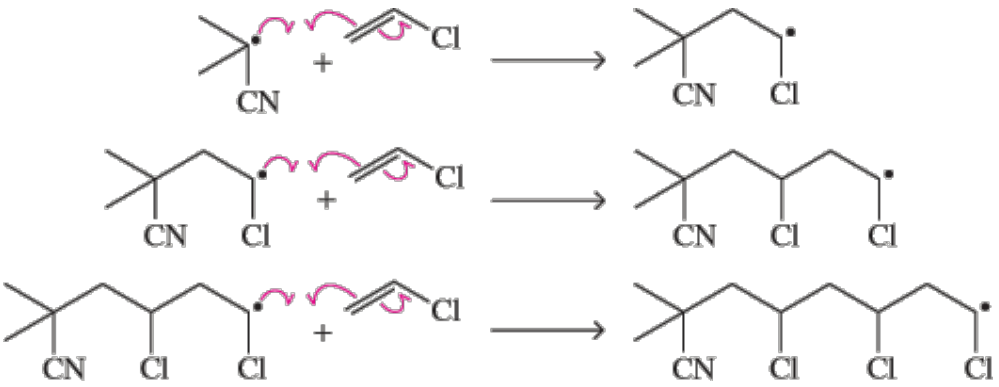
Show the mechanism for the formation of a radical segment of poly(vinyl chloride) containing three units of vinyl chloride, initiated by AIBN.

Analysis and solution

AIBN is a radical initiator, so we are dealing with a chain-growth (addition) polymerisation. In the first step, radicals are generated from AIBN by heat or light. The resulting alkyl radicals attack vinyl chloride so that the more stable secondary radical is formed. The latter attacks another vinyl chloride monomer and so on. In the growing polymer chain, each third carbon atom bears a side chain with a chlorine substituent.



(b) Radical-chain propagation

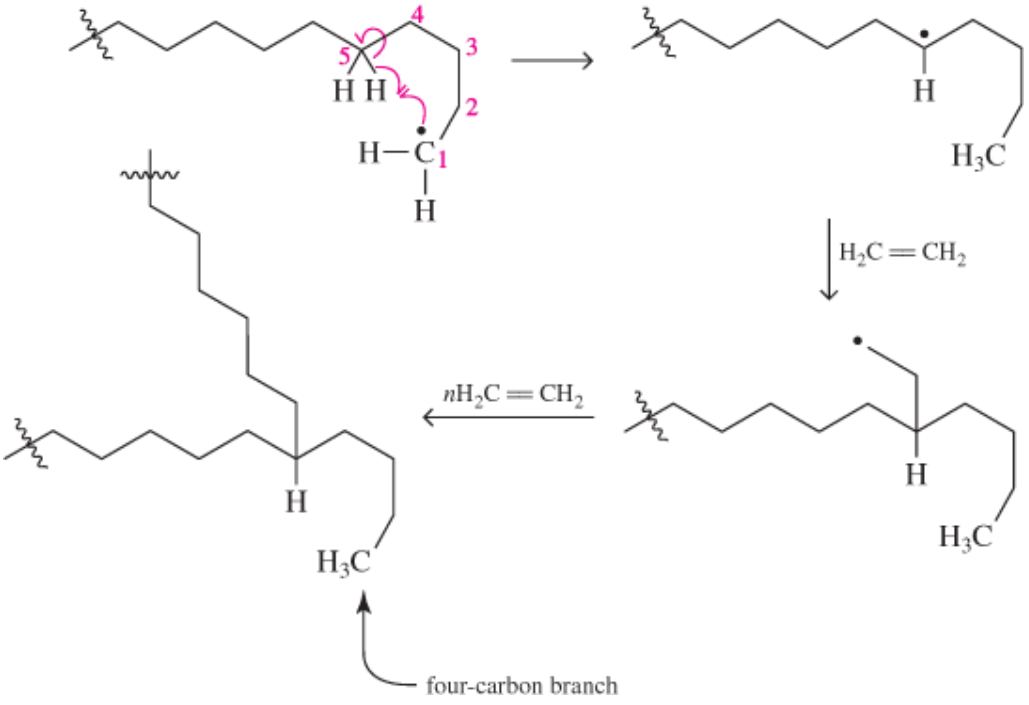


PRACTICE EXERCISE 26.5

Show the mechanism for the formation of a radical segment of polystyrene containing three units of styrene, initiated by diacetyl peroxide.

The first commercial process for ethene polymerisation used peroxide catalysts at temperatures of 500 °C and pressures of 1000×10^5 Pa to produce a soft, tough polymer known as **low-density polyethylene (LDPE or PE-LD)** with a density of between 0.91 and 0.94 g cm^{-3} and a melt transition temperature, T_m, of about 115 °C. Because LDPE's melting point is only slightly above 100 °C, it cannot be used for products that will be exposed to boiling water. At the molecular level, chains of LDPE are highly branched.

The branching on chains of low-density polyethylene results from a 'backbiting' reaction in which the radical end-group takes a hydrogen atom from the fourth carbon atom back, C(5); this converts the less stable 1° radical to a more stable 2° radical. A side reaction such as this is called a **chain-transfer reaction** because the activity of the end-group is 'transferred' from one chain to another. Continued polymerisation of monomers from this new radical centre leads to a branch four carbon atoms long.



Approximately 65% of all LDPE is used for the manufacture of films. LDPE film is inexpensive and can be moulded when heated; this makes it ideal for packaging consumer items such as baked goods, vegetables and other produce, for garbage bags and for insulating electrical equipment and cables.

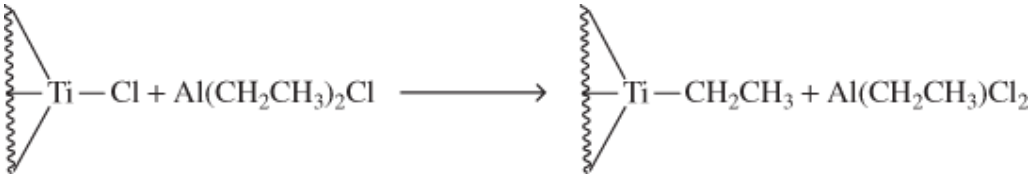
Ziegler–natta Chain-growth Polymerisation

The backbiting mechanism that causes branching in polymer chains is an unavoidable sidereaction in radical polymerisations. This branching greatly affects the properties of polyethylene. For example, whereas linear regions of the polyethylene chain can pack close together to form highly ordered, crystalline regions in the polymer, the branched regions with their structural irregularities cannot participate in this crystallisation. Since closer packing and crystallisation give this material its high density and strength, chain branching means lower density and more flexibility. Since both density and crystallisation properties of polymers are closely connected to their commercial use, the development of a polymerisation process that controls branching and chain length was of great interest to chemists in the first half of the twentieth century. This led to the development of transition metal catalysts, which allow the polymerisation of ethene and substituted ethenes without radicals.

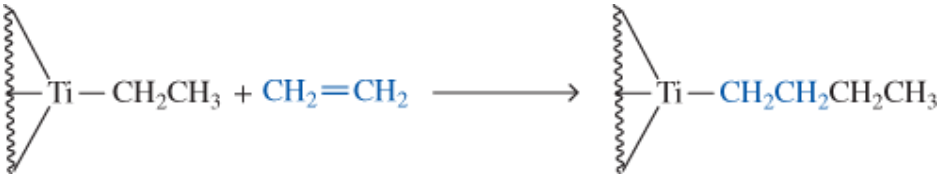
Polyethylene

In the 1950s, Karl Ziegler from Germany and Giulio Natta from Italy developed an alternative method for the polymerisation of alkenes, for which they shared the Nobel Prize in chemistry in 1963. The early **Ziegler–Natta catalysts** were highly active, heterogeneous materials composed of a $MgCl_2$ support, a group 4 transition metal halide such as $TiCl_4$ and an alkylaluminium compound, $Al(CH_2CH_3)_2Cl$. The reaction between $Al(CH_2CH_3)_2Cl$ and $TiCl_4$ below results in an alkyltitanium species (step 1). Once formed, ethene units are repeatedly inserted into the titanium–carbon bond of the alkyltitanium compound to yield polyethylene (steps 2 and 3). These catalysts bring about the polymerisation of ethene and propene at 1–4 × 10^5 Pa and at temperatures as low as 60 °C.

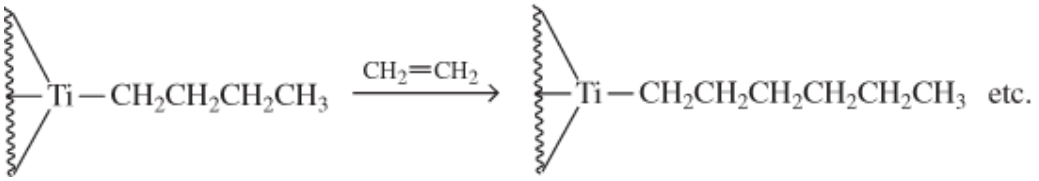
Step 1: Formation of a titanium–carbon bond:



Step 2: Insertion of ethene into the titanium–carbon bond:



Step 3: Repeated insertion of ethene into the titanium–carbon bond:



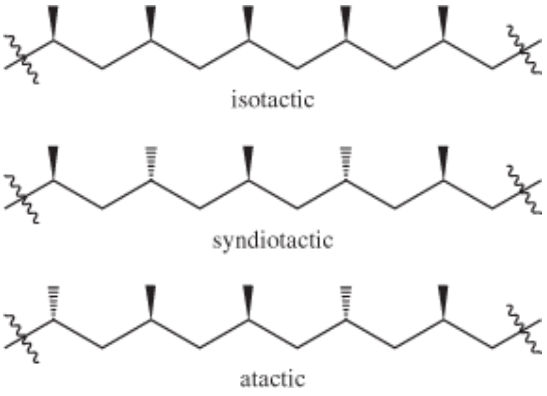
Over 27 billion kilograms of polyethylene are produced worldwide every year with Ziegler– Natta catalysts. Polyethylene from Ziegler–Natta systems, termed **high-density polyethylene (HDPE or PE-HD)**, has a higher density (0.96 g cm^{-3}) and melt transition temperature (133 °C) than low-density polyethylene, is three to ten times stronger, and is opaque rather than transparent. The added strength is due to much less chain branching and, therefore, a higher degree of crystallinity in HDPE than LDPE. As a result of the higher crystallinity, the scattering of light is increased leading to higher opacity of the polymer.

Even greater improvements in properties of HDPE can be realised through special processing techniques. In the melt state, HDPE chains have randomly coiled conformations similar to those of cooked spaghetti. Engineers have developed extrusion techniques that force the individual polymer chains of HDPE to uncoil into linear conformations. These linear chains then align with one another to form highly crystalline materials. HDPE processed in this fashion is stiffer than steel and has approximately four times its tensile strength! Because the density of polyethylene (~1.0 g cm^{-3}) is considerably less than that of steel (8.0 g cm^{-3}), these comparisons of strength and stiffness are even more favourable if they are made on a mass basis.

Polyethylene of ultra-high molar mass, also known as high-performance polyethylene (HPPE) contains extremely long polymer chains with a molar mass of 2–6 million. Polyethylene chains are held together by van der Waals forces, which are not very strong. However, because of the extremely long chains in HPPE, the van der Waals interactions become very strong. HPPE is highly resistant to chemicals and is used in fibre materials and medical applications such as artificial joints (see pp. 1128–9).

Polypropylene

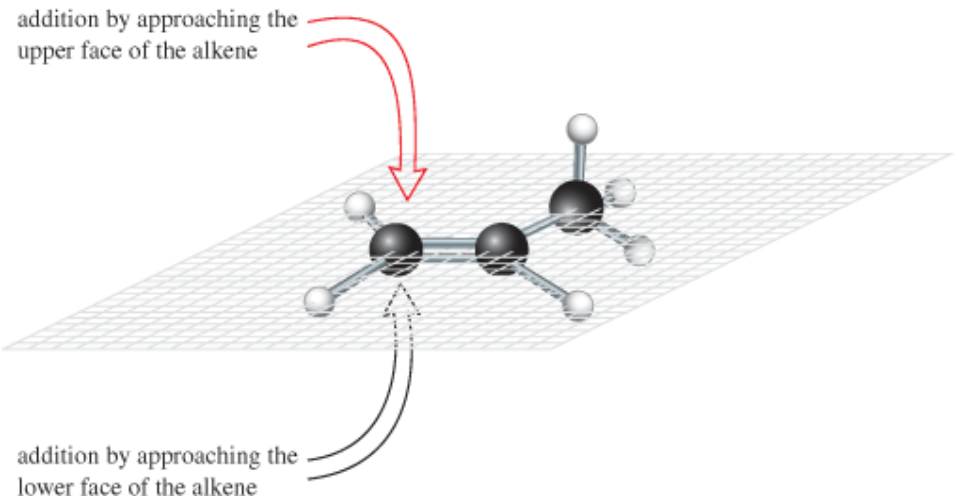
When the asymmetrical alkene propene (see section 26.2) is polymerised, the polypropylene chain has a methyl branch on every second carbon atom — this means that this carbon atom is chiral. The properties of polypropylene are strongly influenced by the three-dimensional arrangement of these methyl branches: that is, whether all methyl groups are on the same side of the chain (**isotactic polypropylene**), alternating (**syndiotactic polypropylene**) or taking positions randomly along the chain (**atactic polypropylene**).



When propene is polymerised through radical polymerisation, mostly atactic polypropylene is obtained. It was, therefore, a big scientific challenge to develop a method that allowed the polymerisation of propene (and other monosubstituted alkenes) in such a way that the chain configuration consists of small regularly oriented units in a single sequential arrangement (called stereoregular). In 1956, Natta developed a modified Ziegler–Natta catalyst consisting of tri ethyl aluminium, $Al(C_2H_5)_3$, and titanium(III) chloride, $TiCl_3$, which yields over 90% of isotactic polypropylene.

Isotactic, syndiotactic and atactic polypropylene are not mirror images of each other. There-fore, they are *diastereomers* (see section 17.1), and these three variations of polypropylene have different physical and chemical properties. The highly ordered carbon chains in isotactic polypropylene result in a material of high strength and stiffness, which is widely used commercially. Atactic polypropylene with polymers of low molar mass (oligomers) is sticky and so is useful in adhesives. Syndiotactic polypropylene is somewhat softer than isotactic polypropylene, but

also tough and clear. It became synthetically (and commercially) available only after the development of certain chiral organometallic catalysts that can distinguish between the two mirror-related faces of propene, as shown below.

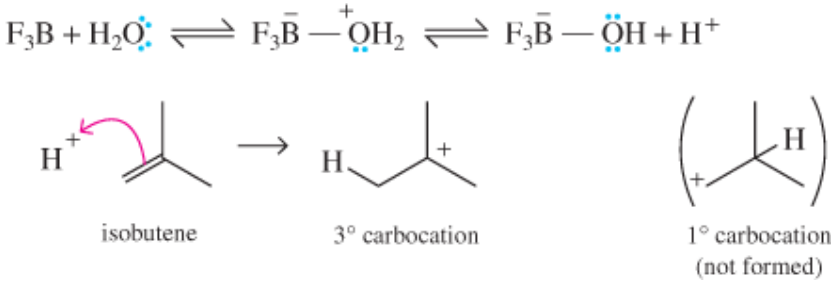


We will not go into more detail here about asymmetric synthesis but you may encounter methods to synthesise only one enantiomer of a chiral compound (see section 17.7) in your future studies in chemistry.

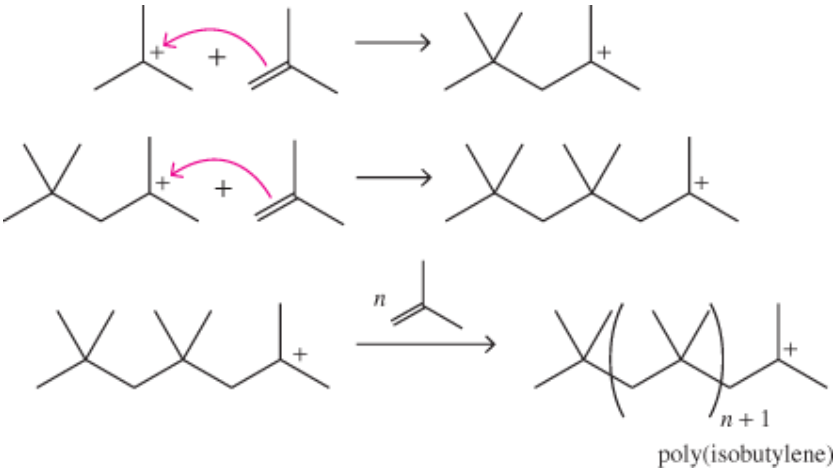
Cationic Polymerisation

Another type of addition polymerisation is **cationic polymerisation**, which is initiated by an electrophile, generally a proton. The proton is derived from a reaction between a Lewis acid, such as $AlCl_3$, $SnCl_4$, BF_3 or $TiCl_4$, and a proton-donating Lewis base, such as water. Cationic polymerisations are used to polymerise electron-rich alkenes, such as styrene, vinyl ethers and isobutene (isobutylene), the last of which we will discuss here.

Step 1: Chain initiation — Reaction of boron trifluoride with water releases a proton, which adds to the sp^2 carbon atom in isobutene, forming the more stable 3° carbocation (see section 16.5).

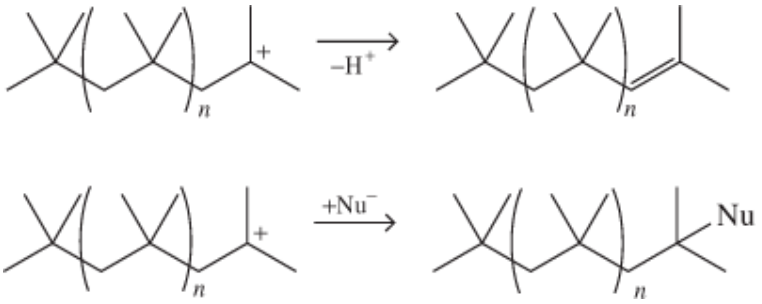


Step 2: Chain propagation — The cation formed in the initiation step reacts with another molecule of isobutene to form a new cation that, in turn, reacts with a third monomer and so on. With every new monomer unit adding to the poly(isobutylene) chain, the positive charge moves to the end of the most recently added monomer unit.



Step 3: Chain termination — Cationic polymerisation can be terminated either by loss of a proton, which leads to

formation of an alkene, or by reaction with a nucleophile.



Poly(isobutylene) is also known as *butyl rubber*. It is an elastomer that is impermeable to air and so has many applications where airtight rubber is required. The first major application of butyl rubber was tyre inner tubes, which is still an important segment of the market today. In addition, butyl rubber is used to make adhesives and cling film, and is used as an additive in petrol and diesel and even in chewing gum.

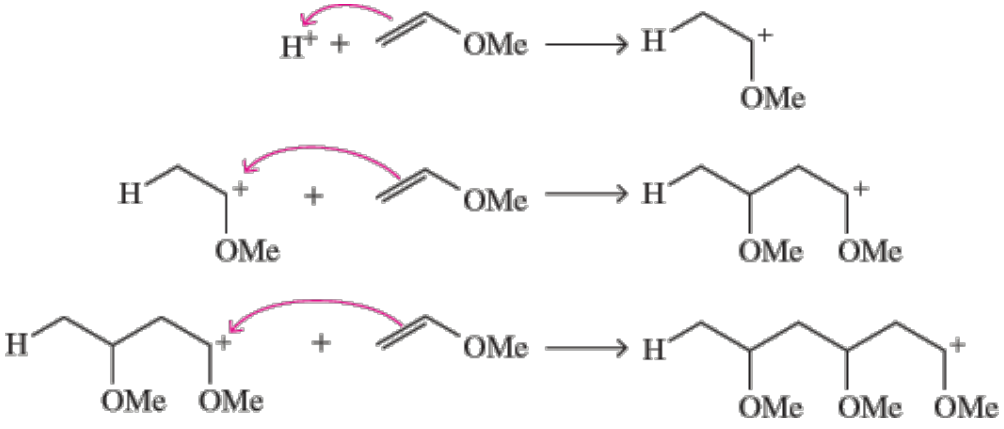
WORKED EXAMPLE 26.6

Synthesising a Polymer Through Cationic Polymerisation

Show the mechanism for the proton-catalysed formation of a cationic segment of poly(methyl vinyl ether) containing three units of methyl vinyl ether.

Analysis and solution

Methyl vinyl ether is an unsymmetrically substituted alkene. The polymerisation is initiated by addition of a proton to the double bond forming the more stable (more highly substituted) carbocation. This is attacked by another molecule of methyl vinyl ether in a stepwise manner to produce the polymer. Each third carbon atom of the polymer backbone is substituted by a methoxy group.

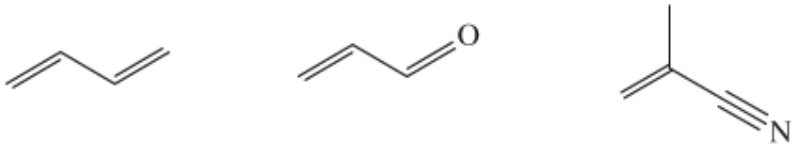


PRACTICE EXERCISE 26.6

Show the mechanism for the cationic, proton-catalysed polymerisation of styrene by developing a segment of polystyrene containing three units of styrene.

Anionic Polymerisation

Addition polymerisation can also be performed with anionic species being the chain carrier. This type of polymerisation uses alkenes with electron-withdrawing groups, which can stabilise negative charges very well, such as through resonance (see section 19.3). Examples include 1,3-butadiene, styrene, acrolein and methyl acrylonitrile.

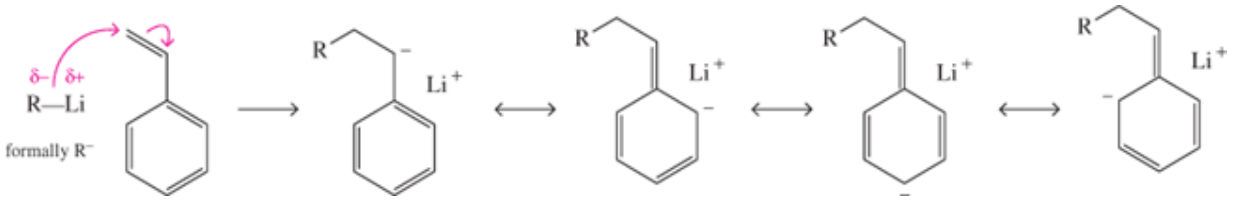


1,3-butadiene | acrolein (2-propenal) | methyl acrylonitrile

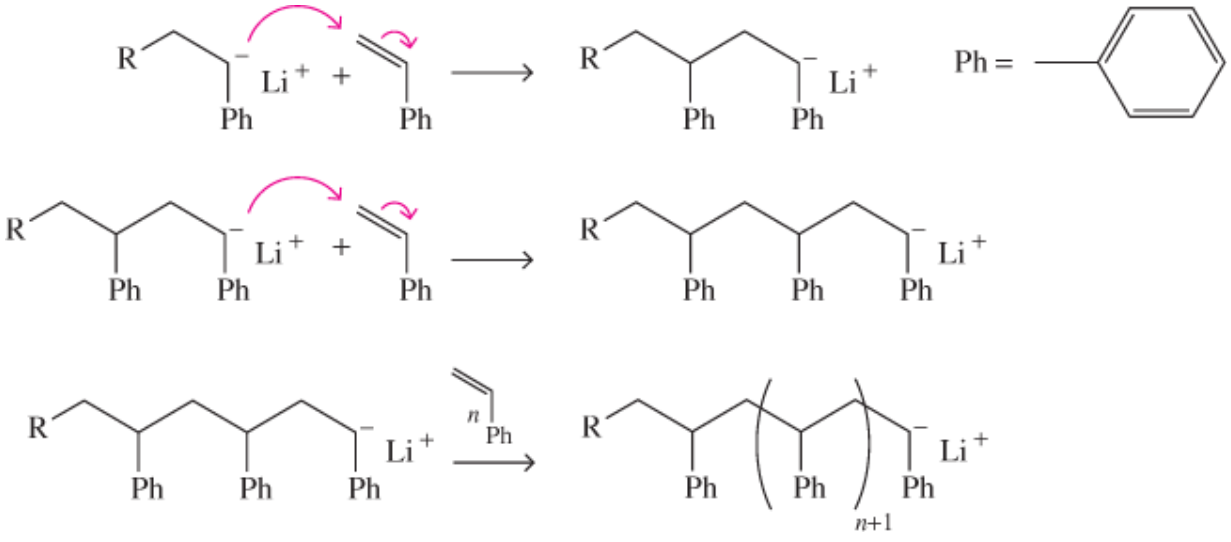
Anionic polymerisations are initiated by the addition of nucleophiles to the alkene. These nucleophiles could be metal amides, hydroxides and alkoxides, as well as organometallic species, such as Grignard reagents (see section 21.5) and alkyllithium compounds, in which the alkyl residue has a negative polarity.

We will discuss here the anionic polymerisation of styrene initiated by addition of an alkyllithium R—Li to the alkene double bond.

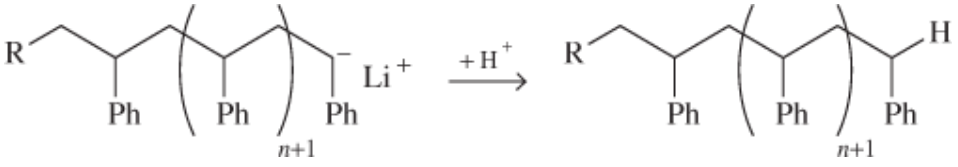
Step 1: Chain initiation occurs by addition of the alkyl residue R^-, leading to formation of a carbanion, which is stabilised by resonance.



Step 2: Chain propagation involves addition of the anion to another molecule of styrene to form a new anion, which in turn reacts with a further styrene monomer. The negative charge moves to the end of the most recently added monomer unit.



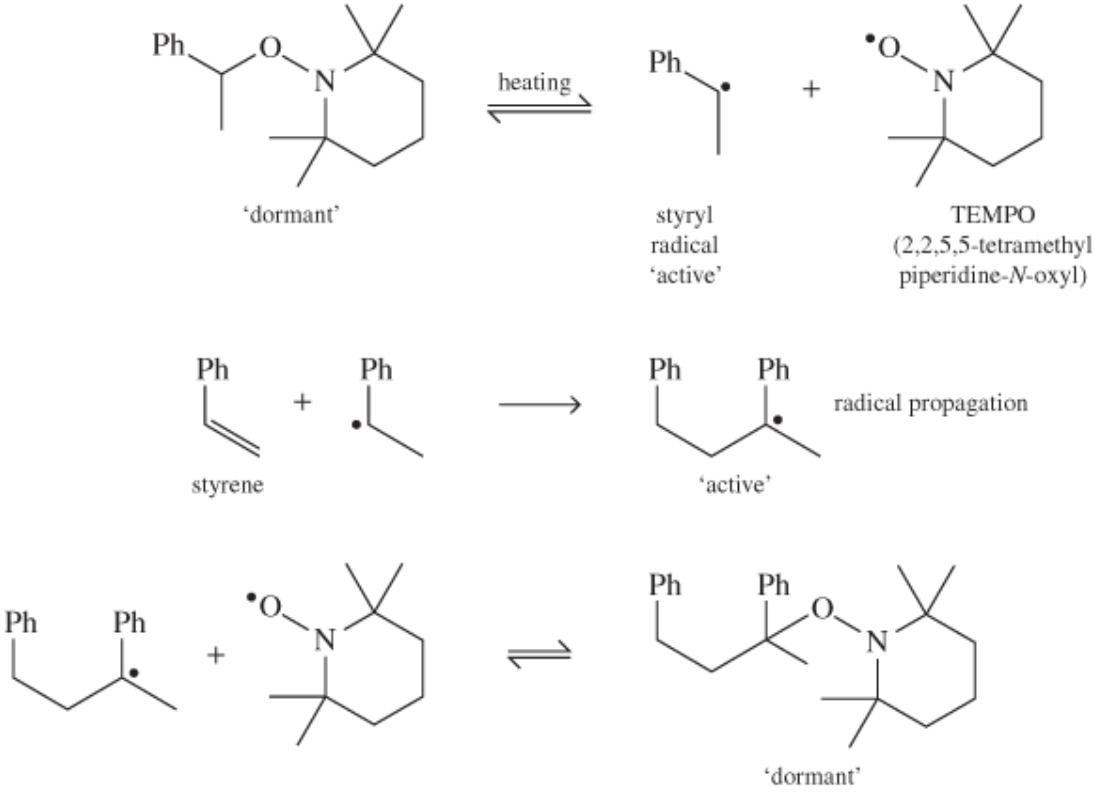
Step 3: Chain termination. Anionic polymerisation has no formal termination pathway. Usually, termination occurs through the presence of impurities, such as water or other electro-philes. Termination through reaction with a Brønsted–Lowry acid (see section 11.1) is shown below.



Reversible-deactivation Radical Polymerisation

Radical polymerisation is a mature technology that is widely used in industry. For example, vinyl polymers are produced on a scale of millions of tonnes per year. However, a major disadvantage is that the high reactivity of the radical chain carriers prevents the industrial production of polymers with controlled architecture (e.g. block copolymers and star polymers, see p. 1118) and low polydispersity (e.g. a highly uniform molecular mass distribution). In the late twentieth century, a new concept was developed which is based on the principle of reversible deactivation of the polymer chain growth during radical polymerisation. These methods rely on a dynamic equilibrium between low concentrations of propagating radicals and various types of dormant species produced through rapid deactivation of growing radicals.

Figure 26.19 illustrates the use of nitroxides as mediators in such reversible-deactivation radical polymerisation. Nitroxides are radical species possessing an unpaired electron at the oxygen atom of an N—O group (the nitroxide). TEMPO (the IUPAC name is 2,2,5,5-tetramethyl-piperidine-*N*-oxyl) is the most well known of these nitroxides; it is a stable orange solid and is commercially available. Reversible recombination of TEMPO with a styryl radical leads to a 'dormant' nonradical species. Heating breaks the C—O bond between the styryl and TEMPO moieties and transforms the dormant compound into the 'active' styryl radical, which can then undergo radical polymerisation. The growing polymer chain can be reversibly trapped by reaction with TEMPO to yield another dormant species. The overall rate of the radical polymerisation is determined by the ratio of activation, deactivation and the actual polymerisation step. Many analogues of TEMPO have been designed for the synthesis of special polymer architectures through this reversible-deactivation radical polymerisation method.



or more generally:

P_n—N $\underset{\text{deactivation}}{\overset{\text{activation}}{\rightleftharpoons}}$ $P_n^{\bullet}$ + N$^{\bullet}$ ↻ polymerisation

P_n = polymer chain
N = nitroxide

FIGURE 26.19 The concept of controlled radical polymerisation using nitroxide-mediated polymerisation.

Chemical Connections

CSIRO's RAFT Technology

Polymers are macromolecules which are composed of discrete chemical units called monomers. Polymers are important because so much of what we are and what we use in our everyday lives is made up of polymers: from natural polymers, such as proteins and our own DNA, through to synthetic polymers, such as plastics, therapeutics, electronics, paints, oils and cosmetics. Polymer synthesis is a complex process that can be classified into two broad categories: addition polymerisation and condensation polymerisation.

In addition polymerisation, polymers are made by adding monomers one by one to an active site on the growing chain. The most common type of addition polymerisation is free radical polymerisation. Polymeric materials made by conventional free radical polymerisation are characterised by a broad mixture of polymer chain lengths, each with a different molecular mass, resulting in a broad molecular mass distribution (figure 26.20).

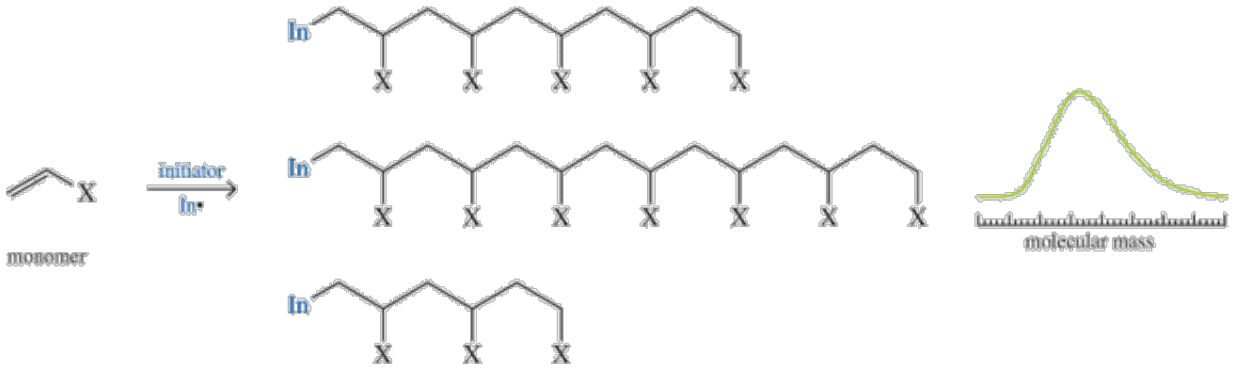


FIGURE 26.20 A schematic showing the process of addition polymerisation, resulting in polymer chains with a wide range of molecular masses.

Polymers made by conventional free radical polymerisation are satisfactory for general purpose applications, such as general paints and plastics, as their properties do not have to be precise. Our modern world, however, is hungry for new, highly functionalised polymers to address the many new and existing challenges that we

face, including the need for new therapeutics and drug delivery systems, multifunctional polymers for personal care uses, and new controlled-release agents to help optimise agricultural yields. To address this level of function and sophistication, polymers of well-defined size, composition and architecture are needed.

CSIRO's RAFT (reversible addition fragmentation chain transfer) technology provides a revolutionary level of control suitable for highly functionalised polymers. RAFT is a type of addition polymerisation in which termination reactions are largely suppressed, and polymer growth can continue until the monomer supply has been exhausted. The polymerisation will resume if more monomers (and initiators) are added to the solution.

This feature of RAFT gives the manufacturer very specific control over the size, composition and architecture of the polymer being formed. It enables the creation of polymer chains that are more uniform in molecular mass (i.e. low polydispersity, see figure 26.21), which means that such polymers exhibit more refined properties.

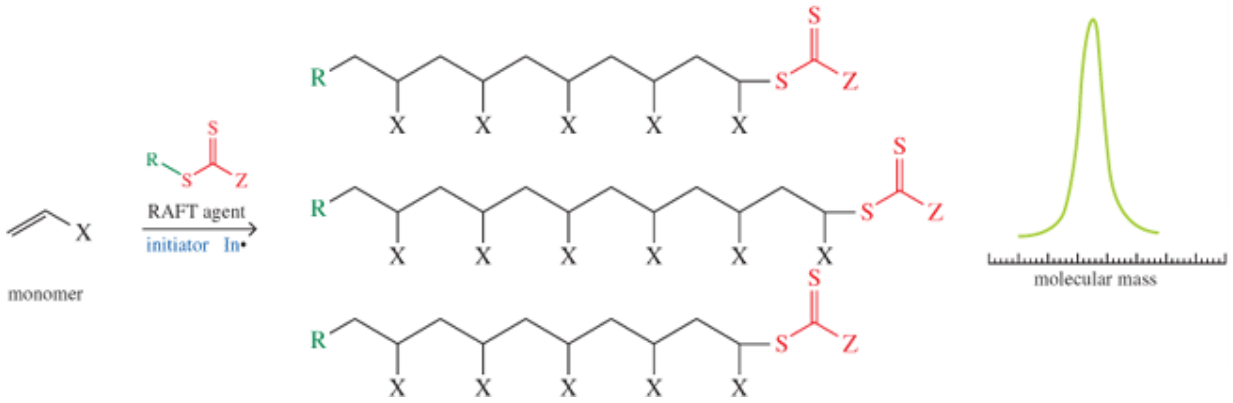
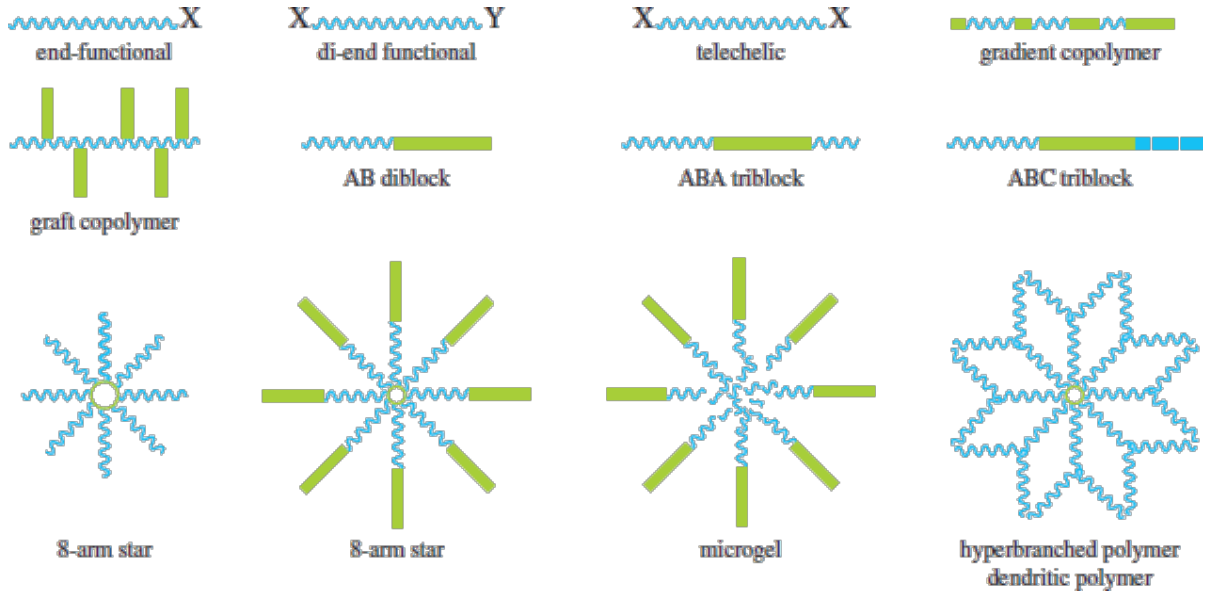


FIGURE 26.21 A schematic showing the process of addition polymerisation using reversible addition fragmentation chain transfer (RAFT) technology, resulting in polymer chains with a narrow range of molecular masses.

RAFT is compatible with a wide range of monomers and monomer mixtures and can be used in all modes of free radical polymerisation, including solution, emulsion and suspension polymerisations. Importantly, polymer manufacture using the RAFT process is compatible with existing industrial plants and processes, which makes its implementation in industry straightforward without the need for new significant capital investment.

RAFT-derived polymers are also characterised by defined end-groups which can be specifically manipulated (see below for examples of the range of possible end-groups). This allows users to deploy such polymers as synthetic intermediates in their own right for myriad applications, including the attachment to other molecules, materials and surfaces. This is plainly not possible with conventionally derived addition polymers. RAFT provides the opportunity to design and synthesise highly functionalised molecules and materials with new properties and features.



In summary, RAFT is a revolutionary technique in the field of polymer design and synthesis. Its ability to control molecular mass, composition and architecture, and to produce polymers that can be attached to other molecules, materials, and surfaces, is truly enabling.

The applications of RAFT are manifold and diverse, and include personal care products, gene silencing for the treatment of human diseases, high-performance paints, circuit boards and electronics, industrial lubricants, flexible electronics and new materials to improve the efficiency and lower the environmental impact of agrichemicals.

> This is a very exciting area of chemistry and we are seeing a huge amount of global interest in this technology. There are over 450 new inventions that use RAFT that have been patented, more than 3000 scientific papers that cite our RAFT work and we have licensed the technology to 15 companies to exploit the technology in a diverse range of fields. We are now seeing the first new products made using RAFT enter the market. (Dr Ezio Rizzardo, CSIRO, lead inventor of RAFT)

CSIRO's RAFT scientists are continuing the research and commercialisation of multi-functional polymers, particularly in the areas of agriculture, drug delivery, biomedical materials, personal care and cosmetics and flexible electronics (figure 26.22). To learn more about RAFT and its applications, go to www.csiro.au/products/RAFT.



FIGURE 26.22 CSIRO is using RAFT technology to develop polymers for use in
(a) personal care products,
(b) spray paints and
(c) drug delivery.

Chemistry Research

Intelligent Materials

Professor Gordon Wallace, University of Wollongong

Traditional polymers have been engineered to provide materials that are low density, mechanically strong and environmentally stable. They have been made to be nonresponsive — they are, in fact, lightweight, dumb materials!

Intelligent polymers are engineered from the molecular level to respond to environmental stimuli in a way that enhances their performance. Imagine, for example, a polymer that changes colour in sunlight to stop transmission of light, or that becomes stronger in response to stress. Consider a polymer coating that releases a corrosion inhibitor in response to the onset of corrosion or even a medical device that releases anti-inflammatory drugs in response to the onset of infection.

Polymers such as polypyrrole conduct electricity and can be reversibly oxidised and reduced according to the processes shown in figure 26.23. Unlike traditional polymers, they are not electronic insulators — they conduct electricity. Also, unlike traditional polymers, they are not inert — they are dynamic (electroactive) structures.

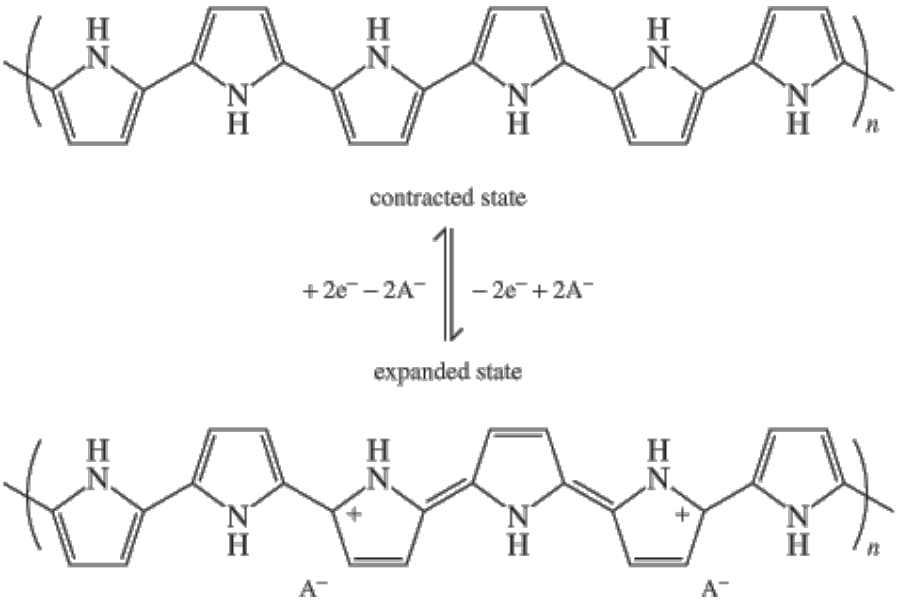


FIGURE 26.23 Polypyrrole dynamic (electroactive) polymer structure (A^- = anion).

The chemical, biological, electrical and mechanical properties of these conducting polymers are critically dependent on the oxidation state of the structure and hence on their working environment. If this dynamic behaviour can be determined by appropriate molecular engineering, truly intelligent polymer structures will emerge.

These dynamic properties of polymers can also be finetuned in the working environment by the application of an external electrical potential. For example, electrical stimulation has been used to initiate an ion flux across a conducting polymer membrane. Simple salts such as NaCl can be pumped across these dynamic membranes using an applied potential, and the ion flux can be switched off at any time by removing the electrical stimulus.

Using a similar but now trilayer membrane structure, electrical stimulation can be used to induce movement in conducting polymers creating so-called artificial muscles (see figure 26.24). Electrical stimulation causes anions to move into the oxidised side of the membrane structure, causing expansion, and expels anions from the other side, causing contraction, resulting in movement (see figure 26.24b). The ability to induce such chemical and mechanical changes *in situ* presents some exciting opportunities for the use of these intelligent polymers in biomedical devices.

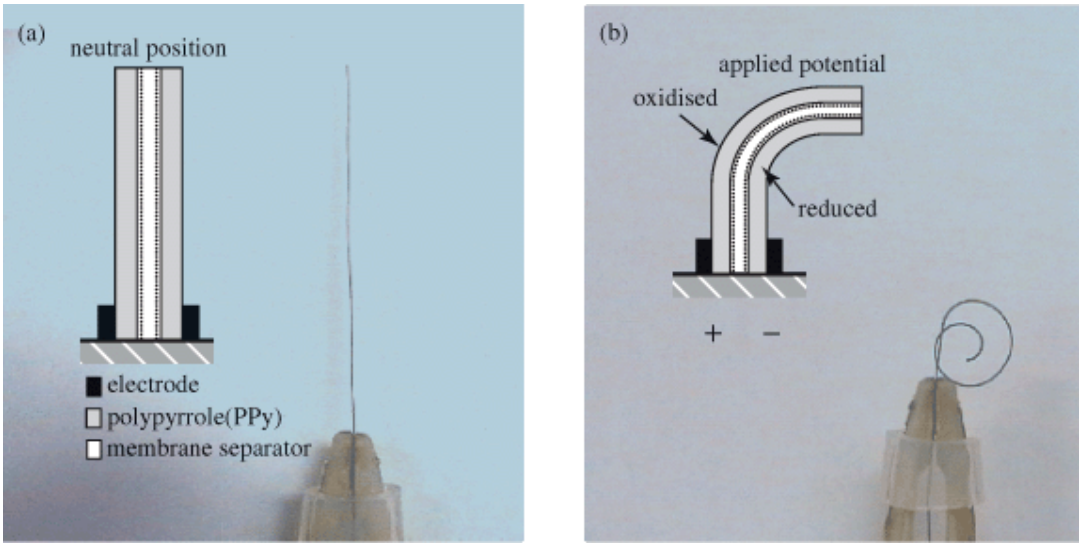


FIGURE 26.24 Electrical stimulation causes dramatic movement (curling) in the polymer. Schematic structure of the conducting polymer actuator in

(a) the neutral position and

(b) the electrically stimulated state.

Recently, researchers at the Intelligent Polymer Research Institute, in collaboration with scientists at the Bionic Ear Institute and St Vincent's Hospital, showed that these polymers can be designed so that they are compatible with nerve cells. Through electrical stimulation, they can release nerve growth factors and facilitate the outgrowth of neurites from these cells (figure 26.25). Such polymers may well find use in improving the electrode–cell interface in medical bionic devices such as the cochlear implant (a 'bionic ear' pioneered by Professor Graeme Clark in Australia).

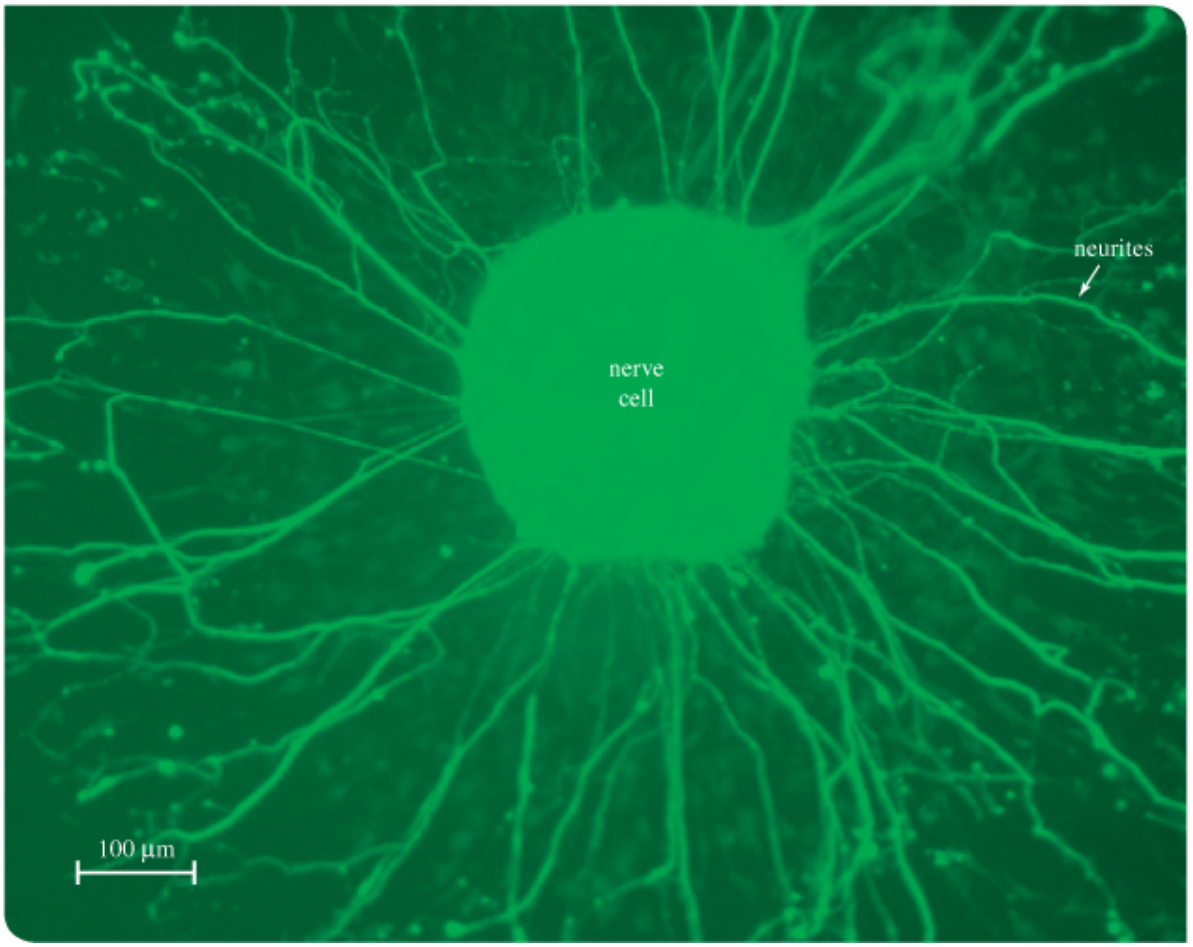


FIGURE 26.25 Electrical stimulation by a conducting polymer causes dramatic improvements in neurite outgrowth from nerve cells.
Gordon Wallace

Also on the medical front, intelligent polymers have been developed that respond to electrical stimuli by producing a force or movement. Such polymers may assist surgeons during implantation of medical devices such as the bionic ear, which is a steerable implant.

As the mechanical strength of intelligent polymers is improved, they may even be used as wearable prosthetics to assist with limb movement. Recently, using nanotechnology, small amounts of carbon nanotubes have been added to a conducting polymer to produce the strongest artificial muscle fibres to date. Some movement is still possible even under stresses of 100 MPa — in excess of what human muscle can withstand.

The ability of conducting polymers to sense the environment is being coupled with an ability to respond, producing truly intelligent systems. A simple example is the development of a conducting polymer trilayer system that responds to oxygen levels to open a valve to monitor the optimum environmental conditions for food packaging during transport.

As we develop our ability to molecularly engineer these systems, some fascinating systems will emerge.

A controlled radical polymerisation process based on *r*eversible *a*ddition *f*ragmentation chain *t*ransfer (RAFT) has been developed by CSIRO in Australia and Rhodia in France. The concept is based on the reversible addition of radicals to carbon–sulfur double bonds in thiocarbonyl thio transfer reagents (R—S(C═S)Z (figure 26.26). Very potent reagents are xanthates, which are esters derived from carbonic acid, where two oxygen atoms are replaced by sulfur, i.e. Z is OR′. The addition of a growing polymer chain radical to the C═S bond is followed by fragmentation of an S—polymer chain bond. This releases a polymer radical, which can undergo further chain growth, until it is again trapped by reversible addition to a C S bond. Today, the RAFT technology is a very powerful tool for designing functional polymer architectures for applications in medicine, electronics and photovoltaics, as well as coatings and paints.

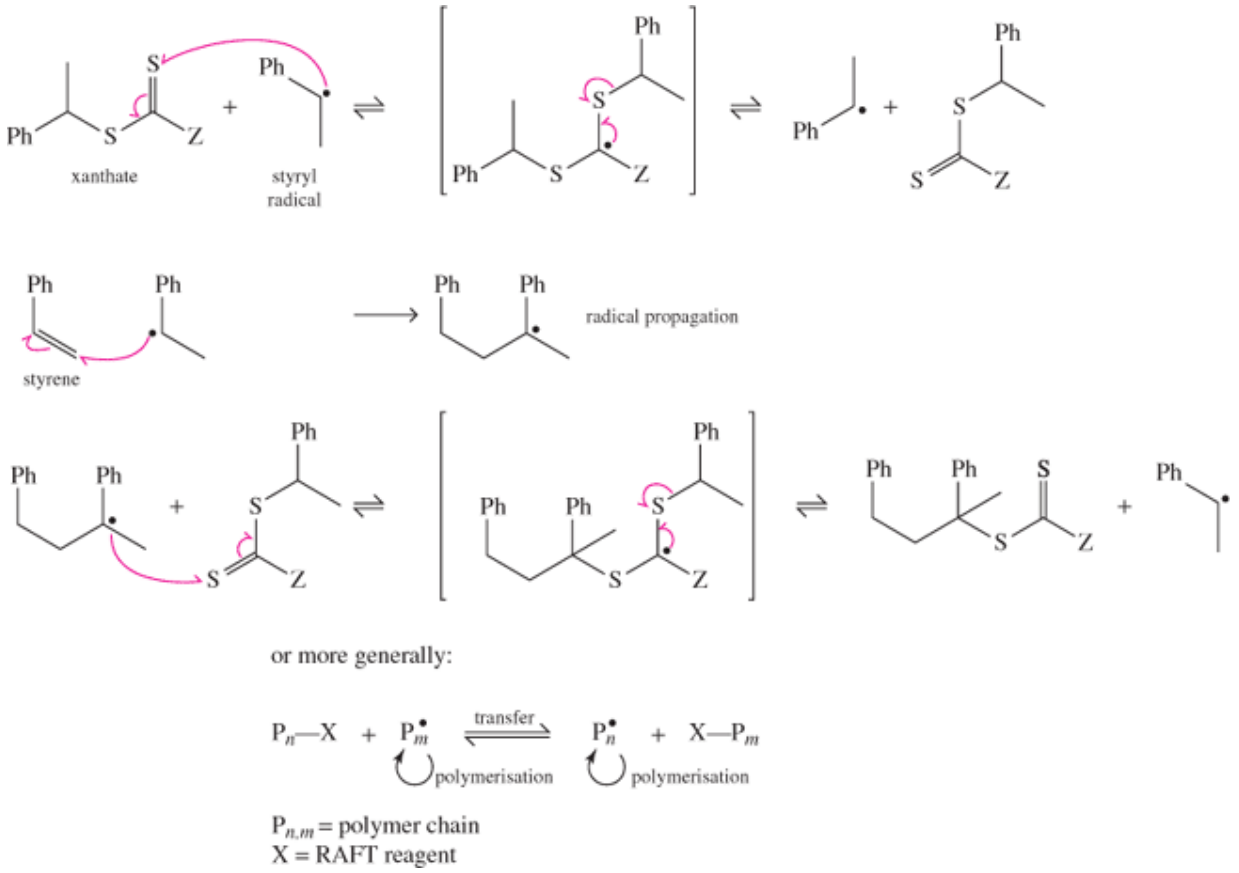
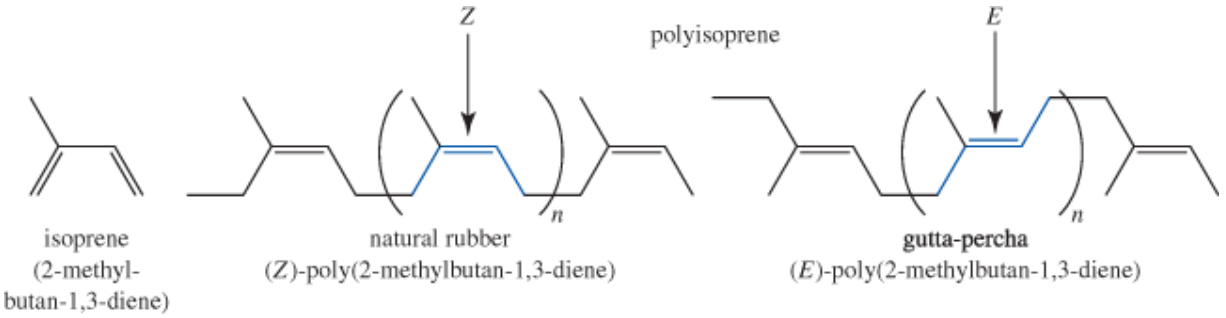


FIGURE 26.26 The RAFT polymerisation process.

Natural Rubber and The Vulcanisation Process

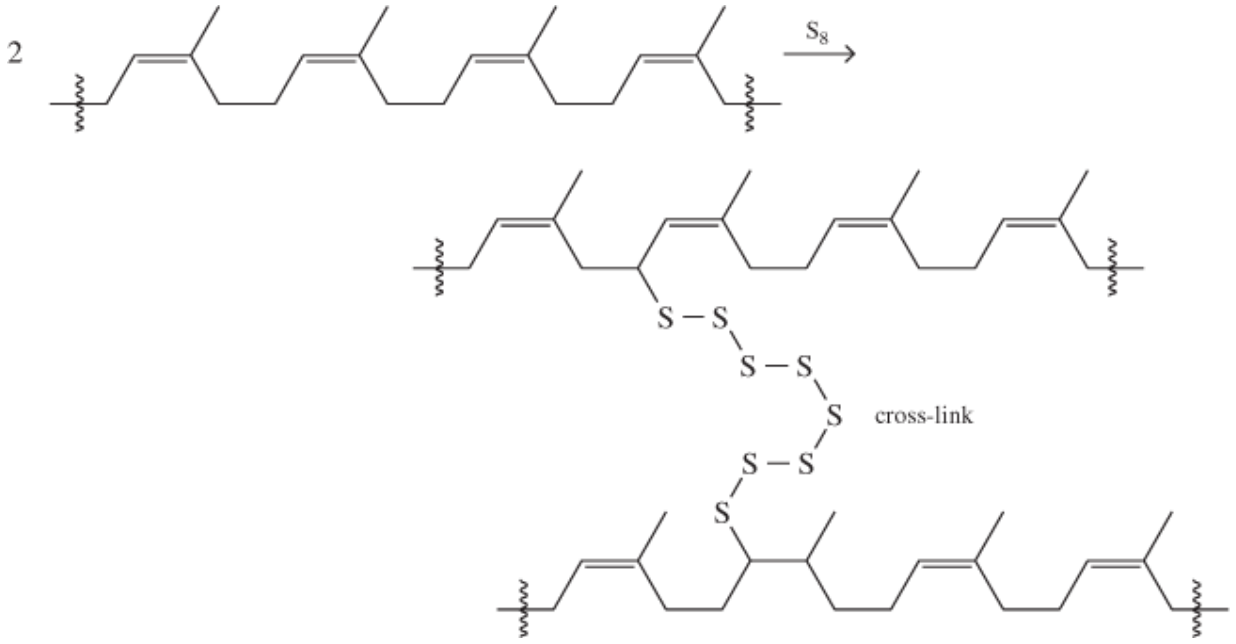
Natural rubber is an important product derived from the latex of the rubber tree *Hevea brasiliensis*. It is a polymer of isoprene (2-methylbutan-1,3-diene, see section 16.3) that features a *Z* geometry at the double bond in each unit. On average, a natural rubber molecule contains up to 5000 units of isoprene. The biological function of rubber latex is to protect the tree after injury by forming a bandage that covers the wound.



Gutta-percha is an isomer of rubber that is found in tropical trees in southeastern Asia and northern Australasia. It is also a polyisoprene, but with *E* configuration at the double bond. Gutta-percha is harder and more brittle than rubber. In 1848, the first golf ball made from guttapercha was produced; it replaced the feather balls within a few years and revolutionised the game. Because it does not readily react within the human body, gutta-percha is also used for a variety of surgical applications and is the filling material that dentists use during root canal therapy.

When natural rubber latex was first discovered, it was not particularly useful. In hot weather it became sticky, and in the cold it became brittle and hard. After many experiments to improve the properties of natural rubber, the American Charles Goodyear discovered in 1839 that, by adding sulfur to the rubber latex and heating, the properties of rubber could be drastically improved. He named his new product **vulcanised rubber** and the process is called **vulcanisation**.

When rubber latex is treated with sulfur, groups of sulfur atoms form bridges, so-called **cross-links**, between the various strands of polyisoprene. (Under the conditions used to treat rubber, sulfur exists substantially as eight-membered rings, S_8.) The mechanism of cross-linking is complicated and will not be discussed here.



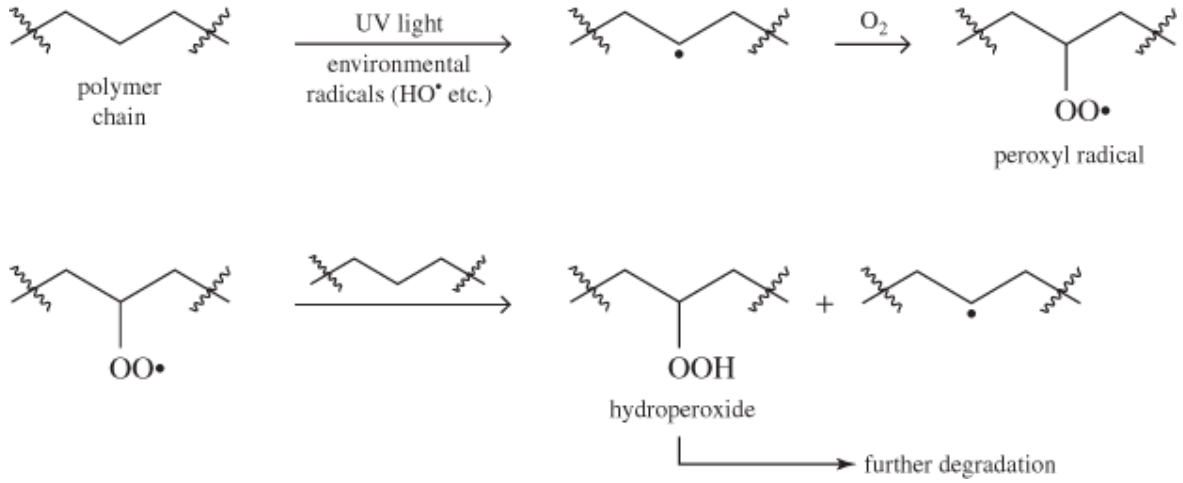
When the strands are linked, they cannot easily slip on each other when it is hot so the rubber does not melt. The increased strength also prevents the polymer from becoming brittle and easily broken when cold. Cross-linking also gives the polymer a ‘memory’, which enables it to snap back into its original shape when released after being stretched; you have experienced this prop-erty when using rubber bands or throwing rubber balls. The amount of sulfur used to vulcanise the rubber latex also affects the properties of the finished product. If only a small amount of sulfur (1–3%) is used, the polymer is soft and elastic. As the extent of cross-linking increases, the product becomes harder and less resilient. Rubber made with 3–10% sulfur is used in the manufacture of tyres. Vulcanised rubber is, like the discovery of Teflon, considered as one of the top 10 accidental inventions.

Degradation of Polymers

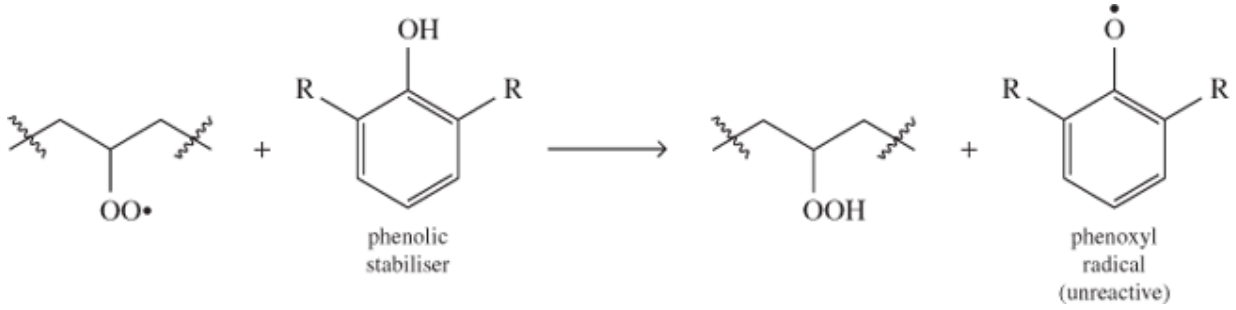
Polymers are exposed to considerable environmental stress. For example, garden furniture starts to lose its appealing

look when it is left outside throughout the year; these and other, formerly white, plastics start to discolour after a while, changing to a dirty yellow colour, which no longer looks attractive. Other polymers become brittle and break into small pieces. Obviously, the environment where commercial polymers are used has a significant effect on their lifespan. In practice, any change in properties of a polymer relative to their initial desired properties, is called **degradation**.

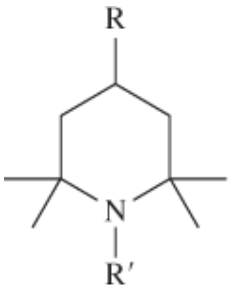
Exposure of plastics to sunlight and some artificial light sources (especially the UV component of the light) can rupture chemical bonds in the polymer. This process is called **photodegradation** and can ultimately lead to cracking, chalking, discolouration and the loss of other physical properties, such as elasticity. Once a chemical bond in the molecule is broken, free radicals are produced, which lead to oxidative degradation of the polymer in a radical-chain process that involves reaction with oxygen in ambient air. In a similar way, chemical degradation by atmospheric radicals, such as hydroxyl radicals (HO•), leads to destruction of the polymer material.



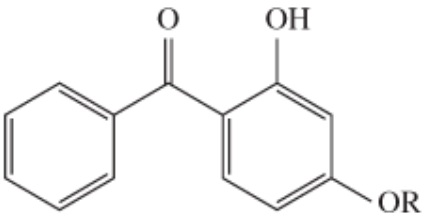
Stabilisers are often added to polymers to prevent such degradation reactions from occurring. Phenolic stabilisers are frequently used because they can intercept the radical-chain degradation process through donation of hydrogen atoms to the intermediate peroxyl radicals. The phenoxyl radical, which is formed during this process, is unreactive. Thus, the **antioxidant** effect of phenol stabilisers (radical scavengers) can transform highly reactive radical species into unreactive compounds which do not propagate further radical-chain degradation.



So-called hindered amine light stabilisers (HALS) are extremely efficient at stabilising most polymers against light-induced degradation. The mechanism of this process is highly complex and not yet fully understood. The advantages of a HALS, compared with a phenolic stabiliser, is that it is constantly regenerated and is not consumed, and, therefore, it provides extremely long-term thermal and light stabilisation to the polymer.



HALS



substituted benzophenone
(UV absorber)

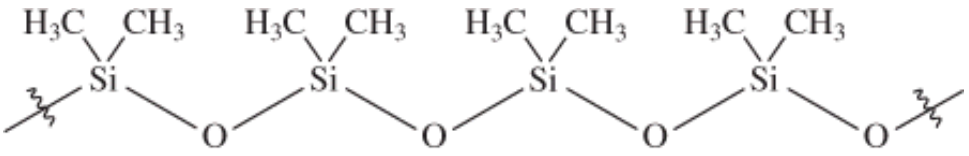
Besides radical-scavenging processes, which deactivate radicals that have already formed, UV light can also be absorbed before any damage to the polymer chain occurs. The concept used to protect polymers is the same as that used to protect our skin from sunburn. Such UV absorbers can be inorganic pigments (such as TiO_2 and ZnO — ingredients in sunscreens) or organic compounds which transform harmful UV radiation into thermal energy through photophysical processes; the details of these are beyond the scope of this chapter.

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26.4 Silicon Polymers

Each polymer discussed so far is classified as an organic polymer because the polymer's back-bone (the main polymer chain) is composed predominantly of carbon atoms, in addition to smaller amounts of nitrogen and oxygen atoms (e.g. polyesters and polyamides). The many applications of the various synthetic organic polymers given in this chapter make it clear that our lives would be very different without them. However, organic polymers have some general disadvantages. For example, they typically become brittle when cold and deteriorate when very hot. They also tend to be flammable, swell in organic solvents and are usually not compatible with living tissue (for example, when used as a medical implant). Because of this, other polymers that are, for example, flexible at low temperatures and able to withstand high temperatures have been developed.

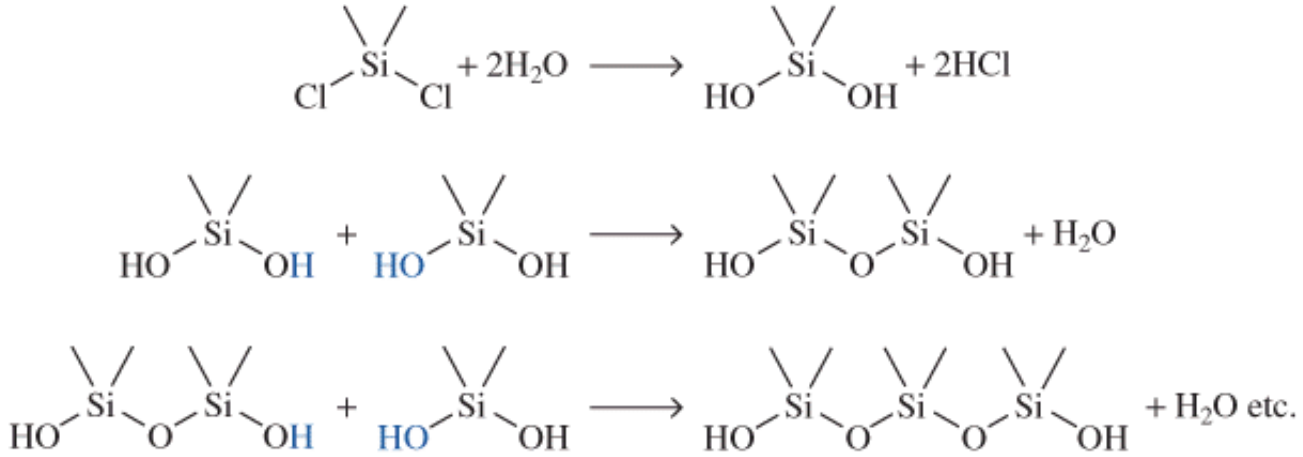
Silicon polymers (**silicones**) have a backbone of alternating silicon and oxygen atoms, with organic groups attached to each silicon atom:



a silicon polymer chain

Because there is no carbon in the backbone, silicones are known as inorganic polymers.

Silicon polymers are formed by condensation polymerisation, beginning with the *hydrolysis* of silicon compounds such as $(CH_3)_2SiCl_2$. This gives Si—OH bonds that subsequently undergo condensation to produce Si—O—Si linkages:



Depending on the chain length and the degree to which chains are cross-linked, silicones can be oils, greases or rubbery solids.

Silicone oil repels water and water-based products. For this reason, it has been used in furniture and car polishes, as waterproofing treatments for fabrics and leather, and for gaskets and sealing rings in jet engines. Silicone greases are used as permanent lubricants in clocks and ball bearings. Silicone rubber has excellent electrical insulating properties and so is used in electric motors and to coat electrical wire. These rubbery materials also retain their flexibility over wide temperature ranges and can be used in place of natural rubber for both high- and low-temperature applications. Silicone rubbers maintain their flexibility at low temperatures, where other elastomers such as natural rubber become hard and stiff, because of the conformational motion of the silicon–oxygen bonds in the backbone of the polymer.

Silicon polymers have become important materials for medical implants, such as breast implants (figure

26.27) used after surgery or for augmentation. There are different types of implants including saline implants, which have a silicone elastomer shell and are filled with sterile saline liquid, and silicone gel implants, which have a silicone shell filled with a viscous silicone gel. In the 1980s, concerns were raised that silicone leaking from breast implants could increase the risk of a range of conditions, such as autoimmune disorders and even cancer. Despite the controversy, there is no unambiguous evidence of an association between silicone gel implants and increased risk of any diseases; certain varieties of both silicone and saline-filled implants are approved for use in Australia and New Zealand.



FIGURE 26.27 Silicon polymers have many medical applications, including their use in breast implants. Bridgeman Art Library/Gabriel Cloquemin

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26.5 Recycling Plastics

Our society is very dependent on polymers in the form of plastics. Durable and lightweight, plastics are probably the most versatile synthetic materials in existence. There are about 40 different plastics or polymers in common use today; Australia produces about 1.2 million tonnes a year, and New Zealand about 242 000 tonnes. Plastics have come under criticism, however, for their contribution to rubbish that ends up as landfill.

If the durability and chemical inertness of most plastics make them ideal for reuse, why are more plastics not being recycled? The answer to this question has more to do with economics and consumer habits than with technological obstacles. In Australia and New Zealand, unlike Europe and North America, recycling bins and drop-off stations for recyclables have only recently become widely established (figure 26.28) and so the amount of used material available for reprocessing has traditionally been small. This limitation, combined with the need for an additional sorting and separation step, rendered the use of recycled plastics in manufacturing more expensive than virgin materials. However, increased recycling has led to greater efficiencies of scale, which bring down costs. In addition, the increase in environmental awareness over the last decade has resulted in greater demand for recycled products.



FIGURE 26.28 Recycling plastics has become routine in most households in Australia and New Zealand.

To help identify different plastics, manufacturers stamp a plastics identification code on their products (figure 26.29). The code is a number inside a triangle formed by three arrows. The most common plastics have the codes 1–7 and are shown in table 26.2.



FIGURE 26.29 A selection of product packaging manufactured from recycled plastics.
Kari-Ann Tapp

TABLE 26.2 Identification codes for plastics in Australia and New Zealand

Plastic identification code				
Australia	New Zealand	Polymer	Common uses	Uses of recycled polymer
		polyethylene terephthalate		

			• soft-drink bottles • filling for sleeping bags • textile fibres	• soft-drink bottles • (multilayer) detergent bottles • clear film for packaging • carpet fibres • fleecy jackets
		high-density polyethylene	• crinkly shopping bags • freezer bags • milk and cream bottles • shampoo bottles • milk crates	• compost bins • crates • agricultural pipes • pallets • rubbish bins • furniture • cargo liners • rulers • packaging materials
		unplasticised poly(vinyl chloride)	• clear cordial and juice bottles • blister packs • plumbing pipes and fittings	• detergent bottles • tiles • plumbing pipe fittings
		plasticised poly(vinyl chloride)	• garden hose • shoe soles • blood bags	• hose inner core • industrial flooring
		low-density polyethylene	• lids of ice-cream containers • garbage bags • rubbish bins • black plastic sheeting	• film for builders, industry, packaging and plant nurseries • bags
		polypropylene	• ice-cream containers • potato chip bags • drinking straws • hinged lunch boxes	• compost bins • kerbside recycling crates • worm factories
		polystyrene	• yoghurt containers • plastic cutlery • imitation crystal ‘glassware’	• clothes pegs • coat hangers • office accessories • rulers • CD cases
		expanded polystyrene	• hot-drink cups	• synthetic timber

6 PS-E		• takeaway food containers • meat trays • packaging	
7 OTHER	7 OTHER	includes all other plastics, such as acrylic and nylon	• car parts • packaging • computers • concrete aggregate • outdoor furniture • agricultural pipes

Plastics and Chemicals Industries Association

Most plastics can be recycled, but, due to the difficulty in collecting, sorting, cleaning and reprocessing (figure 26.30), it is economically viable to recycle only three types of plastics from domestic sources: PET, HDPE (PE-HD in New Zealand) and PVC (also V for vinyl in Australia). Of these, HDPE is the most often recycled plastic.

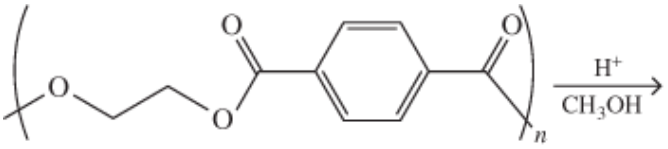


FIGURE 26.30 Worker sorting rubbish at a recycling depot.
Todd Martyn Jones

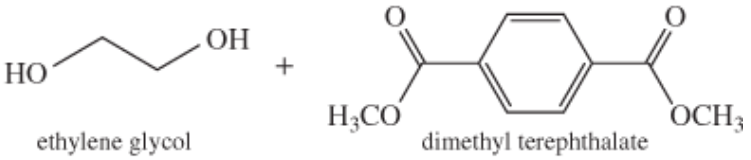
The process of recycling most plastics is simple, with separation of the desired plastics from other contaminants being the most labourintensive step. For example, PET soft-drink bottles (p. 1128) usually have a paper label and adhesive that must be removed before the PET can be reused. The recycling process begins with hand or machine sorting, after which the bottles are shredded into small chips. An air cyclone then removes paper and other lightweight materials. Any remaining labels and adhesives are eliminated with a deter-gent wash, and the PET chips are then dried. PET produced by this method is 99.9% free of contaminants and sells for about half the price of the virgin material. PET

chips can be melted and spun into fibres. Unfortunately, plastics with similar densities cannot be separated with this technology, and plastics composed of several polymers cannot be broken down into pure components. However, recycled mixed plastics can be moulded into plastic 'timber' that is strong, durable and resistant to graffiti.

Besides these mechanical methods of polymer recycling and purification, chemical recycling (*monomer recycling*) can be used to essentially reverse the condensation polymeris ation reaction that was used to create the polymer. This yields the same mix of chemicals that formed the original polymer, which can be purified and used to synthesise new polymer chains of the same type. For example, Eastman Kodak salvages large amounts of its PET film scrap by a transesterification reaction. The scrap is treated with methanol (*methanolysis*) in the presence of an acid catalyst to give ethylene glycol and dimethyl tere phthalate, monomers that are purified by distillation or recrystallisation and used as feedstocks for the production of more PET film:



poly(ethylene terephthalate)
(PET)



ethylene glycol
(1,2-ethanediol)

dimethyl terephthalate

Another potential option for chemical recycling of plastics is the conversion of assorted polymers into petroleum hydrocarbons by a so-called thermal depolymerisation process. Long-chain polymers containing carbon, hydrogen and oxygen are decomposed under pressure and heat into petroleum hydrocarbons with chain lengths of around 18 carbon atoms. Thermal depolymerisation mimics the natural geological processes that produced fossil fuels. Thus, like natural petroleum, the recycled chemicals produced can be made into fuels as well as polymers. Such a process could accept almost any polymer or mix of polymers.

The problems associated with plastic recycling can principally be circumvented by using **biodegradable polymer**, which can be broken down by enzymes produced by micro-organisms. The carbon–carbon bonds in chain-growth polymers are inert to enzyme-catalysed degradation, so they are not biodegradable. However, if the polymer contains small units with bonds that can be broken by enzymes, the polymer is degraded by micro-organisms once it is buried as waste. The polyester PET, for example, can be made degradable by incorporating aliphatic ester units into its structure; this creates weak spots in the polymeric chains and makes them susceptible to degradation by hydrolysis.

Chemical Connections

Polymer Banknotes

Australia is the world leader in the technology that is used to make plastic banknotes. After a 21-year research effort, Australia released the world's first polymer banknote in 1988 (figure 26.31). The technology was further improved in the following years and by 1996 all notes in Australia were plastic. Today they are used in more than 22 countries from New Zealand (figure 26.32) to Mexico, and many more, including the United States, are considering their introduction.



FIGURE 26.31 The world's first polymer banknote.



FIGURE 26.32 New Zealand polymer banknotes.
Allan Blackman

The polymer banknote technology was developed by the CSIRO Division of Chemicals and Polymers and Note Printing Australia (which is a part of the Reserve Bank of Australia). The research scientist who invented the plastic note technology was CSIRO's David Solomon, now a professorial fellow in the Polymer

Science Group at the University of Melbourne. (Solomon is currently working on a polymer film to cover large water storages to prevent evaporation.)

Traditional paper banknotes wear out quickly, and tend to disintegrate if they get wet. They are also easily counterfeited. In fact, it was the widespread counterfeiting of the $10 note shortly after Australia converted to decimal currency in 1966 that prompted the research that led to the development of the polymer note. The counterfeiting problem became worse with the development of high-quality colour scanners and photocopiers that made it easy to produce convincing counterfeit paper money.

Polymer notes are much more durable than paper; for example, the plastic $5 note survives almost 3.5 years in circulation, whereas the old paper notes lasted only about 6 months. Interestingly, once polymer notes are taken out of circulation, they are shredded and then recycled into products such as compost bins.

Polymer notes have proven much more difficult to counterfeit than paper notes. The polymer substrate starts as a biaxially oriented polypropylene film of a type that is not available commercially. It is supplied to the Reserve Bank (RBA) and other currency producers by a joint venture between the RBA and the Belgium-based chemical firm Union Chemie Belge. Multiple coatings are then applied to the clear film to make it opaque and to embed security features such as diffractive optically variable devices (including the image in the ‘holographic’ window that changes appearance depending on the viewing angle and the light). The polymer also allows most of the usual paper-note printing techniques and features, such as intricate patterns and details, see-through registration (similar to a watermark), fluorescent features, and the use of different inks. In fact, a combination of several different printing techniques is used to further complicate any counterfeiting attempts. The notes are then finished with a special protective coating to keep them clean and resistant to moisture.

Work is continuing to develop better polymer substrates and ways to make counterfeiting even more difficult.

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SUMMARY

The Architecture of Polymers

Polymerisation is the process of joining many small monomers into high-molar-mass polymers. The properties of polymeric materials depend on the structure of the repeating unit, as well as on the chain architecture and morphology of the material.

Polymers have different architectures and can be classified as linear or branched, or having a comb, ladder or star structure. The introduction of covalent cross-links between individual polymer chains leads to additional structural variations. Thermoplastics are polymers that, when melted, become sufficiently fluid that they can be moulded into shapes that are retained when they are cooled. Thermosetting plastics (or thermosets) are polymers that cure irreversibly through the addition of energy (as provided by heat, light or a chemical reaction) to a stronger form. Polymers may be composed of both ordered crystalline domains (crystallites) and disordered amorphous domains. The relative amounts of crystalline and amorphous domains differ from polymer to polymer and frequently depend on how the material is processed.

Polymer Notation and Nomenclature

When drawn, the structure of a polymer is usually shown by placing parentheses around the repeating unit, which is the smallest molecular fragment that contains all the nonrepeating structural features of the chain. The most common method of naming a polymer is to add the prefix *poly*- to the name of the monomer from which the polymer is synthesised.

Formation of Polymers

Polymers are formed by various techniques. Step-growth polymerisations involve the stepwise reaction of difunctional monomers. Important commercial polymers synthesised through step-growth processes include polyamides, polyesters, polycarbonates, polyurethanes and epoxy resins.

Chain-growth polymerisation proceeds by the sequential addition of monomer units to an active end-group on the chain. Radical chain-growth polymerisation consists of three stages: chain initiation, chain propagation and chain termination. In chain initiation, radicals are formed from nonradical molecules. In chain propagation, a radical and a monomer react to give a new radical. The chain length is the number of times a cycle of chain-propagation steps repeats. In chain termination, radicals are destroyed. New concepts enable controlled radical polymerisation, which produces polymers with defined architecture and low polydispersity. Ziegler–Natta chaingrowth polymerisations form an alkyl–transition metal compound; then alkene monomers are repeatedly inserted into the transition metal–carbon bond to yield a saturated polymer chain.

Modified Ziegler–Natta catalysts allow the stereoregular polymerisation of unsymmetrical alkenes, such as propene. This leads to isotactic, atactic and syndiotactic polypropylenes, which have different arrangements of the methyl group on the carbon polymer chain and, therefore, different chemical and physical properties.

Cationic polymerisations, usually of electron-rich alkenes, are initiated by cationic reagents that give carbocations, which act as polymerisation chain carriers. The chain is terminated by reaction with a nucleophile, usually an anion.

Anionic polymerisation reactions usually use electron-deficient alkenes, which can stabilise negatively charged intermediates (through resonance, for example). These polymerisations are initiated by addition of a nucleophile (such as a metallorganic compound) to give carbanions, which act as chain carriers. Anionic polymerisation reactions have no formal termination pathway, but reactions with electrophilic

species which may be present as impurities usually lead to termination.

Natural rubber is a polymer of isoprene, which is sticky at high temperature but brittle and hard when it is cold. Its properties can be improved by vulcanisation, a process by which the polyisoprene chains become cross-linked with sulfur chains. The amount of sulfur in vulcanised rubber determines its properties — small amounts make the polymer elastic; more increases the number of cross-links, making the rubber hard and less resilient.

Silicon Polymers

Silicon polymers have a noncarbon backbone that consists of silicon and oxygen atoms. They maintain their flexibility even at very low and very high temperatures. Because of their chemical resistance, they are used in medical applications such as implant materials.

Recycling Plastics

Recycling increases the life of plastics, either by mechanical degradation and melting into a new shape or by chemical recycling through depolymerisation techniques. A plastics identification code is used to help identify different plastics. Biodegradable polymers are modified polymers that contain labile units that can be enzymatically degraded by micro-organisms.

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KEY CONCEPTS AND EQUATIONS

Polymerisation reactions forming condensation or step-growth polymers *(section 26.3)*

In this polymerisation technique, a small molecule is usually eliminated when the two monomer units are joined. The structure of the polymer can be predicted from the structure of the monomers.

Polymerisation reactions forming addition or chain-growth polymers *(section 26.3)*

In this polymerisation technique, two monomer units are joined without the loss of atoms. The structure of the polymer can be predicted from the structure of the monomers.

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REVIEW QUESTIONS

The Architecture of Polymers

26.1 Why are branched polymers more flexible than linear polymers?

26.2 Give one example each of polymers with chains that are associated by each of the following.

(a) van der Waals forces

(b) hydrogen bonding

(c) stacking of aromatic rings

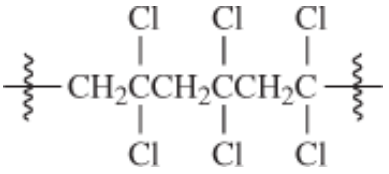
26.3 List the differences between thermosetting and thermoplastic polymers.

26.4 What are elastomers?

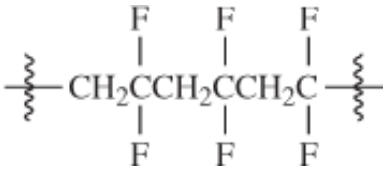
Polymer notation and nomenclature

26.5 The following are structural formulae for sections of two polymers:

(a)



(b)



From what alkene monomer is each polymer derived?

26.6 Draw a chain of three segments of each of the following polymers.

(a) Teflon

(b) poly(vinyl fluoride)

(c) polyacrylonitrile

26.7 What is the repeating unit in the polymers in question 26.6?

Formation of Polymers

26.8 Explain the general difference between step-growth and chain-growth polymers.

26.9 Why is an initiator required in chain-growth polymerisations?

26.10 Why are cationic polymerisations generally performed with electron-rich alkenes?

26.11 Why are anionic polymerisations usually performed with electron-poor alkenes?

26.12 Explain the structural difference between atactic, isotactic and syndiotactic polypropylene.

26.13 Explain the backbiting mechanism that leads to branching in the polymerisation of ethene.

Silicon Polymers

26.14 Outline the general structure of a silicon polymer.

26.15 Why are silicon polymers more flexible than carbon-based polymers at low temperature?

Recycling Plastics

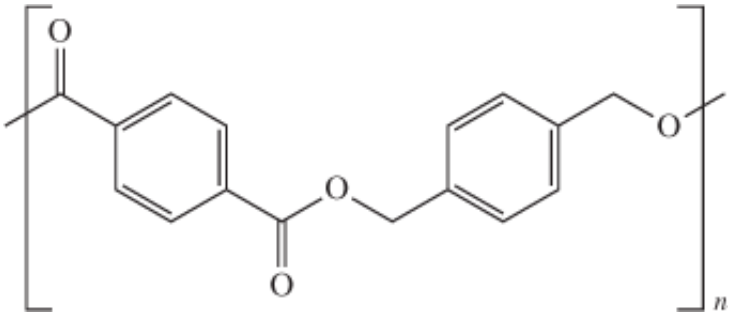
26.16 Explain the difference between mechanical and chemical recycling of polymers.

26.17 What is the difference between biodegradable and nonbiodegradable polymers?1

26.18 What is the main way of making a polymer biodegradable?

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26.19 Consider the following polymer.



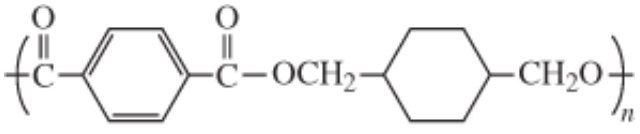
(a) Identify what monomers you would use to make this polymer.

(b) Which type of bond links the monomer units together?

(c) Would you use acidic conditions or basic conditions for this polymerisation process?

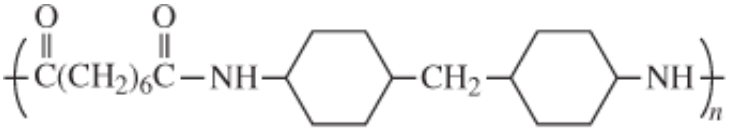
26.20 Identify the monomers required for the synthesis of each of the following step-growth polymers.

(a)



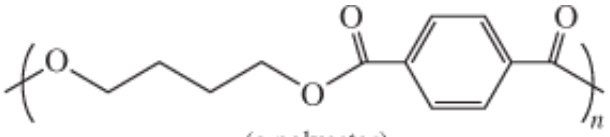
Kodel®
(a polyester)

(b)



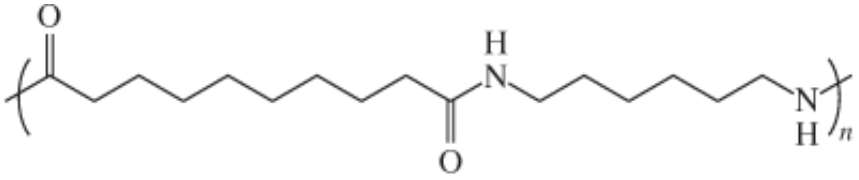
Quiana
(a polyamide)

(c)



(a polyester)

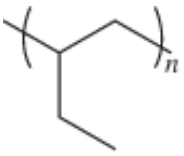
(d)



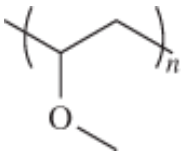
nylon 6,10
(a polyamide)

26.21 Draw the structure of the alkene monomer used to make each of the following chain-growth polymers.

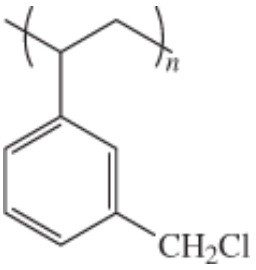
(a)



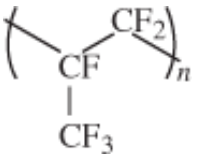
(b)



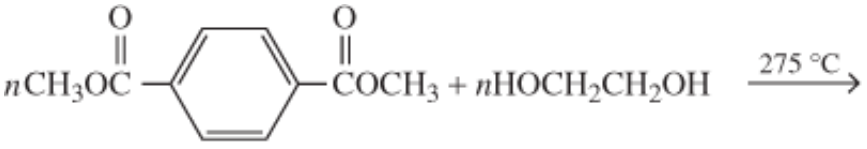
(c)



(d)



26.22 Poly(ethylene terephthalate) (PET) can be prepared by the following reaction. Propose a mechanism for the step-growth reaction in this polymerisation.



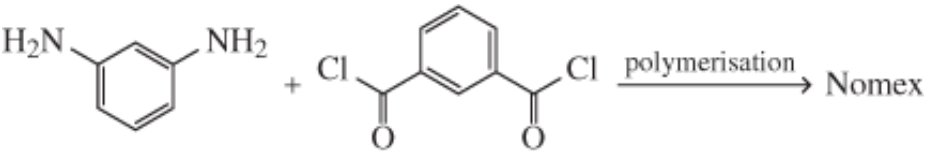
dimethyl terephthalate — ethylene glycol



poly(ethylene terephthalate) — methanol

26.23 Polyethylene can be used for the production of solid food containers as well as flexible cling film. Which of these two items is made from more highly branched polyethylene? Explain.

26.24 Nomex® is an aromatic polyamide (aramid) prepared by the polymerisation of 1,3-benzenediamine and the acid chloride of 1,3-benzenedicarboxylic acid:

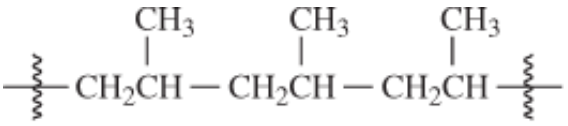


1,3-benzenediamine — 1,3-benzene-dicarbonyl chloride

The physical properties of the polymer make it suitable for high-strength, high-temperature applications such as parachute cords and jet aircraft tyres. Draw the structural formula for the repeating unit of Nomex.

26.25 Nylon 6,10 (see question 26.20d) can be prepared by reacting a diamine and a diacid chloride. Draw the structural formula of each reactant.

26.26 The following is the structural formula of a section of polypropylene corresponding to three units of the propene monomer:



polypropylene

Draw the structural formula for a comparable section of:

(a) poly(vinyl chloride)

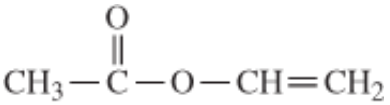
(b) polytetrafluoroethylene (PTFE)

(c) poly(methyl methacrylate).

26.27 Currently, about 30% of PET soft-drink bottles are being recycled. In one recycling process, scrap PET is heated with methanol in the presence of an acid catalyst. The methanol reacts with the polymer, liberating ethylene glycol and dimethyl terephthalate. These monomers are then used as feedstock for the production of new PET products. Write an equation for the reaction of PET with methanol to give ethylene glycol and dimethyl terephthalate.

26.28 LDPE (PE-LD) has a higher degree of chain branching than HDPE (PE-HD). Explain the relationship between chain branching and density.

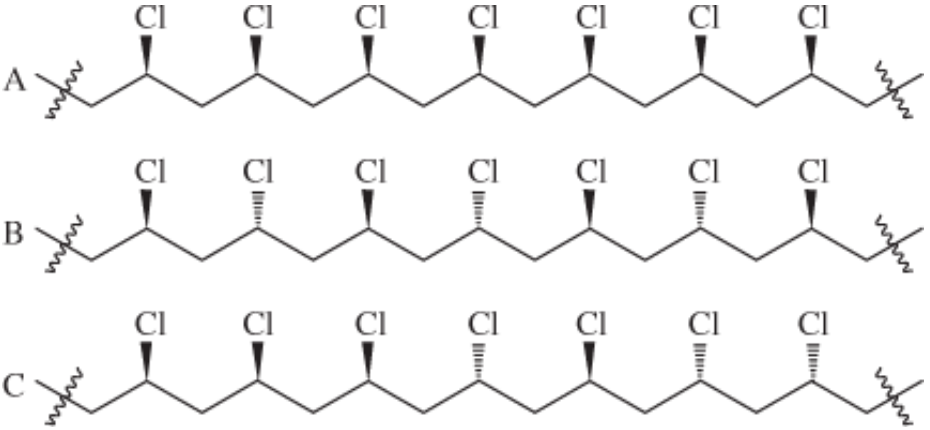
26.29 Polymerisation of vinyl acetate gives poly(vinyl acetate). Hydrolysis of this polymer in aqueous sodium hydroxide gives poly(vinyl alcohol). Draw the repeating units of both poly(vinyl acetate) and poly(vinyl alcohol).



vinyl acetate

26.30 Poly(vinyl alcohol) is made by the polymerisation of vinyl acetate, followed by hydrolysis in aqueous sodium hydroxide (see question 26.29). Why is poly(vinyl alcohol) made by this process and not by the polymerisation of vinyl alcohol, $CH_2{=}CHOH$?

26.31 Consider the following three polymers.



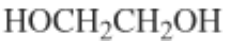
(a) Which do you expect to be the most rigid?

(b) Which do you expect to be the most transparent? (Assume equal molar masses.)

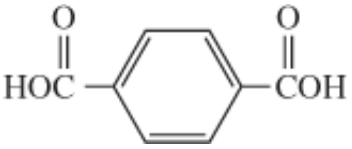
26.32 The structure of vinyl acetate is shown in question 26.29. This compound forms an addition polymer in the same way as ethene and propene. Draw a segment of the poly(vinyl acetate) polymer that contains three of the repeating units.

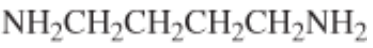
26.33 If the following two compounds polymerised in the same way that PET forms, what would be the repeating unit of their polymer?





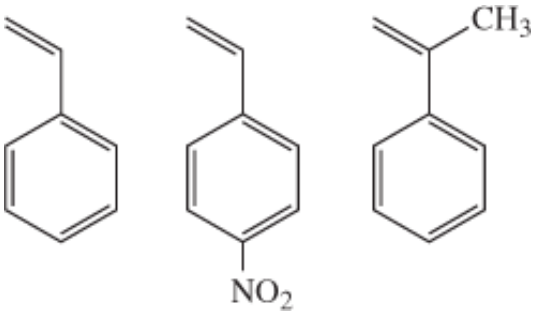
26.34 If the following two compounds polymerised in the same way that nylon forms, what would be the repeating unit in the polymer?



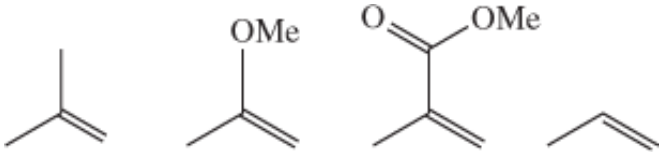


26.35 List the compounds in each of the following groups of monomers in order of increasing ability to undergo cationic polymerisation.

(a)



(b)



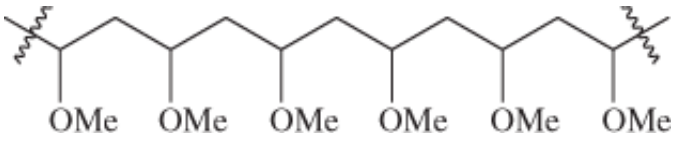
Now, list each group of compounds in order of decreasing ability to undergo anionic polymerisation.

26.36 Draw a segment of (a) poly(vinyl chloride) and (b) polystyrene that contains head-to-head and tail-to-tail linkages, rather than the normal head-to-tail linkages.

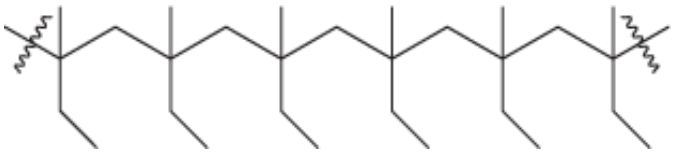
26.37 Which polymer would be more likely to form segments with head-to-head linkages: polystyrene or poly(vinyl chloride)?

26.38 Which monomers are required to form each of the following polymers. Can each of these polymers be made from one single type of monomer?

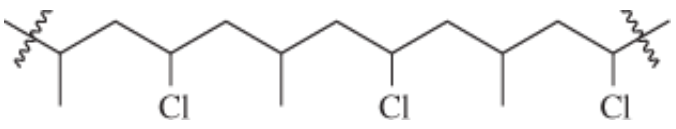
(a)



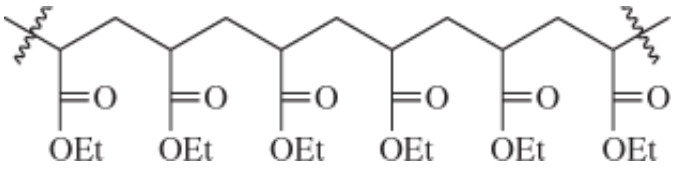
(b)



(c)



(d)



26.39 Draw a short segment of nylon 5.

26.40 Draw a short segment of nylon 5,5.

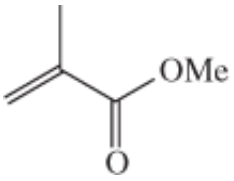
26.41 What happens to a T-shirt made of polyester if aqueous NaOH is spilled on it?

26.42 Draw the repeating unit of the polymers derived from each of the following monomers.

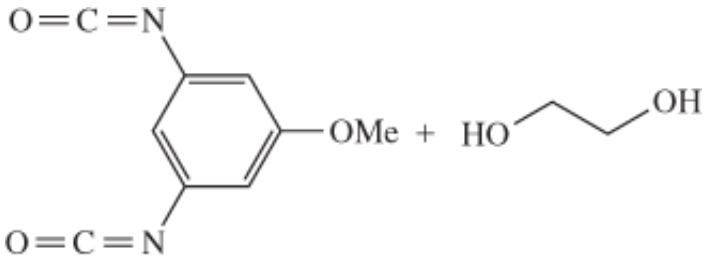
(a)



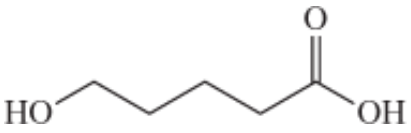
(b)



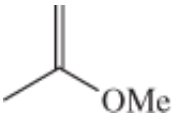
(c)



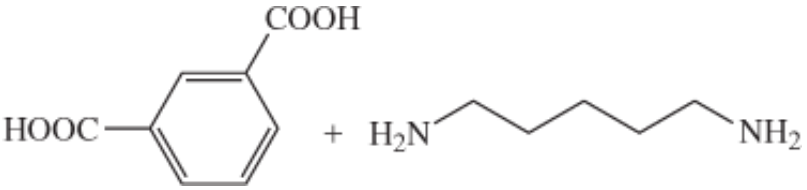
(d)



(e)

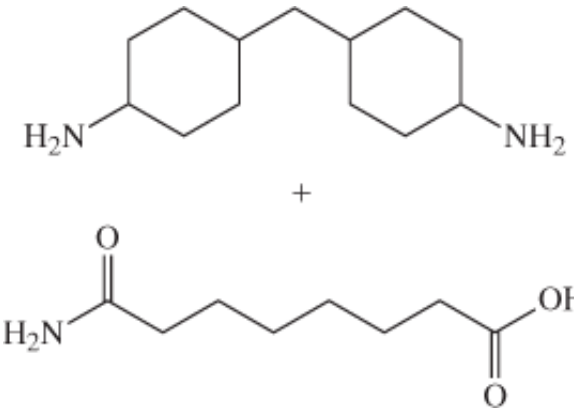


(f)



26.43 Explain why poly(isobutylene) is not isotactic, syndiotactic or atactic.

26.44 Quiana is a synthetic polymer that can be used to make fabric that mimics the texture of silk. It can be prepared from the following monomers.



(a) Draw the structure of Quiana.

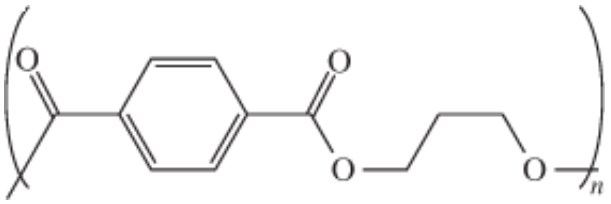
(b) Is Quiana a polyester, a polyamide, a polycarbonate or a polyurethane?

(c) Is Quiana a step-growth polymer or a chain-growth polymer?

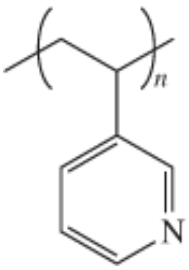
(d) Is Quiana an addition polymer or a condensation polymer?

26.45 Draw the structure of the monomer or monomers used to synthesise the polymers with each of the following repeating units. Indicate whether each polymer is a chain-growth or a step-growth polymer.

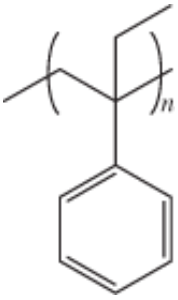
(a)



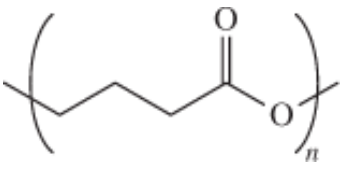
(b)



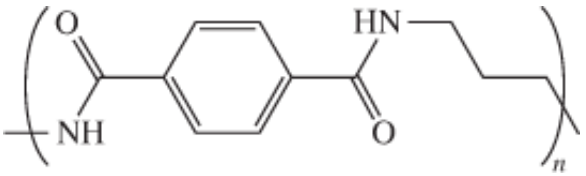
(c)



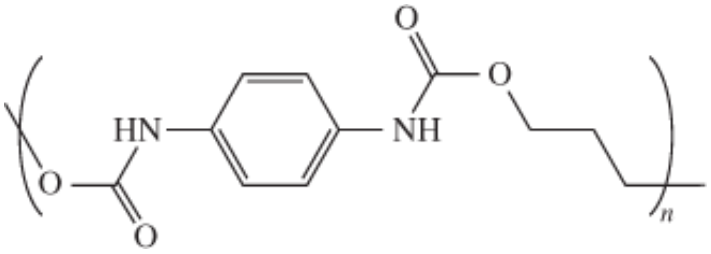
(d)



(e)



(f)



26.46 Polystyrene is formed by adding a small amount of a peroxide to styrene. If a small amount of 1,4-divinylbenzene is added to the reaction mixture, a stronger and more rigid polymer is formed. Explain the reason for this. Draw a small segment of this more rigid polymer.



1,4-divinylbenzene

26.47 A student has started two polymerisation reactions. A chain-growth polymerisation is occurring in one flask and a step-growth polymerisation in another flask. Both reactions are terminated early in the polymerisation process and the contents of the flasks are analysed. Flask A contains a high-molecular-mass polymer and very little material of intermediate mass; flask B contains mainly material with intermediate mass and very little high-molecular-mass polymer. Which type of polymer is found in each flask? Explain your answer.

26.48 Polyformaldehyde, sold under the trade name Delrin, is a strong polymer used in the manufacture of many guitar picks. It is prepared via the acid-catalysed polymerisation of formaldehyde.

(a) Draw the structure of polyformaldehyde.

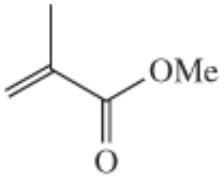
(b) Would you describe polyformaldehyde as a polyether or a polyester?

(c) Is polyformaldehyde a step-growth polymer or a chain-growth polymer?

26.49 When a solution of aqueous sodium hydroxide is spilled on polyester clothing, a hole develops in the fabric. Describe how the polyester is destroyed.

26.50 A cling-wrap is synthesised through chain-growth copolymerisation of 1,1-dichloroethene and vinyl chloride (chloroethene). Draw a short segment of the polymer chain.

26.51 Plexiglas is a transparent plastic with excellent optical properties. It is polymerised from methyl methacrylate using free radical initiation. Write the mechanism for the radical polymerisation of methyl methacrylate to give three segments of poly(methyl methacrylate).



methyl methacrylate

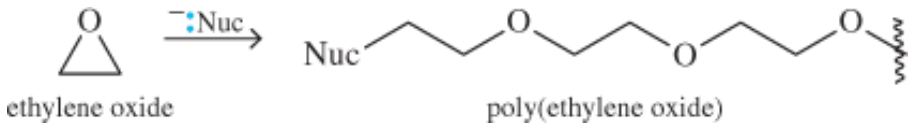
26.52 Consider the structure of polystyrene on p. 1122.

(a) Draw structural formulae for segments of the chains of iso-tactic, syndiotactic and atactic

polystyrene.

(b) If solutions of each of these forms of polystyrene are made, which would you expect to show optical activity?

26.53 When ethylene oxide is treated with a strong nucleophile, the epoxide ring is opened to form an alkoxide ion that can function as a nucleophile to attack another molecule of ethylene oxide. This process repeats itself, and a polymer is formed.



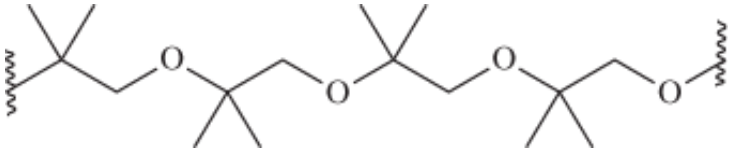
ethylene oxide poly(ethylene oxide)

The resulting polymer is called poly(ethylene oxide) or poly(ethylene glycol). It is sold under the trade name Carbowax and is used as an adhesive and a thickening agent.

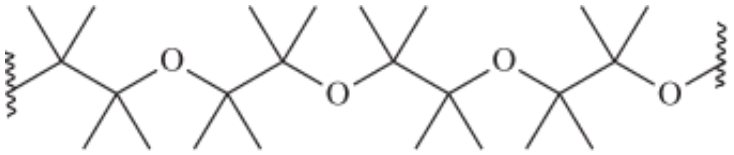
(a) Draw a mechanism showing the formation of a segment of poly(ethylene oxide).

(b) Ethylene oxide can also be polymerised when treated with an acid. Draw the mechanism of formation of a segment of poly(ethylene oxide) under acidic conditions.

(c) Identify the monomer you would use to prepare the following polymer.



(d) Determine whether you would use basic conditions or acidic conditions to prepare the following polymer. Explain your choice.

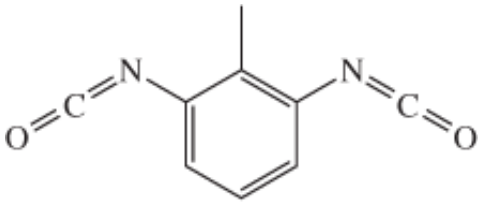


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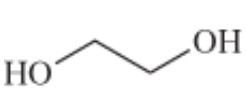
ADDITIONAL EXERCISES

26.54 Is a repeating unit required for a compound to be called a polymer?

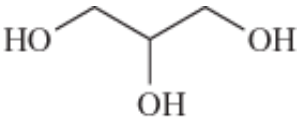
26.55 Addition of a small amount of glycerol (propane-1,2,3-triol) to the reaction mixture of toluene-2,6-diisocyanate and ethylene glycol during the synthesis of a polyurethane foam produces a much stiffer polymer. Explain this finding.



toluene-2,6-diisocyanate

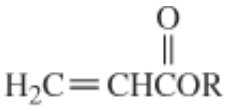


ethylene glycol



glycerol

26.56 Unsaturated esters and acrylonitrile are successfully polymerised using free-radical or anionic initiation. However, polymerisation does not occur when cationic initiators are used. Explain.



unsaturated ester



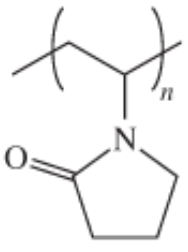
acrylonitrile

26.57 Which polymer should be more resistant to strong base: nylon 6,6 or the polyester in question 26.45a? Explain.

26.58 Gutta-percha is not very elastic, even after it is vulcanised. Explain.

26.59 Glyptal is a particularly strong polymer used to make electronic parts. It is manufactured from phthalic acid (1,2-benzene dicarboxylic acid) and glycerol. Draw a small segment of the polymer and explain why it is so strong.

26.60 Poly(vinyl pyrrolidone) was once used as an extender for blood plasma.



poly(vinyl pyrrolidone)

(a) Which monomer is used for the synthesis of this polymer?

(b) Would you synthesise this polymer using free-radical initiation or cationic initiation? Explain.

(c) Propose a mechanism for the polymerisation of a segment consisting of three repeating units.

(d) Poly(vinyl pyrrolidone) clearly contains amide linkages. Is this, therefore, a polyamide? Explain.

26.61 A typical polyurethane can be made by polymerising adipic acid with excess ethylene glycol. The resulting polyester is then treated with toluene-2,6-diisocyanate (see question 26.55).

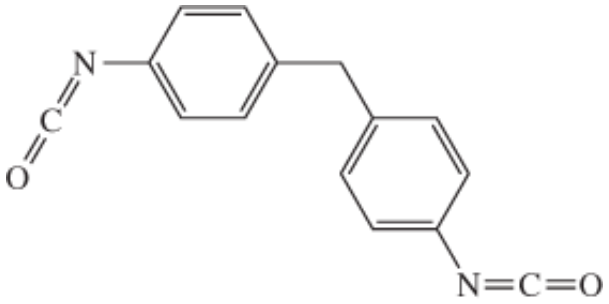
(a) Draw a segment of the polyester.

(b) Draw a segment of the polyurethane.

(c) Why is excess ethylene glycol used in making the polyester?

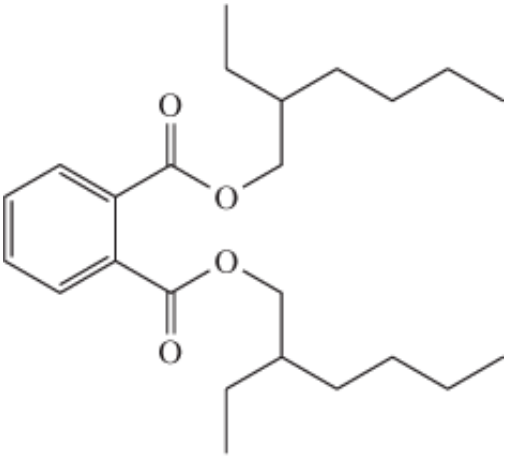
26.62 Nitroethene, $CH_2{=}CHNO_2$, is a very labile compound that must be prepared with care. If purification of nitroethene is attempted, generally only small amounts are recovered, but the inner walls of the distillation apparatus are covered with a white film. Explain.

26.63 Draw the structure of the repeating unit of a polyurethane prepared by reaction of glycerol with methane diphenyldiisocyanate (MDI).



methane diphenyldiisocyanate
(MDI)

26.64 Poly(vinyl chloride), PVC, is used for rigid structures such as window frames. If PVC is used for more flexible products such as plastic bags, about 20 –30% dialkyl phthalates, such as the compound shown below, are incorporated during polymerisation. Explain.

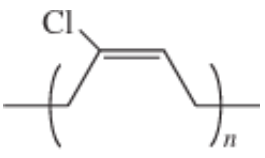


dialkyl phthalate

26.65 Neoprene (shown below) is a chemically inert polymer of chloroprene. It is used in many applications, such as wetsuits.

(a) Draw the structure of the monomer of neoprene.

(b) Name the monomer chloroprene according to the IUPAC rules.



neoprene

26.66 (a) Describe the type of isomeric possibilities in the free-radical polymerisation of styrene?

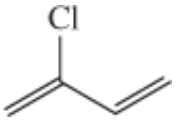
Draw structures of any possible isomers.

(b) Would the free-radical polymerisation of styrene distinguish between the isomer possibilities to favour one?

26.67 Draw the structure (repeating unit) of the polymer that would be formed from 1,5-pentanedioic acid and ethylene glycol. What functional groups link the units of the chain?

26.68 What would happen in the polymerisation of nylon 6,6 if adipic acid (1,6-hexanedioic acid) contained acetic acid as an impurity?

26.69 (a) Draw several segments of the structure of neoprene (polychloroprene). Note that the double bond has *E* configuration.



chloroprene

(b) Draw several segments of the structure of the polymer chain with *Z* configuration at the double bond. Suggest how this change in stereochemistry at the double bond might affect the properties of this polymer.

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KEY TERMS

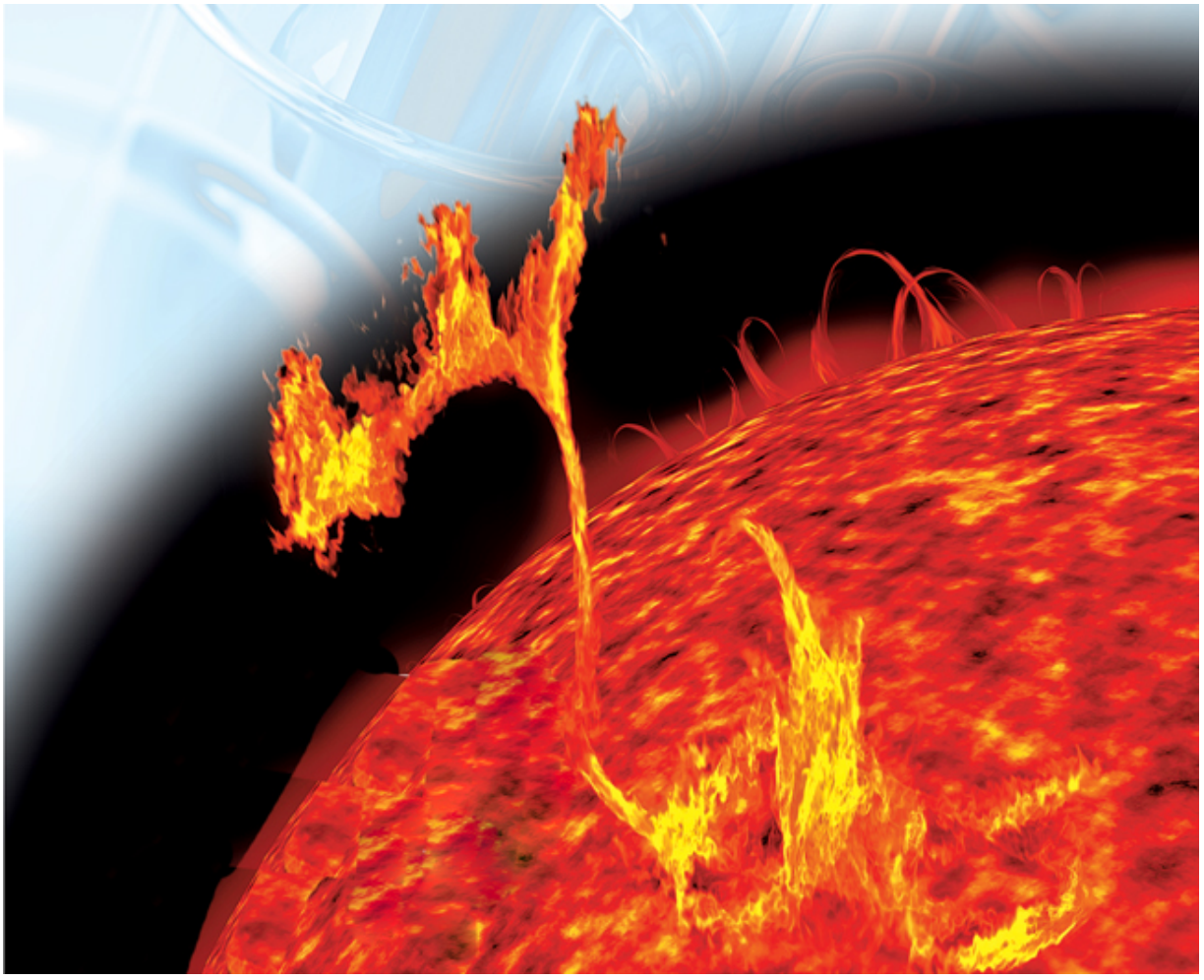
addition polymerisation
alternating
amorphous domains
antioxidant
aramid
atactic polypropylene
biodegradable polymers
biopolymers
block
cationic polymerisation
Chain initiation
chain length
Chain propagation
Chain termination
chain-growth polymerisation
chain-transfer reaction
condensation polymerisation
cross-links
crystalline domains
degradation
elastomers
epoxy resins
fishhook (single-headed) arrows
high-density polyethylene (HDPE or PE-HD)
isotactic polypropylene
low-density polyethylene (LDPE or PE-LD)
macromolecules
melt transition temperature (T_m)
monomers
Natural rubber
photodegradation
plastic
polyamides
Polycarbonates
Polyesters
polymer
addition polymerisation
Polyurethanes
Radical chain-growth polymerisation
radicals
repeating unit
Silicon polymers
silicone
statistical
step-growth polymerisation
syndiotactic polypropylene
thermoplastic
thermosetting plastic
vulcanisation
vulcanised rubber
Ziegler–Natta catalysts

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CHAPTER

27 Nuclear Chemistry

Life on Earth is predominantly solar-powered. As we saw in chapter 12, green plants use solar photons with wavelengths in the visible region as an energy source to convert carbon dioxide and water to carbohydrates, which ultimately provide the basis for essentially all life. But from where do the solar photons obtain their energy? The answer to this question is found in the atomic nucleus. Our Sun is powered by nuclear reactions (as shown in the photo below) which involve the fusing of hydrogen nuclei to give helium nuclei under conditions of extremely high temperature and pressure. This nuclear process consumes a quite astonishing 600 million tonnes of hydrogen *per second* and emits an enormous amount of energy. Another possible energy source involving the atomic nucleus arises from the fact that some heavy atomic nuclei are also inherently unstable and break apart to give lighter nuclei, again with the emission of significant amounts of energy; a variation of this process is used in the production of nuclear power. In this chapter, we will discuss some of the processes which occur in atomic nuclei. We will investigate why some nuclei are stable and some are radioactive, and we will detail some of the uses of radioactive materials.



KEY TOPICS

27.1 Nuclear stability
27.2 Unstable nuclei
27.3 Synthesis of new elements
27.4 Radioactive dating methods

27.4 Radioactive dating methods
27.5 Applications of nuclear processes

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27.1 Nuclear Stability

As described in chapter 1, atomic nuclei can be divided into two types: stable and radioactive. Radio active nuclei undergo spontaneous decay, and therefore we say that they are *unstable*. However, before we begin our discussion of nuclear stability, we must first define exactly what we mean by the word 'stable' in the context of an atomic nucleus. This is most easily done by defining its opposite, 'unstable'. As an example, consider the radioactive neodymium nucleus ^{144}Nd. This has a half-life of 2.29×10^{15} years. As we learned in chapter 15, this means that any sample of this isotope decays by half over this period, and it takes 2.29×10^{16} years to decay completely. These lengths of time, by our everyday standards, are almost incomprehensible (indeed they are about a million times the age of the universe!). To us, a sample of ^{144}Nd would show no obvious change and appear to be stable over the period of our lifetime. Despite this, we still say that the ^{144}Nd nucleus is unstable, even though its rate of decay is extremely slow. There are radioactive nuclei with half-lives of fractions of a second and others with half-lives of 10^{19} years, but they are all unstable as they all undergo a nuclear process that results in their radioactive decay. Therefore, a stable nucleus is one in which such nuclear processes do not occur.

One of the important factors that determines whether or not a particular nucleus is stable is the ratio of protons to neutrons in the nucleus. This is evident when we consider figure 27.1, which shows all the stable nuclei on a plot of the number of neutrons (N) versus the number of protons (Z). These data have a definite pattern that shows that all stable nuclei fall within a **band of stability** (the shaded region in figure 27.1). Any nucleus with a ratio of neutrons to protons that falls outside the band of stability is unstable and decomposes spontaneously. Lighter nuclei lie on or close to the $N = Z$ line, but, as the atomic number increases, the N:Z ratio of stable nuclei rises slowly until it reaches 1.54. The trend is illustrated by the N:Z ratios (in parentheses) of the following stable nuclei:

$^{4}_{2}$He (1.00), $^{31}_{15}$P (1.07), $^{56}_{26}$Fe (1.15), $^{81}_{35}$Br, $^{197}_{79}$Au (1.49) and $^{208}_{82}$Pb (1.54).

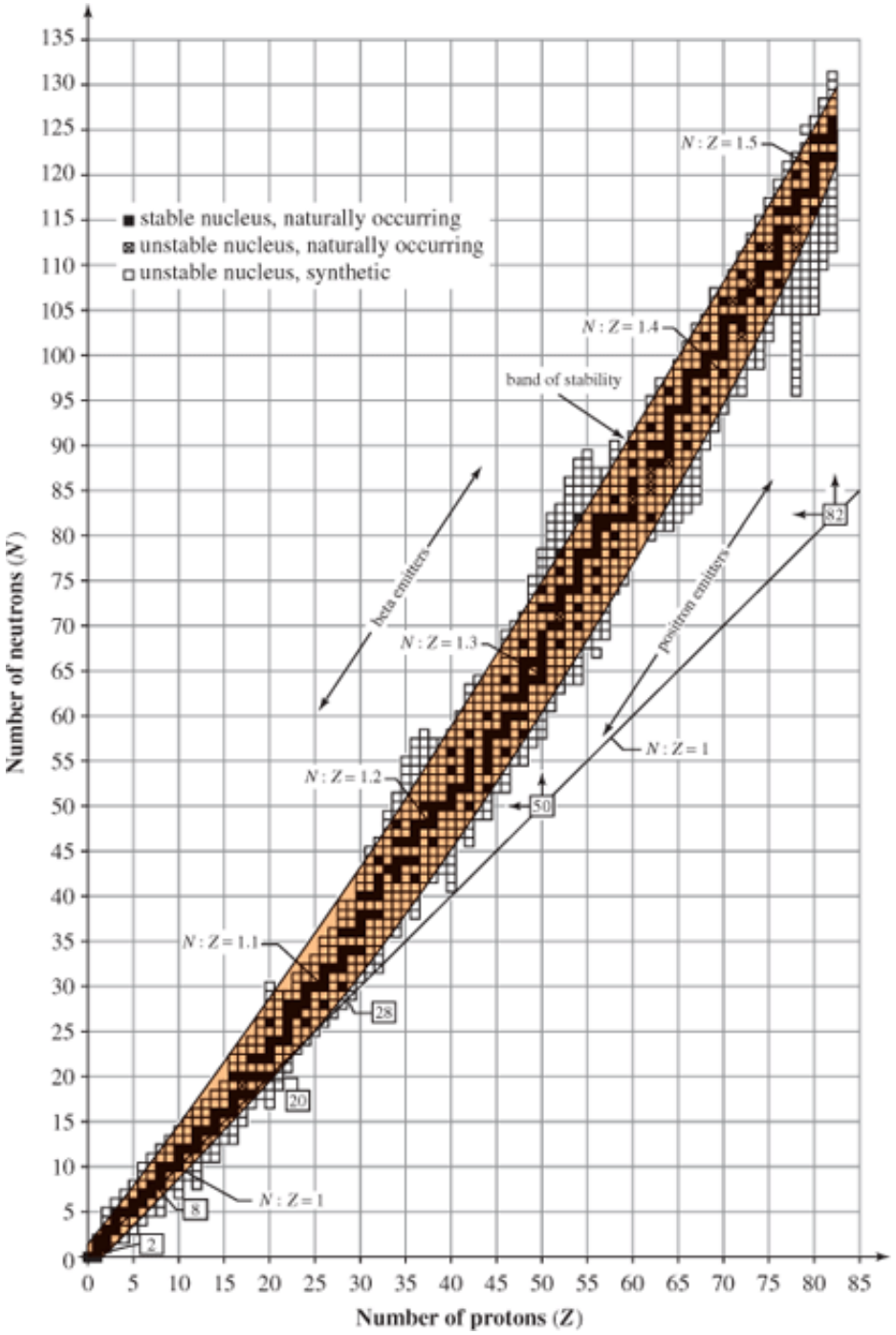


FIGURE 27.1 Plot of number of neutrons versus number of protons for all the elements from H (Z = 1) to Pb (Z = 82). The numbers in square boxes indicate magic numbers (see p. 1163).

The attractive force that holds the nucleus together is called the **strong nuclear force**; it acts between protons and neutrons and operates through the exchange of subatomic particles called mesons. The strong nuclear force operates only at very small distances to hold protons and neutrons together within the nucleus, and, at these distances, it is about 100 times stronger than proton–proton repulsion. As Z increases, the effect of electrical repulsion increases, and, therefore, more neutrons are required to generate enough nuclear force to stabilise the nucleus. This accounts for the gradual increase in the slope of the plot in figure 27.1. However, when Z increases beyond a certain point, added neutrons can no longer stabilise the nucleus, and this is suggested in figure 27.1 by the fact that there are no stable nuclei beyond lead, Z = 82 (the $^{209}_{83}Bi$ nucleus was, for many years, thought to be stable, but was shown in 2003 to undergo alpha decay, with a half-life of 1.9×10^{19} years). Some elements with higher Z are found on Earth, notably radium (Z = 88), thorium (Z = 90) and uranium (Z = 92), but all such elements are unstable (all their isotopes are radioactive) and eventually disintegrate into nuclei with $Z < 83$. Consequently, the set of stable nuclei, those that make up the world of ‘normal’ chemistry and provide

the material for all terrestrial chemical reactions, is a small subset of all possible nuclei. Careful inspection of figure 27.1 shows that there are no stable nuclei having $Z = 43$ or $Z = 61$. These correspond to the elements technetium (Tc) and promethium (Pm), neither of which occurs naturally on Earth. The (relatively) short half-lives of all known isotopes of these elements means that any originally present on Earth have decayed over the intervening 4 billion years.

Although stable nuclei do not undergo spontaneous radioactive decay, not all stable nuclei are equally 'stable' — in other words, they do not all have the same energy. We can in fact calculate the **nuclear binding energy**, the energy that holds the nucleus together. We do this using the most well-known equation in all of science, Einstein's equation $E = mc^2$, which quantifies the equivalence of mass and energy. The key to this calculation is the accurate measurement of the mass of an atomic nucleus, and also the masses of the components of the atomic nucleus, the proton and the neutron. If we add the masses of the individual protons and neutrons in an atomic nucleus, we find that it always adds up to slightly *more* than the actual mass of the nucleus itself. The mass difference (sometimes called the **mass defect**) is due to mass that is converted to energy on formation of the atomic nucleus from its components, and we can calculate this liberated energy using Einstein's equation. If we wished to break the nucleus apart into its constituent nucleons, i.e. protons and neutrons (see p. 8), we would need to supply an amount of energy equal to the nuclear binding energy; therefore, the greater the nuclear binding energy, the more stable the nucleus. The calculation is illustrated in worked example 27.1.

WORKED EXAMPLE 27.1

Calculating the Nuclear Binding Energy

The ^4_2He nucleus consists of two protons and two neutrons. Use the following data to calculate the nuclear binding energy of the ^4_2He nucleus.

$$\begin{aligned} \text{mass of the } ^4_2\text{He nucleus} &= 4.001\,506\,\text{u} \\ \text{mass of a proton} &= 1.007\,276\,467\,\text{u} \\ \text{mass of a neutron} &= 1.008\,664\,916\,\text{u} \end{aligned}$$

Analysis

We are given the mass of the ^4_2He nucleus, as well as those of a proton and a neutron. We start by calculating the mass of two protons and two neutrons, and comparing this with the actual mass of the ^4_2He nucleus to determine the mass defect. We then use Einstein's equation to convert the mass defect to the equivalent energy, which is the nuclear binding energy.

Solution

We can calculate the mass defect as follows:

$$\begin{aligned} \text{mass of 2 protons} &= 2 \times 1.007\,276\,467\,\text{u} = 2.014\,552\,934\,\text{u} \\ \text{mass of 2 neutrons} &= 2 \times 1.008\,664\,904\,\text{u} = 2.017\,329\,808\,\text{u} \\ \text{mass of 2 protons and 2 neutrons} &= 4.031\,882\,766\,\text{u} \\ \text{mass defect} &= 4.031\,882\,766\,\text{u} - 4.001\,506\,\text{u} = 0.030\,377\,\text{u} \end{aligned}$$

Before we can use Einstein's equation, we must convert 0.030 377 u into kg. We use the conversion factor 1 u = 1.660 54 × 10^{-27} kg to calculate that 0.030 377 u = 5.0442 × 10^{-29}

kg. Knowing that the speed of light, c, = 2.998×10^8 m s^{-1}, we can now calculate the energy equivalent of 5.0442×10^{-29} kg using Einstein's equation:

$$\begin{aligned} E &= mc^2 \\ &= 5.0442 \times 10^{-29}\,\text{kg} \times \left(2.998 \times 10^8\,\text{m s}^{-1}\right)^2 \\ &= 4.534 \times 10^{-12}\,\text{kg m}^2\,\text{s}^{-2} \\ &= 4.534 \times 10^{-12}\,\text{J} \end{aligned}$$

This is the nuclear binding energy of a single ^4_2He nucleus. In other words, formation of one ^4_2He nucleus from two isolated protons and two isolated neutrons releases 4.534×10^{-12} J, which appears to be a negligible amount of energy. However, when we convert this to the amount of energy released on formation of 1 mole (4 g) of ^4_2He nuclei from its constituent nucleons, we obtain a value of 2.73×10^{12} J, equivalent to the energy contained in 650 tonnes of the highly explosive TNT.

Is our answer reasonable?

In predominantly arithmetical problems like this, we can only check that we have substituted the correct numbers into the equations and carried out the arithmetic correctly. While the amount of energy liberated does seem extraordinary, we have done all manipulations correctly and we can therefore be confident of the answer.

PRACTICE EXERCISE 27.1

The mass of the ^3_2He nucleus is 3.014 932 u. Calculate the nuclear binding energy of 1 mole of this nucleus.

You can see from worked example 27.1 that the energies involved in the atomic nucleus are substantial. Should we ever be able to harness those energies in a controllable way, we would have a virtually limitless source of energy. There are two possible nuclear processes that we can exploit as sources of energy. **Nuclear fusion** is the joining together of light nuclei to form heavier nuclei, while **nuclear fission** is the splitting of heavy nuclei into nuclei of lower mass number. Both processes produce significant amounts of energy.

Calculations show that, as the mass number increases, so does the nuclear binding energy of the nucleus. However, the **binding energy per nucleon** is more important for the overall stability of the nucleus. This quantity is the nuclear binding energy divided by the mass number, A, and it measures how tightly each nucleon is bound to the nucleus. As the binding energy per nucleon becomes more positive, nuclei become energetically more stable. Figure 27.2 shows the binding energy per nucleon plotted versus mass number.

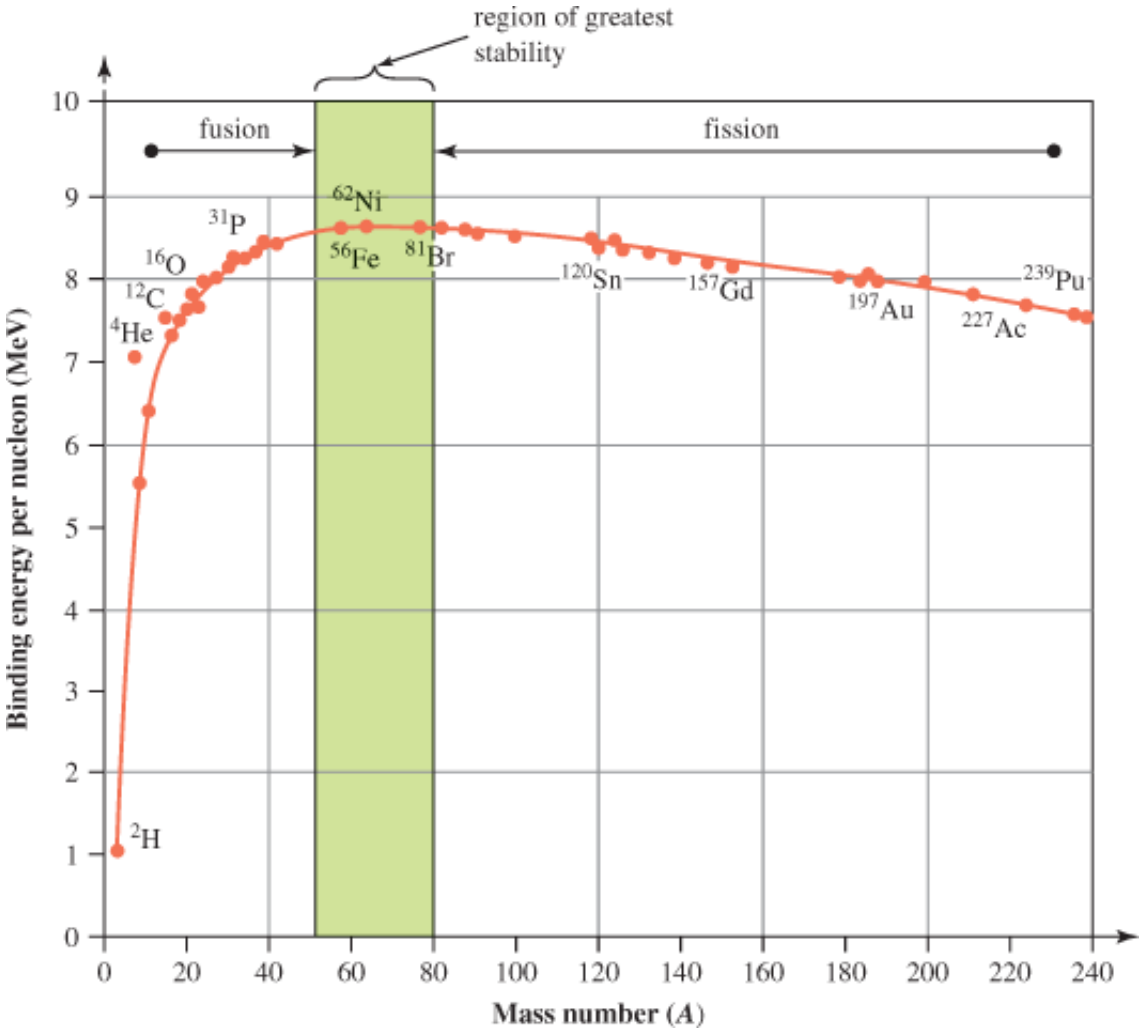


FIGURE 27.2 Binding energies per nucleon. The energy unit here is the megaelectron volt or MeV (1 MeV = 1.602×10^{-13} J).

The curve in figure 27.2 reaches a maximum at $^{62}_{28}\text{Ni}$, which means that these nuclei are the most energetically stable of all. However, the plot does not have a sharp maximum, so elements with mass numbers in the range 50 to 80 contain the most energetically stable isotopes in nature. Lighter nuclei are, therefore, more unstable than these and we would expect such nuclei to undergo fusion reactions to approach the region of greatest stability. Fusion reactions do in fact occur in stars and it has been proposed that all the elements on Earth up to and including $^{62}_{28}\text{Ni}$ are products of such reactions. As we continue to follow the plot of figure 27.2 to the highest mass numbers, the nuclei decrease in stability as the binding energies per nucleon decrease. Among the heaviest atoms, therefore, we would expect to find isotopes that change to more stable forms by breaking up in fission reactions.

Careful inspection of figure 27.1 shows that, when the numbers of neutrons and protons in a nucleus are both even, the isotope is far more likely to be stable than when both numbers are odd. Of the 263 stable isotopes, only five have odd numbers of both protons and neutrons, whereas 157 have even numbers of both. The rest have an odd number of one nucleon and an even number of the other. To see this, notice how, in figure 27.1, the horizontal lines with the largest numbers of dark squares (stable isotopes) most commonly correspond to even numbers of neutrons. Similarly, the vertical lines with the most dark squares most often correspond to even numbers of protons. This is related to the spins of nucleons, a concept analogous to electron spin, which we first encountered in chapter 1. Protons and neutrons also behave as though they have spin, and, when two protons or two neutrons have opposite spins (paired), their combined energy is lower than when the spins are the same (unpaired). Only when there are even numbers of both protons and neutrons can all spins be paired, thereby resulting in a lower energy nucleus. Therefore, the least stable nuclei tend to be those in which the number of protons and neutrons

are odd.

Another rule of thumb for nuclear stability is based on **magic numbers** of nucleons. Isotopes with specific numbers of protons or neutrons, the magic numbers, are more stable than the rest. The magic numbers of nucleons are 2, 8, 20, 28, 50, 82 and 126, and figure 27.1 shows, with the exception of number 126, where they fall. When the numbers of both protons and neutrons are the same magic number, as they are in $^{4}_{2}\text{He}$, $^{16}_{8}\text{O}$ and $^{40}_{20}\text{Ca}$, the isotope is very stable. The heaviest known stable isotope, $^{208}_{82}\text{Pb}$, involves two different magic numbers, 82 protons and 126 neutrons. The existence of magic numbers supports the hypothesis that a nucleus has a shell structure with energy levels analogous to electron energy levels. Electron levels, as we have seen, are associated with their own special numbers, those that equal the maximum number of electrons allowed in a principal energy level: 2, 8, 18, 32, 50, 72 and 98 (for principal quantum numbers n = 1, 2, 3, 4, 5, 6 and 7, respectively). The total numbers of electrons in the atoms of the most chemically stable elements — the noble gases — also make up a special set: 2, 10, 18, 36, 54 and 86 electrons. Thus, special sets of numbers are not unique to nuclei.

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27.2 Unstable Nuclei

We have seen in figure 27.1 that there are relatively few combinations of protons and neutrons that give rise to stable nuclei. Any other *N*:*Z* ratios give unstable nuclei in which either the number of neutrons or the number of protons is too great. These unstable nuclei spontaneously undergo **radioactive decay** to give nuclei with more favourable *N*:*Z* ratios. There are a number of possible radioactive decay paths available to an unstable atomic nucleus and we summarise these on the next few pages.

Alpha Decay

We first mentioned alpha particles in chapter 1 when we discussed Rutherford's gold foil experiment. An **alpha particle** is a helium nucleus, comprising two protons and two neutrons, and is symbolised as $^{4}_{2}\mathrm{He}$. It has a 2+ charge, although this is usually not included in the symbol. Alpha particles are the most massive of any commonly emitted by radionuclides. When ejected from the nucleus, alpha particles move through the atom's electron cloud, reaching emerging speeds of up to one-tenth the speed of light. Their size, however, prevents them from going far. By the time they have travelled at most only a few centimetres in air, alpha particles have collided with molecules in the air, lost kinetic energy, picked up electrons and become neutral helium atoms. Alpha particles cannot penetrate the skin, although enough exposure causes a severe skin burn. However, if a radioactive substance that emits alpha particles is inhaled or ingested, it can end up in the soft tissues of the lungs or the intestinal tract and can cause serious harm. This was graphically illustrated by the death of the Russian expatriate Alexander Litvinenko, who was poisoned by the alpha emitter $^{210}\mathrm{Po}$ in London in late 2006.

When a nucleus emits an alpha particle, *Z* decreases by 2, and the atom is converted to another element. Alpha decay is the preferred decay method of most nuclei having $Z > 82$. We can illustrate this decay process using a **nuclear equation** , which, in contrast to a balanced chemical equation, requires only that both *A* and *Z* are balanced on either side of the arrow. Thus, we can show the alpha decay of the uranium isotope $^{238}_{92}\mathrm{U}$ as:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

Notice that the product of alpha decay is a different chemical element, with an atomic number 2 less than that of the parent nucleus. A general diagram of alpha decay is given in figure 27.3.

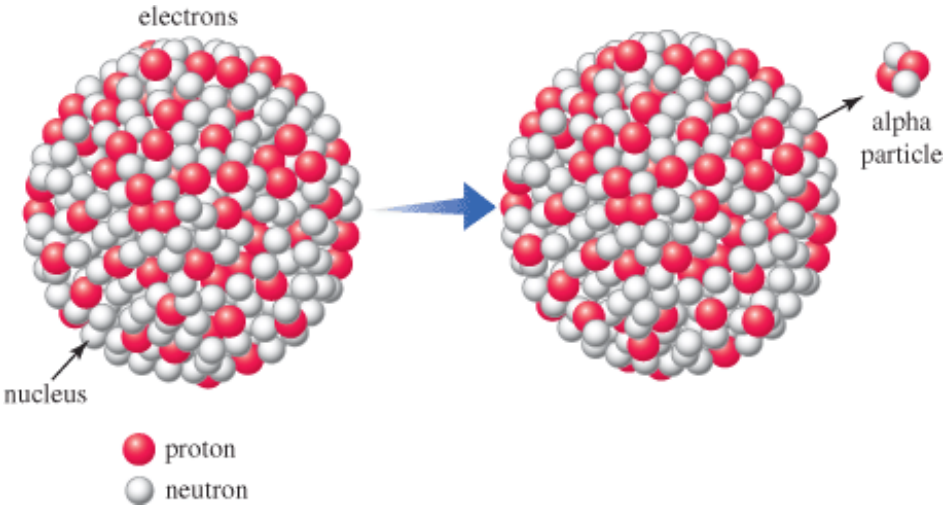


FIGURE 27.3 Emission of an alpha particle from an atomic nucleus.

Beta Decay

A **beta particle** is simply an electron. In nuclear chemistry, it is symbolised as $^{0}_{-1}e$. It may seem somewhat counterintuitive to say that an atomic nucleus can decay by emission of an *electron*, but this only serves to show the extraordinary workings of the nucleus. And, in fact, beta decay involves more than just the emission of a beta particle; a particle called an antineutrino is also ejected. In contrast to alpha particles, which are all emitted with the same discrete energy from a given radionuclide, beta particles emerge from a given beta emitter with a continuous range of energies from zero to a characteristic fixed upper limit for each radionuclide. This fact once gave nuclear physicists considerable trouble, partly because it was an apparent violation of energy conservation. To solve this problem, Wolfgang Pauli (1900 -1958, Nobel Prize in physics, 1945) proposed in 1927 that beta emission is accompanied by yet another decay particle, this one electrically neutral and almost massless. Enrico Fermi (1901–1954, Nobel Prize in physics, 1938) suggested the name 'neutrino' ('little neutral one'), but eventually it was named the 'anti-neutrino', symbolised as $\bar{\nu}_e$.

We will illustrate beta decay with reference to tritium, the radioactive isotope of hydrogen:

$$^{3}_{1}H \rightarrow {}^{3}_{2}He + {}^{0}_{-1}e + \bar{\nu}_e$$

The emitted beta particle and antineutrino $\bar{\nu}_e$ (figure 27.4) actually arise as a result of the conversion of a neutron to a proton in the decay process as follows:

$$^{1}_{0}n \rightarrow {}^{0}_{-1}e + {}^{1}_{1}p + \bar{\nu}_e$$

The entire decay process is depicted in figure 27.4.

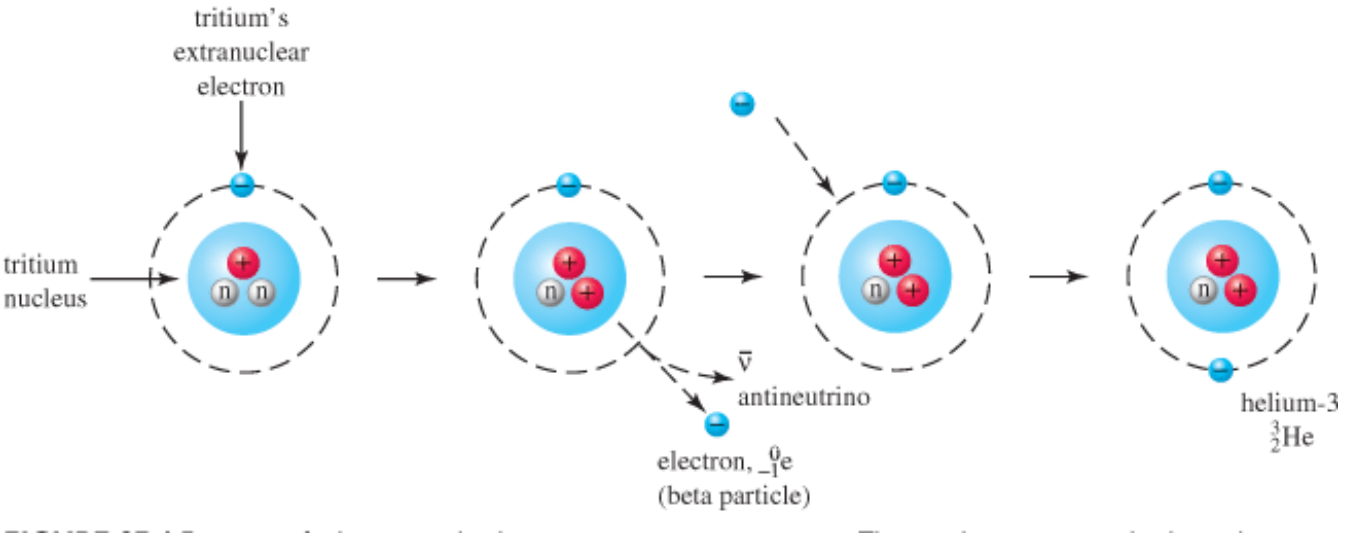


FIGURE 27.4 Emission of a beta particle changes a neutron into a proton. This results in a positively charged ion, which picks up an electron to become a neutral atom.

Again, we find that beta decay results in the conversion of one chemical element to another.

As an electron is extremely small, a beta particle is less likely than an alpha particle to collide with the molecules of anything through which it travels. Depending on its initial kinetic energy, a beta particle can travel up to 3 m in dry air. However, only the highest energy beta particles can penetrate the skin. Nuclei lying above the band of stability (figure 27.1) tend to undergo radioactive decay via beta emission, as this increases *Z* without changing *A*, thereby decreasing the neutron to proton ratio and moving the nucleus closer to the band of stability. For example, by beta decay, $^{20}_{9}F$ decreases its neutron to proton ratio from 11 : 9 to 10 : 10.

$$^{20}_{9}F \rightarrow {}^{20}_{10}Ne + {}^{0}_{-1}e + \bar{\nu}_e$$

The surviving $^{20}_{10}Ne$ nucleus is closer to the centre of the band of stability. Figure 27.5, an enlargement of the relevant part of figure 27.1, explains this change further. Figure 27.5 also shows how the beta decay of $^{27}_{17}Mg$ to $^{27}_{13}Al$ lowers the neutron to proton ratio.

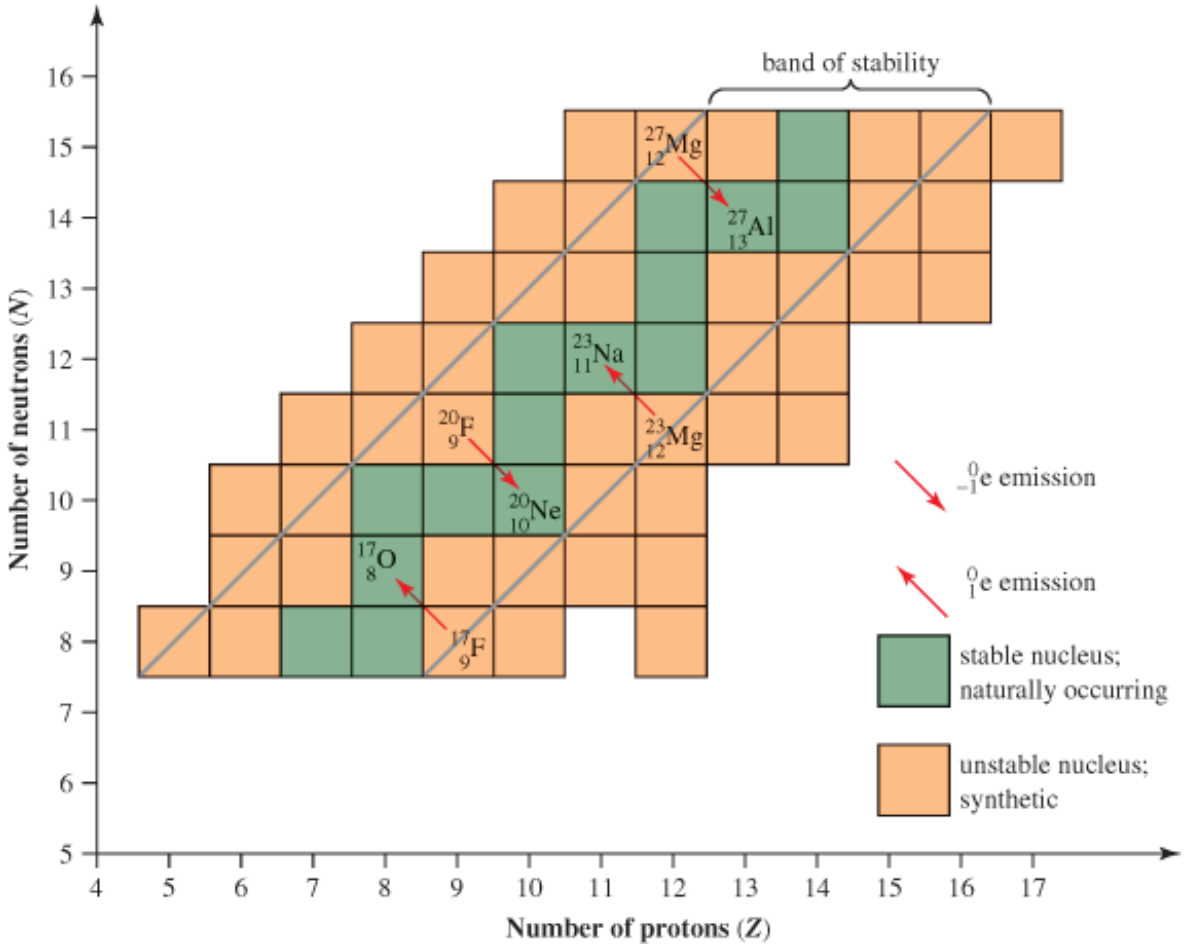


FIGURE 27.5 An enlarged section of the band of stability. Beta decay from $^{27}_{12}Mg$ and $^{20}_{9}F$ reduces their neutron to proton ratio and moves them closer to the band of stability. Positron emission (see below) from $^{23}_{12}Mg$ and $^{17}_{9}F$ also increases this ratio and moves these nuclei closer to the band of stability.

Gamma Decay

Gamma radiation, which often accompanies either alpha or beta radiation, consists of highenergy photons. A gamma-ray photon is given the symbol $^{0}_{0}\gamma$ or, often, simply γ. Gamma radiation is extremely penetrating and is effectively blocked only by very dense materials such as lead. The emission of gamma radiation involves transitions between energy levels within the nucleus; when a nucleus emits an alpha or beta particle, it is sometimes left in an excited energy state, and subsequent emission of a gamma-ray photon allows the nucleus to relax to a lower energy state.

Positron Emission

This is a relatively rare form of radioactive decay and involves emission of a **positron**, a positively charged electron, symbolised as $^{0}_{1}e$. A positron forms in the nucleus by the conversion of a proton to a neutron, as shown in figure 27.6.

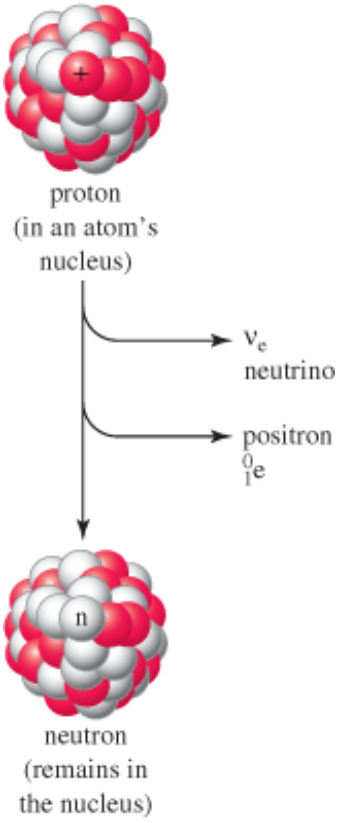


FIGURE 27.6 The emission of a positron and neutrino results in the conversion of a proton to a neutron in the nucleus.

Positron emission, like beta emission, is accompanied by a chargeless and virtually massless particle, a neutrino (ν_e). For example, $^{54}_{27}Co$ is a positron emitter and decays to a stable isotope of iron:

$$^{54}_{27}Co \rightarrow {}^{54}_{26}Fe + {}^{0}_{1}e + \nu_e$$

The ejected positron eventually collides with an electron, and the two particles annihilate each other with production of two gamma-ray photons, called annihilation radiation photons, according to the nuclear equation:

$$^{0}_{1}e + {}^{0}_{-1}e \rightarrow 2{}^{0}_{0}\gamma$$

Because a positron destroys a particle of ordinary matter (an electron), it is called a particle of **antimatter**. To be classified as antimatter, a particle must have a counterpart of ordinary matter, and the two must annihilate each other when they collide. For example, the antiproton and the antineutron are the antimatter equivalents of the proton and the neutron. Similarly, the anti neutrino ejected during beta decay is the antimatter counterpart of the neutrino ejected in positron emission. Positron emission is most often found in nuclei lying below the band of stability (figure 27.1), as this increases the neutron to proton ratio, so the resulting nucleus lies closer to the band of stability. A $^{17}_{9}F$ nucleus, for example, increases its neutron to proton ratio by emission of a positron and a neutrino to give $^{17}_{8}O$ as shown in figure 27.5:

$$^{17}_{9}F \rightarrow {}^{17}_{8}O + {}^{0}_{1}e + \nu_e$$

Figure 27.5 also shows that positron decay by $^{23}_{12}Mg$ to give $^{23}_{11}Na$ produces a similar shift towards the centre of the band of stability.

Neutron Emission

This is simple emission of a neutron, which does not change *Z*. The extremely unstable $^{7}_{2}He$ nucleus (half-life 3×10^{-21} s) decays via **neutron emission**:

$$^{7}_{2}\text{He} \rightarrow {}^{6}_{2}\text{He} + {}^{0}_{1}\text{n}$$

Electron Capture

As the name suggests, electron capture involves the nucleus capturing an electron from the surrounding inner shells of electrons. It is very rare among natural isotopes but common among synthetic radionuclides. For example, $^{50}_{23}\text{V}$ nuclei can capture electrons, thereby converting to titanium nuclei, with the emission of X-rays and neutrinos:

$$^{50}_{23}\text{V} + {}^{0}_{-1}\text{e} \rightarrow {}^{50}_{22}\text{Ti} + \nu_e + \text{X-rays}$$

The net effect of **electron capture** is conversion of a proton in the nucleus to a neutron, as shown for the $^{7}_{4}\text{Be}$ nucleus in figure 27.7:

$$^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \rightarrow {}^{1}_{0}\text{n}$$

Electron capture changes *Z* but not *A*. It leaves a hole in the inner electron shells, and the atom emits X-ray photons as other orbital electrons drop down to fill the hole. Moreover, the nucleus that has just captured an orbital electron may be in an excited energy state and so can emit a gamma-ray photon.

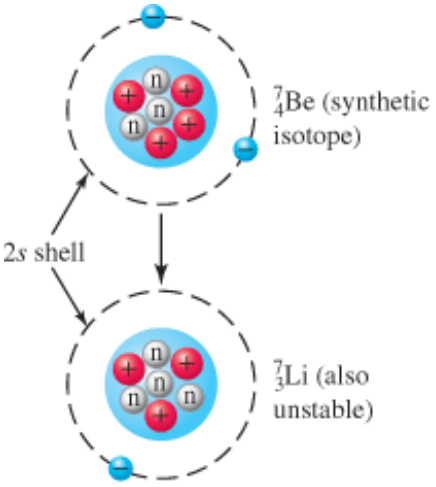


FIGURE 27.7 Electron capture occurs when an orbital electron collapses into the nucleus, thereby converting a proton into a neutron.

WORKED EXAMPLE 27.2

Writing a Balanced Nuclear Equation

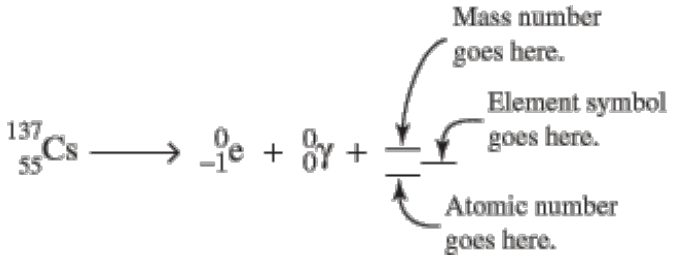
$^{137}_{55}\text{Cs}$, one of the radioactive products from a nuclear power plant, emits beta and gamma radi ation. Write the nuclear equation for its decay.

Analysis

We start with an incomplete equation using the given information and then determine any other data needed to complete the equation, remembering that both *Z* and *A* must balance on both sides of the equation.

Solution

The incomplete nuclear equation is:



The element symbol can be obtained from the periodic table after we have determined the atomic number of the product. This may be found using the fact that the atomic number (55) on the left-hand side of the equation must equal the sum of the atomic numbers on the right-hand side.

$$55 = (-1) + 0 + Z$$

Hence $Z = 56$, and from the periodic table we can determine that the product is Ba (barium). To determine which isotope of barium forms, we recall that the sums of the mass numbers on either side of the equation must also be equal. Letting A be the mass number of the barium isotope:

$$137 = 0 + 0 + A$$

Hence $A = 137$. The balanced nuclear equation is therefore:

$$^{137}_{55}\text{Cs} \rightarrow {}^{0}_{-1}\text{e} + {}^{0}_{0}\gamma + {}^{137}_{56}\text{Ba}$$

Is our answer reasonable?

Besides double-checking that element 56 is barium, the answer satisfies the requirements of a nuclear equation; that is, the sums of both the mass and atomic numbers, on both sides of the equation, are the same.

PRACTICE EXERCISE 27.2

Marie Curie (figure 27.8) was awarded the Nobel Prize for chemistry in 1911 for the discovery of the elements polonium and radium, and for the study of radium and its compounds. She is one of only four women to be awarded the Nobel Prize for chemistry. She had earlier been awarded the 1903 Nobel Prize for physics, jointly with her husband Pierre and Henri Becquerel (see p. 5). Marie Curie is one of only four people to be awarded two Nobel Prizes.



FIGURE 27.8 Marie Curie (1867–1934), one of only four people to be awarded two Nobel Prizes (physics in 1903 and chemistry in 1911).

Radium was originally used in the treatment of cancer. $^{226}_{88}Ra$ is an alpha and gamma emitter. Write a balanced nuclear equation for its decay.

PRACTICE EXERCISE 27.3

Write the balanced nuclear equation for the decay of $^{90}_{38}Sr$, a beta emitter. ($^{90}_{38}Sr$ is one of the many radionuclides present in the wastes of operating nuclear power plants, and is particularly dangerous as it can substitute for its fellow group 2 element calcium in human bones, thereby leading to irradiation of neighbouring tissue.)

Rates of Radioactive Decay

The methods of radioactive decay outlined in this section all involve ejection of a particle or a photon. If we can measure the numbers of these that are emitted over a period of time, we can measure the rate of radioactive decay. This is possible using the following devices.

- ***Geiger counter:*** The Geiger–Müller tube, one part of a Geiger counter (figure 27.9), detects beta and gamma radiation with energy high enough to penetrate the tube's window. Inside the tube is a gas under low pressure in which ions form when radiation enters. The ions permit a pulse of electricity to flow, which activates a current amplifier, a pulse counter and an audible click.



FIGURE 27.9 A Geiger counter is often used to ensure safety in laboratories that use radioactive reagents. This counter measures radiation in units of microsieverts per hour. The sievert (Sv) is an SI derived unit, with 1 Sv equivalent to 1 J kg^{-1}.AFP/Genya Savilov

- ***Scintillation counters:*** A scintillation counter (figure 27.10) has a surface coated with a phosphorescent chemical that emits a tiny flash of light when struck by a particle of radiation. These flashes can be magnified electronically and automatically counted.



FIGURE 27.10 A scintillation counter being used to test radiation levels outside a nuclear facility.Darrin Gray

- ***Dosimeters:*** People who work near radiation sources wear dosimeters to measure their total exposure. If exposure exceeds a predetermined limit, they are reassigned to an unexposed workplace for a period of time. Initially, film dosimeters were used. The darkening of a photographic film exposed to radiation

over a period of time is proportional to the total quantity of radiation received. Film dosimeters have largely been replaced by more modern technologies (figure 27.11): thermoluminescent dosimeters (TLDs) and optically stimulated luminescence (OSL) dosimeters.



FIGURE 27.11 Thermoluminescent dosimeters contain a crystal of lithium fluoride or calcium fluoride that absorbs radiation. The crystal is heated in a specialised machine that can determine the radiation dose. Optically stimulated luminescence dosimeters measure exposure to different types of radiation using various filters and a thin layer of aluminium oxide. To read the dose, a blue laser is used to stimulate the aluminium oxide, causing it to become luminescent. The luminescence is proportional to the quantity of radiation received.Lynsey Addario

We define the **activity** of a radioactive substance as the number of disintegrations it undergoes per second. The SI unit of activity is the **becquerel (Bq)**, named appropriately after Henri Becquerel, (1852–1908, Nobel Prize in physics, 1903) who discovered radioactivity; 1 becquerel is 1 disintegration per second. As a guide, 1 litre of air has an activity of about 0.04 Bq, due to ^{14}C in its carbon dioxide, while 1 gram of natural uranium has an activity of about 2.6×10^4 Bq. Our bodies themselves are also radioactive owing to the presence of naturally occurring isotopes such as ^{40}K — thankfully, the low natural abundance (0.01%) and long half-life (~10^9 years) of this isotope means that we are not very radioactive.

For a sufficiently large sample of a radioactive material, the activity is experimentally found to be proportional to the number of radioactive nuclei, N:

$$\text{activity} = kN$$

where the proportionality constant, k, is called the **decay constant k**. The decay constant is characteristic of the particular radioactive nuclide, and it gives the activity per nuclide in the sample. Since activity is the number of nuclei that disintegrate per second, we can write:

$$\text{activity} = -\frac{\Delta N}{\Delta t} = kN$$

which is called the **law of radioactive decay**. ΔN is the change in the number of radioactive nuclei over the time interval Δt and is defined as $N_{\text{final}} - N_{\text{initial}}$. As ΔN is therefore negative, a negative sign is introduced to make activity a positive number. The above equation is an example of a first-order kinetic process (chapter 15); all radioactive decay processes are, in fact, first-order, meaning that the activity of a radionuclide is directly proportional to the number of nuclei present. The most important facet of a first-order process with respect to radioactivity is that the **half-life** $\left(t_{\frac{1}{2}}\right)$ of a radioactive material, the time taken for exactly half of the sample to decay, is independent of the amount of the material present. The concept of half-life is depicted in figure 27.12 (see also p. 634), which shows the typical amount versus time decay curve for a radioactive nucleus, in this case ^{32}P, a nuclide widely used in labelling biological samples.

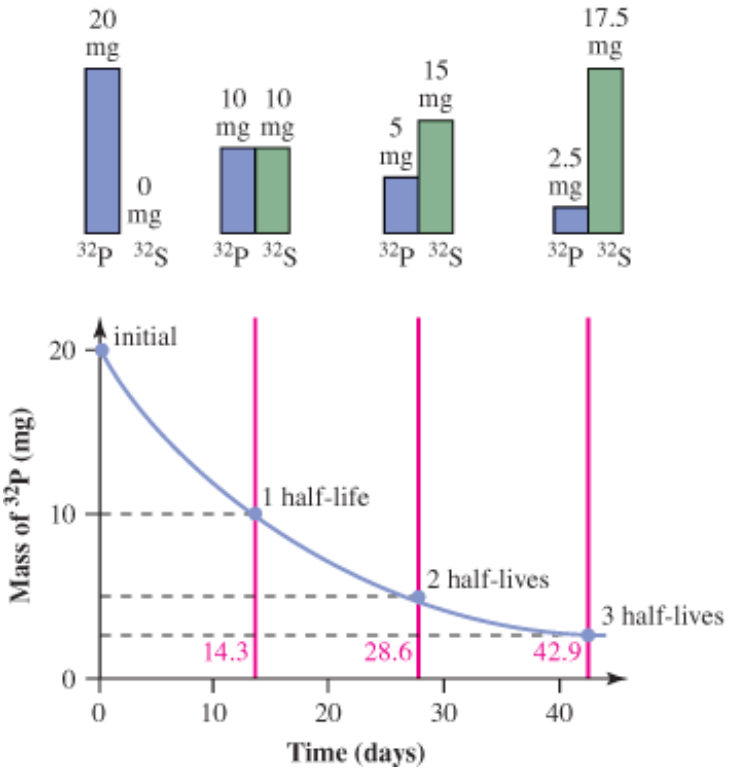


FIGURE 27.12 Decay of ^{32}P, a radioactive nuclide with a half-life of 14.3 days. The amount of the nuclide present halves every 14.3 days.

This nuclide has a half-life of 14.3 days, and decays via beta emission to give ^{32}S. Therefore, after the first 14.3-day period, exactly half of the sample has decayed, so we have a 50 : 50 mixture of ^{32}P and ^{32}S. After a further 14.3-day period, exactly half of the *remaining* ^{32}P has decayed, meaning that the sample is now 75% ^{32}S and 25% ^{32}P. After 10 half-lives (143 days), there is 0.098% of the original ^{32}P sample remaining. Table 27.1 gives the half-lives of some naturally occurring and synthetic radioactive nuclei and their modes of decay.

TABLE 27.1 Half-lives and decay modes of some radioactive nuclei.

Element	Isotope	Half-life	Mode of decay
Naturally occurring radionuclides			
potassium	$^{40}_{19}K$	1.25×10^9 years	beta, electron capture, gamma
tellurium	$^{123}_{52}Te$	9.2×10^{16} years	electron capture
neodymium	$^{123}_{52}Te$	2.29×10^{15}years	alpha
rhenium	$^{187}_{75}Re$	4.12×10^{10} years	beta
radon	$^{222}_{88}Rn$	3.82 days	alpha
radium	$^{226}_{88}Ra$	1.6×10^3 years	alpha, gamma
thorium	$^{230}_{90}Th$	7.54×10^4 years	alpha
uranium	$^{238}_{92}U$	4.47 × 109 years	alpha
Synthetic radionuclides			
tritium	$^{3}_{1}H$	12.32 years	beta
oxygen	$^{15}_{8}O$	122 seconds	positron

phosphorus	$^{32}_{15}P$	14.3 days	beta
technetium	$^{99m}_{43}Tc$	6.01 hours	gamma
iodine	$^{131}_{53}I$	8.03 days	beta
caesium	$^{137}_{55}Cs$	30.08 years	beta
strontium	$^{90}_{38}Sr$	28.9 years	beta
plutonium	$^{238}_{94}Pu$	87.7 years	alpha
americium	$^{243}_{95}Am$	7.37×10^3 years	alpha

You can see from these data that the half-lives range from seconds to quadrillions of years, and obviously, therefore, nuclear decay reactions can occur at vastly different rates.

Sometimes one radionuclide does not decay to a stable isotope but decays instead to another unstable radionuclide. The decay of one radionuclide after another continues until a stable isotope forms. The sequence of such successive nuclear reactions is called a **radioactive disintegration series**. Four series occur naturally, and ^{238}U is at the head of the one shown in figure 27.13.

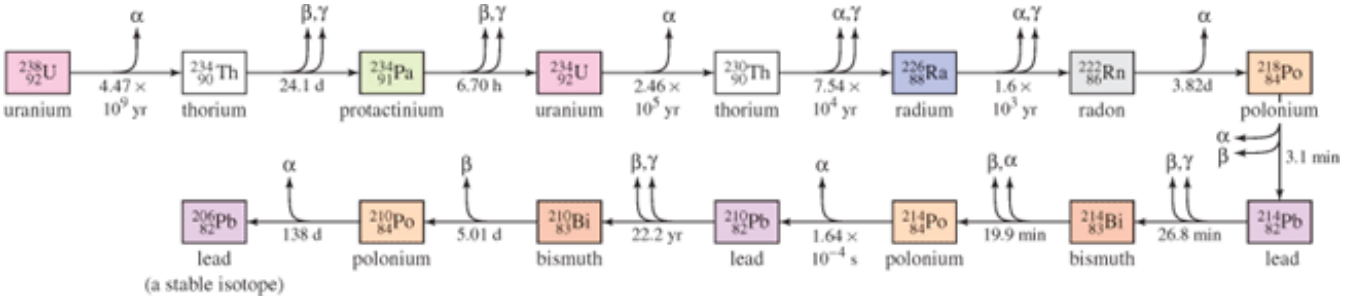


FIGURE 27.13 The $^{238}_{92}U$ radioactive disintegration series. The time given beneath each arrow is the half-life of the preceding isotope.

WORKED EXAMPLE 27.3

Decay Sequences

$^{222}_{86}Rn$ is an unstable nuclide that has been detected in the air of some stone houses, owing to the decay of naturally occurring uranium in the stone. Its presence is a concern because of high health hazards associated with exposure to its radioactivity. Gaseous radon easily enters the lungs, and, once it decays, its solid products remain embedded in lung tissue. $^{222}_{86}Rn$ changes to a stable nuclide by emitting α and β particles. The first four steps are α, α, β and β. Write this sequence of nuclear reactions and identify each product.

Analysis

Charge number and mass number must be conserved in each reaction. Thus, each α particle decreases the nuclear charge by 2 units and the mass number by 4 units. Similarly, each β emission increases the nuclear charge by 1 unit but leaves the mass number unchanged. Consult a periodic table to identify the element symbol of each product nuclide.

Solution

The starting nuclide is ^{222}Rn, which, according to the decay sequence, emits an α particle:

$$^{222}_{86}\text{Rn} \rightarrow {}^{A}_{Z}X + {}^{4}_{2}\text{He}$$

The product has A = 222 - 4 = 218 and Z = 86 - 2 = 84. Element 84 is Po, so ^{222}Rn decomposes to give an α particle and ^{218}Po:

$$^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$$

The polonium nucleus is unstable, and the sequence indicates that it decays via α emission:

$$^{218}_{84}\text{Po} \rightarrow {}^{214}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

The decay sequence indicates that $^{214}_{82}\text{Pb}$ is unstable as well. This nuclide converts a neutron to a proton by β emission:

$$^{214}_{82}\text{Pb} \rightarrow {}^{A}_{Z}X + {}^{0}_{-1}\text{e}$$

For this product, A = 214 - 0 = 214 and Z = 82 - (-1) = 83. The product nucleus is bismuth, element 83:

$$^{214}_{82}\text{Pb} \rightarrow {}^{214}_{83}\text{Bi} + {}^{0}_{-1}\text{e}$$

The fourth decay in the sequence is also β emission, which produces ^{214}Po, another isotope of element 84:

$$^{214}_{83}\text{Bi} \rightarrow {}^{214}_{84}\text{Po} + {}^{0}_{-1}\text{e}$$

Is our answer reasonable?

You can confirm that both A and Z are conserved in these processes. Extra-heavy nuclides like ^{222}Rn frequently decay through sequences of α and β decays, because to reach the band of stability they must not only shed mass (α decay) but also decrease their N:Z ratios (β decay).

PRACTICE EXERCISE 27.4

The decay sequence in worked example 27.3 continues with four more steps: α, β, β, and α. Determine the correct equations for these reactions.

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27.3 Synthesis of New Elements

Chemistry as a true scientific discipline had its beginnings only in the late seventeenth and early eighteenth centuries. Prior to this, man's major chemical ambition was to be able to turn metal elements such as lead and mercury into gold, a nonscience called alchemy. Not surprisingly, despite the centuries of effort expended in this exercise, all attempts ended in failure. However, this changed in the early years of the twentieth century when Ernest Rutherford, in turning nitrogen into oxygen by bombarding it with alpha particles, became the first successful alchemist. Changing one element into another is called **transmutation**, and, as we have seen, is a result of the natural alpha and beta decay of radioactive elements. Transmutation can also be induced, as Rutherford did, by the bombardment of nuclei with high-energy particles, such as alpha particles from natural emitters, neutrons from nuclear reactors, or protons made by stripping electrons from hydrogen. The particles used to effect transmutations must usually be accelerated to high speeds to penetrate the electron cloud and the nucleus of an atom; this can be achieved using electric fields in linear and circular accelerators (figure 27.14).

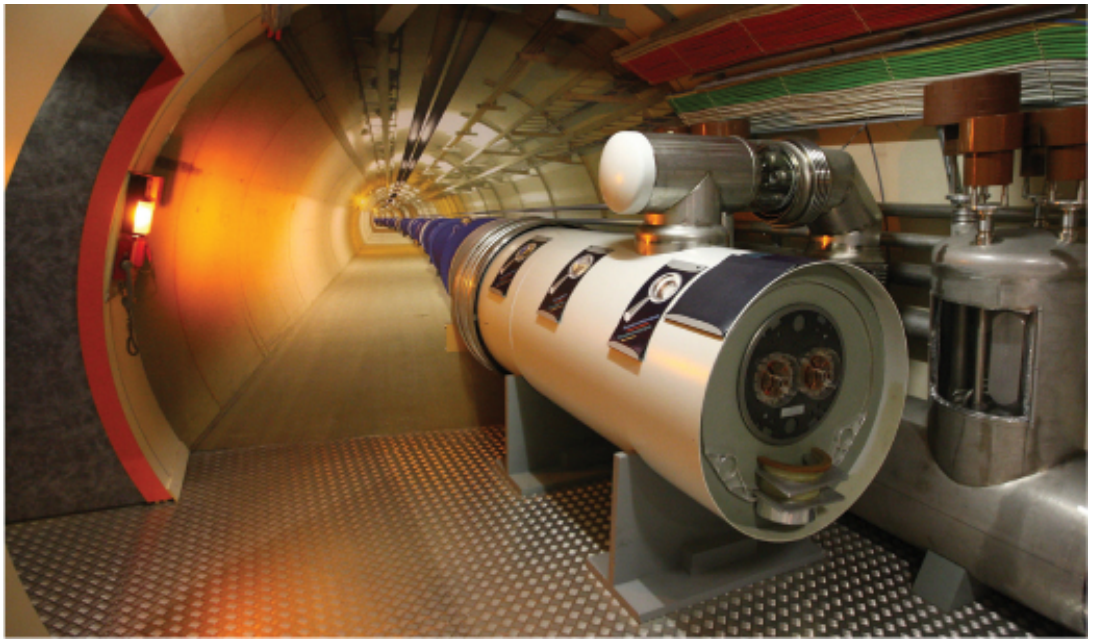


FIGURE 27.14 In this linear accelerator (the Large Hadron Collider at CERN in Switzerland), protons can be accelerated to just under the speed of light and given up to 33 GeV of energy before they strike their target (1 GeV = 10^9 eV = 1.6 x 10^{-10} J).Johannes Simon

A linear accelerator gives particles greater energy and enables them to sweep through the target atom's electron cloud and become buried in its nucleus (although beta particles can be accelerated, they are repelled by a target atom's own electrons). Both the energy and the mass of a bombarding particle enter the target nucleus at the moment of capture. The energy of the new nucleus, called a **compound nucleus**, quickly becomes distributed among all of the nucleons, but the nucleus is nevertheless rendered somewhat unstable. To get rid of the excess energy, a compound nucleus generally ejects something — a neutron, proton or electron — and often emits gamma radiation as well. This leaves the new nucleus of an isotope different from the original target, so an overall transmutation has occurred.

In 1917, Ernest Rutherford observed the first example of artificial transmutation. When he let alpha particles pass through a chamber containing nitrogen atoms, an entirely new radiation was generated, one much more penetrating than alpha radiation. It was found to consist of protons. Rutherford was able to show that the protons came from the decay of the compound nucleus $^{18}_{9}F^{*}$ produced when a $^{14}_{7}N$ nucleus captured a bombarding alpha particle:

$$\underset{\text{alpha particle}}{^{4}_{2}He} + \underset{\text{nitrogen nucleus}}{^{14}_{7}N} \rightarrow \underset{\text{compound nucleus}}{^{18}_{9}F^{*}} \rightarrow \underset{\text{oxygen nucleus}}{^{17}_{8}O} + \underset{\text{high-energy progon}}{^{1}_{1}p}$$

where the asterisk in $^{18}_{9}F^{*}$ denotes a compound nucleus. This process is illustrated in figure 27.15 and also on the New Zealand postage stamp pictured in figure 27.16.

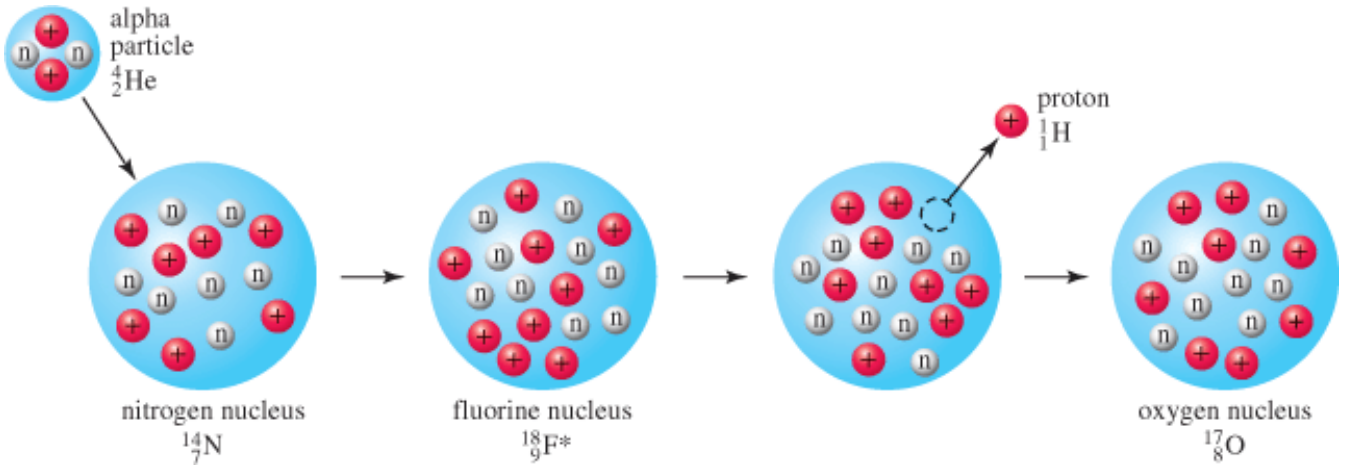


FIGURE 27.15 Transmutation of nitrogen into oxygen. When the nucleus of $^{14}_{7}N$ captures an alpha particle, it becomes a compound nucleus of $^{18}_{9}F^{*}$. This then expels a proton and becomes the nucleus of $^{17}_{8}O$.



FIGURE 27.16 One of two New Zealand postage stamps released in 1971 to honour the centenary of Rutherford's birth.New Zealand Post Limited

More than 1000 isotopes have been made by transmutations. Most do not occur naturally, and these appear in the band of stability (figure 27.1) as small open squares, nearly 900 in number. The naturally occurring isotopes above atomic number 82 all have very long half-lives. Others might have existed, but their half-lives probably were too short to permit them to last into our era. All of the elements from neptunium (atomic number 93) upwards, the **transuranium elements**, are synthetic. Elements from atomic numbers 93 to 103 complete the actinoid series of the periodic table, which starts with element 90, thorium. Beyond this series, the elements up to 118 have been made synthetically. Bombarding particles larger than neutrons, such as alpha particles or the nuclei of heavier atoms, are used to make the heaviest elements. For example, darm-stadtium (Ds, element 110) was made when a neutron was ejected from the compound nucleus formed by the fusion of $^{62}_{28}Ni$ and $^{208}_{82}Pb$:

$$^{62}_{28}Ni + {}^{208}_{82}Pb \rightarrow {}^{270}_{110}Ds^{*} \rightarrow {}^{269}_{110}Ds + {}^{1}_{0}n$$

Some atoms of the most recently named element, copernicium (element 112), were formed when a neutron was lost from the compound nucleus made by bombarding $^{208}_{82}Pb$ with $^{70}_{30}Zn$ in a reaction very similar to that above. The newest element on the periodic table, Uus (element 117), was reported in 2010. Five atoms of $^{293}_{117}Uus$ and one of $^{294}_{117}Uus$ were prepared from the bombardment of $^{249}_{987}Bk$ with $^{48}_{20}Ca$, and and these had half-lives of tens of milliseconds. The name of element 117, ununseptium, as well as those for elements 113 to 116 and 118, are temporary, and these elements will not be assigned ‘proper’ names until their syntheses have been independently verified.

The synthesis of artificial isotopes is not merely an academic exercise, and many artificial isotopes have

important uses. For example, the technetium isotope ^{99m}Tc finds extensive use as an imaging agent in medicine. The ^{239}Pu isotope is fissionable, and can therefore be used as a fuel in nuclear power stations. The smoke detectors in most houses in Australia and New Zealand contain tiny amounts of element 95, americium (Am). ^{60}Co is a gamma emitter and is used to irradiate foodstuffs to increase their shelf lives. In addition, the synthesis of new elements helps us to understand the structure of the nucleus; Glenn Seaborg (1912–1999, Nobel Prize in chemistry, 1951) predicted that there should be an 'island of stability' among the normally short-lived transuranium elements, and that, like the $^{208}_{82}\mathrm{Pb}$ nucleus, the as yet unknown element $^{310}_{126}\mathrm{Ubh}$ should show unusual stability because of the presence of magic numbers of both protons and neutrons. With this in mind, much time and money is being expended in the synthesis of new heavy elements.

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27.4 Radioactive Dating Methods

The determination of the age of a geological deposit or an archaeological find by the use of radionuclides that are naturally present is called **radiological dating**. It is based partly on the premise that the half-lives of radionuclides have been constant throughout the entire geological period. This premise is supported by the finding that half-lives are insensitive to all environmental forces such as heat, pressure, magnetism and electrical stresses. In geological dating, a pair of isotopes is sought that are related as a 'parent' to a 'daughter' in a radioactive disintegration series, such as the $^{238}_{92}U$ series (figure 27.13). $^{238}_{92}U$ (as 'parent') and $^{206}_{82}Pb$ (as 'daughter') have been used as a radiological dating pair of isotopes. The long half-life of $^{238}_{92}U$ (~5×10^9 years) is a necessary criterion for geological dating. After the concentrations of $^{238}_{92}U$ and $^{206}_{82}Pb$ are determined in a rock specimen, the ratio of the concentrations together with the half-life of $^{238}_{92}U$ is used to calculate the age of the rock. Probably the most widely used isotopes for dating rock are the $^{40}_{19}K$ / $^{40}_{18}Ar$ pair. $^{40}_{19}K$ is a naturally occurring radionuclide with a half-life nearly as long as that of $^{238}_{92}U$. One of its modes of decay is electron capture, which results in the production of $^{40}_{18}Ar$:

$$^{40}_{19}K + {}^{0}_{-1}e \rightarrow {}^{40}_{18}Ar$$

The argon produced by this reaction remains trapped within the crystal lattices of the rock and is freed only when the rock sample is melted. The amount of argon can be measured with a mass spectrometer (chapter 20); the age of the specimen is then estimated using the observed ratio of $^{40}_{18}Ar$ to $^{40}_{19}K$, together with the half-life of the parent. Because the half-lives of $^{238}_{92}U$ and $^{40}_{19}K$ are so long, samples have to be at least 300 000 years old for either of these two parent–daughter isotope pairs to work.

^{14}C Dating

^{14}C dating is used to estimate the age of organic remains, such as wooden or bone objects from ancient tombs. The ratio of ^{14}C (a beta emitter) to stable carbon, ^{12}C, in an ancient sample is measured and compared with the ratio in recent organic remains. The data can then be used to calculate the age of the sample.

Chemistry Research

Sequencing the Early Solar System

Dr Claudine Stirling, University of Otago, Dunedin

Our solar system evolved from a giant molecular cloud of dust and gas that collapsed gravitationally more than 4.5 billion years ago. What triggered this collapse is the subject of debate, but one leading theory invokes shockwaves from a nearby massive exploding star — a supernova. Our research at the University of Otago aims to investigate the role of a supernova in triggering the birth of our solar system and reconcile the precise timescale of events leading to its formation. This is achieved using multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS, figure 27.17) to search for minute (one part in 10 000) variations in the uranium isotopic composition of meteorites derived from asteroidal-sized objects that were formed at the start of the solar system; these variations were previously too small to detect.



FIGURE 27.17 The MC-ICPMS instrument used to measure uranium isotopes.David A Hardy, www.astroart.org

The supernova hypothesis: Did a massive exploding star trigger the birth of our solar system?

By far the most likely astrophysical site for the formation of uranium and the other radioactive actinoids is a supernova, as the high fluence of the neutrons released from the explosion allows synthesis of the very heavy elements. This contrasts with lighter elements, which can be produced in a range of different astrophysical environments. Therefore, the detection of specific actinoids in condensates of the first solar system that are preserved in meteorites provides a unique 'fingerprint' of supernova events that occurred close to the 'proto-solar molecular cloud', the region of space that evolved to become our solar system. A critically important actinoid is the short-lived isotope ^{247}Cm, which decays to ^{235}U with a half-life of 16 million years. Given its short half-life, ^{247}Cm is presently extinct, but its former existence can be detected by searching for small excesses in its ^{235}U daughter isotope. If anomalies in the abundance of ^{235}U (measured relative to ^{238}U as ^{238}U/^{235}U) are found that can be related to ^{247}Cm decay, then it becomes possible to use the ^{247}Cm–^{235}U radioactive decay system to date the timing of the last supernova event and evaluate its role in triggering the birth of our solar system.

Solar system evolution and the uranium–lead dating method

The uranium–lead geological dating method has been widely used to define the timescale and sequence of events across the Earth and solar system. The uranium–lead dating method is based on a combination of the ^{238}U and ^{235}U radioactive disintegration series and the slow decay of the radioactive ^{238}U and ^{235}U 'parent' isotopes (with half-lives of 4.5×10^9 years and 7×10^8 years, respectively) to their stable 'daughter' isotopes of ^{206}Pb and ^{207}Pb, respectively. Like most radioactive dating techniques, the accuracy and precision of the uranium–lead method has experienced ongoing improvements in recent years as instrumentation has advanced. In fact, the modern uranium–lead method defines the most precise age of the solar system at 4.5672 ± 0.0006 billion years and provides compelling new evidence that the debris in the early solar system evolved rapidly from dust-sized particles to large planetesimals exceeding 100 km across in only 2 to 3 million years. Until very recently, the uranium–lead dating method assumed a constant ratio between the ^{238}U and ^{235}U parent

isotopes; uranium was not expected to 'fractionate' isotopically due to its very heavy mass. However, new techniques in mass spectrometry, allowing the $^{238}U/^{235}/U$ ratio to be measured up to 100 times more precisely than previously, have shown significant variability in the $^{238}U/^{235}U$ ratio of some terrestrial rocks, and the fundamental timescale of the early solar system will need to be drastically revised if uranium isotopic variations are also found in meteorites.

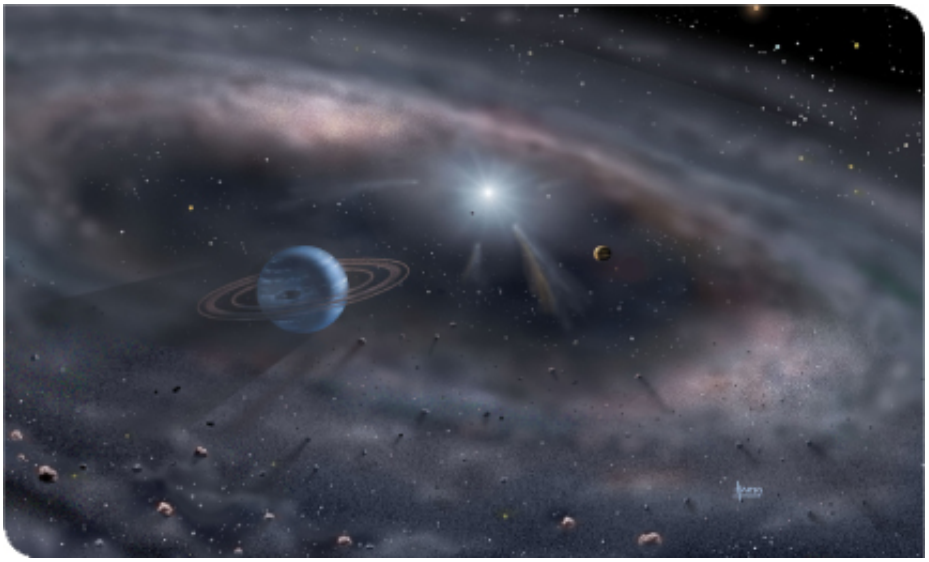


FIGURE 27.18 Planets take shape in the dusty disk around a young star in an artist's conception. The scene is an example of what things might be like around MWC 419, a blue star about 2100 light-years from Earth.

There are two approaches to ^{14}C dating. The older method, which was introduced by its discoverer Willard F Libby (1908 -1980, Nobel Prize in chemistry, 1960), measures the radioactivity of a sample taken from the specimen. The radioactivity is proportional to the concentration of ^{14}C. However, the newer and current method of ^{14}C dating, accelerator mass spectrometry, can count single ^{14}C nuclei in the presence of ˜10^{15} stable atoms. This approach permits the use of smaller samples (0.5–5 mg versus 1–20 g for the Libby method), it works at much higher efficiencies, and it gives more precise dates. The half-life of the ^{14}C nucleus (5730 years) means that objects up to 60 000 years old can be dated, but estimation is more accurate for objects less than 7000 years old.

^{14}C has been produced in the atmosphere for many thousands of years by the action of cosmic rays on atmospheric nitrogen. Primary cosmic rays are streams of particles from the Sun, mostly protons but also the nuclei of many elements as high as atomic number 26. Their collisions with atmospheric atoms and molecules generate secondary cosmic rays, which include all subatomic particles. Secondary cosmic rays contribute to our background radiation, and people living at high altitudes receive more of this radiation than others.

Neutrons of the proper energy in secondary cosmic rays can transmute nitrogen atoms into ^{14}C atoms according to the equation:

$$\underset{\text{neutron (in cosmic ray)}}{{}^{1}_{0}n} + \underset{\text{nitrogen atom in the atmosphere}}{{}^{14}_{7}N} \rightarrow \underset{\text{compound nucleus}}{{}^{15}_{7}N^{*}} \rightarrow \underset{\text{carbon–14 atom (a beta emitter)}}{{}^{14}_{6}C} + \underset{\text{high-energy proton}}{{}^{1}_{1}p}$$

The newly formed ^{14}C diffuses into the lower atmosphere, where it is absorbed as $^{14}CO_2$ by green plants

during photosynthesis. Thus, ^{14}C becomes incorporated into plant substances and into the animals that eat plants. The ^{14}C decays but more is ingested by the living organism. The net effect is an overall equilibrium involving ^{14}C in the global system. As long as the plant or animal is alive, its ratio of ^{14}C atoms to ^{12}C atoms is constant. At death, the amount of ^{14}C in an organism's remains is at its maximum, and it slowly loses this ^{14}C by decay. The decay is a first-order process with a rate independent of the number of original carbon atoms. The ratio of ^{14}C to ^{12}C, therefore, can be related to the time that has elapsed between the death of the organism and the time of the measurement. The critical assumption in ^{14}C dating is that the steady-state availability of ^{14}C from the atmosphere has remained largely unchanged over the period for which measurements are valid. In contemporary biological samples, the ratio ^{14}C : ^{12}C is about 1.3×10^{-12}. Thus, each fresh 1.0 g sample of biological carbon in equilibrium with the $^{14}CO_2$ of the atmosphere has a ratio of 5.8×10^{10} atoms of ^{14}C to 4.8×10^{22} atoms of ^{12}C. The ratio decreases by a factor of 2 every 5730 years, the half-life of ^{14}C. Knowing the ^{14}C : ^{12}C ratio in the sample allows us to calculate its age using the first-order kinetic treatment that we saw in chapter 15. If we let r_0 stand for the ^{14}C : ^{12}C ratio at the time of death of the carbon-containing species and r_t stand for the ^{14}C : ^{12}C ratio now, it can be shown that:

$$\ln\frac{r_0}{r_t} = (1.21 \times 10^{-4}\,\text{yr}^{-1})t$$

where t is the age of the sample in years. Radiocarbon dating has been used with great success to defuse a number of controversies, as shown in worked example 27.4.

WORKED EXAMPLE 27.4

Radiocarbon Dating

In 1996, the Jinmium Aboriginal rock shelter in the Kimberley region of the Northern Territory was dated at around 120 000 years old using a technique called thermoluminescence, meaning that human habitation of Australia would have occurred at least 60 000 years earlier than previously thought. However, the method used was later called into question, and ^{14}C dating of charcoal fragments was used to reveal the true age of the site. The ^{14}C:^{12}C ratio in a charcoal sample was 1.08×10^{-12}, while the same ratio in living objects is 1.33×10^{-12}. How old is the sample?

Analysis

We know the ^{14}C : ^{12}C ratio in both the charcoal sample and in living objects. Therefore, we simply use these values in the equation given above to find t.

Solution

Using the equation:

$$\ln\frac{r_0}{r_t} = \left(1.21 \times 10^{-4}\,\text{yr}^{-1}\right)t$$

and substituting the values above gives:

$$\ln\frac{1.33 \times 10^{-12}}{1.08 \times 10^{-12}} = \left(1.21 \times 10^{-4}\,\text{yr}^{-1}\right)t$$

Hence:

$$t = \frac{2.08 \times 10^{-1}}{1.21 \times 10^{-4}\,\text{yr}^{-1}} = 1.72 \times 10^{3}\,\text{yr}$$

The true age of the upper levels in deposits at the site was of the order of 1000–3000 years, while lower levels were dated at no older than 10 000 years. The earliest known date of human habitation of Australia, therefore, remains at around 50 000–60 000 years ago.

Is our answer reasonable?

In problems like this, involving the substitution of data into an equation, always go back and check that you have put the correct numbers in the correct places. We appear to have done this, and the answer we obtained is plausible, so we can be confident we are correct.

PRACTICE EXERCISE 27.5

In 1988, the Shroud of Turin (figure 27.19), claimed by some to have been used to bury Christ, was dated by isotopic analysis of its carbon content. The ^{14}C : ^{12}C ratio of a sample from the shroud was 1.22×10^{-12}, while the same ratio in living objects is 1.33×10^{-12}. How old is the shroud?



FIGURE 27.19 The shroud of Turin.

Calculations of ages, as illustrated in worked example 27.4, assume that the level of ^{14}C in the atmosphere at the time of death was the same as it is today. To check the validity of ^{14}C dating, its age estimates have been compared with those obtained by tree-ring dating, which involves fewer assumptions than radiocarbon dating. A large number of such comparisons show small but consistent differences, indicating that the fractional amount of ^{14}C in the atmosphere has changed slowly but steadily with time. Archaeologists use a small multiplying factor to correct for this small drift when they

use radiocarbon dating on objects that do not retain tree rings, such as charcoal and cloth.

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27.5 Applications of Nuclear Processes

There are few more emotive words in the English language than ‘nuclear’. On the one hand, nuclear power can potentially provide energy for the planet for the foreseeable future. On the other hand, Hiroshima and Nagasaki serve to remind us that nuclear processes can potentially destroy life on Earth. The nuclear debate has raged for over 60 years and will doubtless continue for many more. It is important that all participants in this debate are well informed, so, in this section, we aim to explain the processes that allow us access to the huge energies of the nucleus through nuclear fission and nuclear fusion. We also take a brief look at nuclear medicine, in which radioactive materials are used in a controlled fashion for diagnosis and treatment of disease.

Nuclear Fission

We have already seen that nuclear transmutation reactions can be induced by bombardment of particular nuclei with alpha particles. Because of their electrical neutrality, neutrons penetrate an atom's electron cloud easily, so they can enter the nucleus. Enrico Fermi discovered in the early 1930s that slow-moving thermal neutrons, those with an average kinetic energy that puts them in thermal equilibrium with their surroundings at room temperature, can be captured by nuclei. When Fermi directed thermal neutrons at a uranium target, several different species of nuclei were produced, a result that Fermi could not explain. None had an atomic number above 82. He and other physicists did not follow up on a suggestion by chemist Ida Noddack-Tacke that nuclei of much lower atomic number probably formed; at that time, the forces holding a nucleus together were considered too strong to permit such a result.

In 1939, Otto Hahn (1879–1968, Nobel Prize in chemistry, 1944) and Fritz Strassman finally verified that the process above produces several isotopes much lighter than uranium, such as $^{140}_{56}\mathrm{Ba}$. Shortly thereafter, Lise Meitner (after whom element 109, meitnerium, is named) and Otto Frisch showed that a nucleus of one of the rare isotopes in natural uranium, $^{235}_{92}\mathrm{U}$, splits into roughly two equal parts after it captures a slow neutron. They named this break-up nuclear fission. An isotope that can undergo fission after neutron capture is called a **fissile isotope**. $^{235}_{92}\mathrm{U}$ is the naturally occurring fissile isotope of uranium used in nuclear reactors and has an abundance of 0.72%. Two other fissile isotopes, $^{233}_{92}\mathrm{U}$ and $^{239}_{94}\mathrm{Pu}$, can be made in nuclear reactors. The general fission reaction of $^{235}_{92}\mathrm{U}$ can be represented as:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow X + Y + b\,{}^{1}_{0}\mathrm{n}$$

X and *Y* can be a large variety of nuclei, with more than 30 having been identified. The co efficient *b* has an average value of 2.47, the average number of neutrons produced by fission events. A typical specific fission is:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U}^{*} \rightarrow {}^{94}_{36}\mathrm{Kr} + {}^{139}_{56}\mathrm{Ba} + 3\,{}^{1}_{0}\mathrm{n}$$

The compound nucleus $^{236}_{92}\mathrm{U}^{*}$ is the one that actually undergoes nuclear fission. It has 144 neutrons and 92 protons for a neutron : proton ratio of roughly 1.6. Initially, the emerging krypton and barium isotopes have the same ratio, and this is much too high for them. The neutron : proton ratio for stable isotopes with 36 to 56 protons is nearer 1.2 to 1.3 (figure 27.1). Therefore, the initially formed, neutron-rich krypton and barium nuclides promptly eject neutrons, called secondary neutrons, that generally have much higher energies than thermal neutrons. These secondary neutrons become thermal neutrons as they are slowed by collisions with surrounding materials. They can now be captured by unchanged $^{235}_{92}\mathrm{U}$ atoms and the process is repeated. Because each fission event produces, on average, more than two new neutrons, the potential exists for a nuclear chain reaction (figure 27.20).



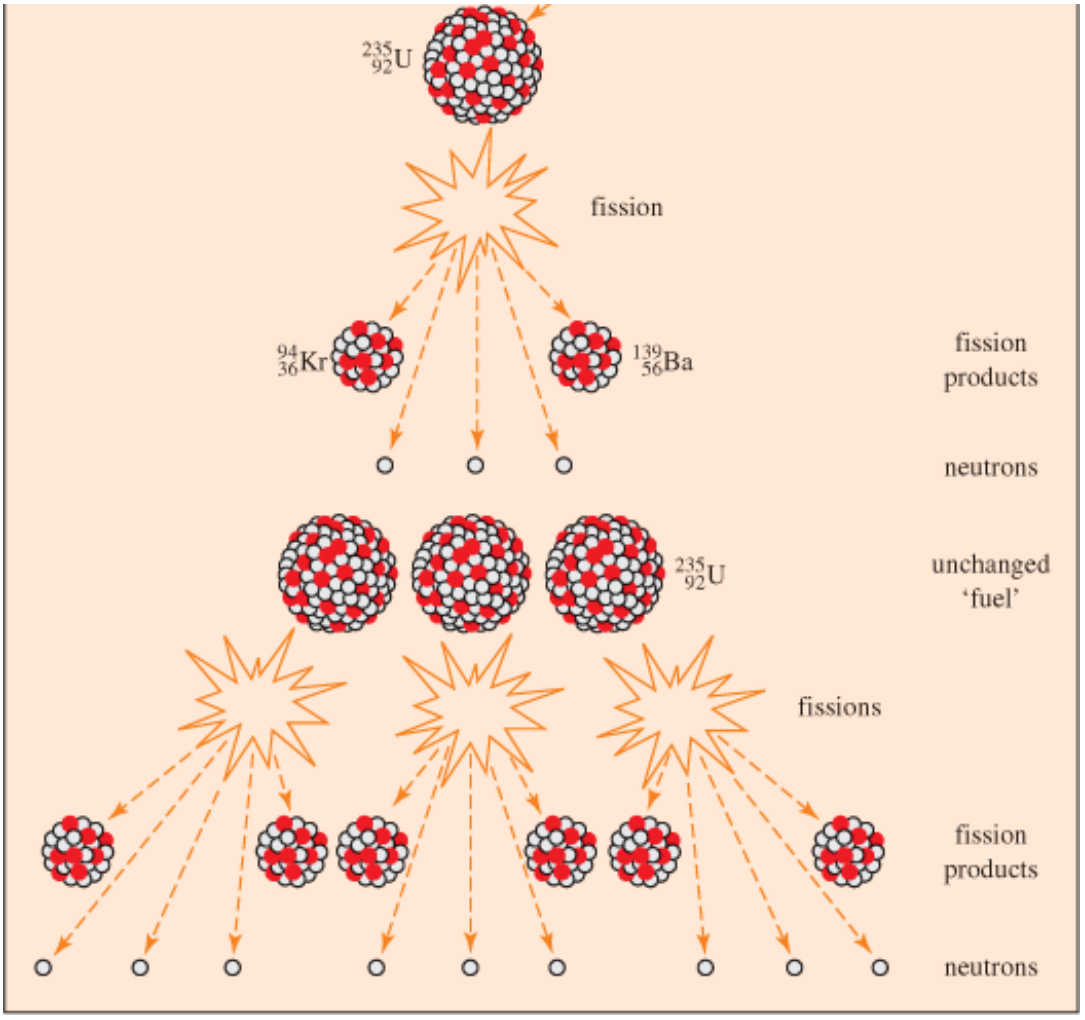


FIGURE 27.20 A nuclear chain reaction. Whenever the concentration of a fissile isotope is high enough (at or above the critical mass), the neutrons released by one fission can be captured by enough unchanged nuclei to cause more than one additional fission event. In civilian nuclear reactors, the fissile isotope is too dilute for this to get out of control. In addition, control rods of nonfissile materials that are able to capture excess neutrons can be inserted or withdrawn from the reactor core to ensure that the heat generated can be removed as fast as it develops.

A chain reaction is a self-sustaining process where products from one event cause one or more repetitions of the process. If the sample of $^{235}_{92}$U is small enough, the loss of neutrons to the surroundings is sufficiently rapid to prevent a chain reaction. However, at a certain **critical mass** of $^{235}_{92}$U, a few kilograms, this loss of neutrons is insufficient to prevent a sustained reaction. A virtually instantaneous fission of the sample ensues resulting in an explosion that releases an enormous amount of energy. The energy produced by the fission of 1 kg of $^{235}_{92}$U (about the size of a golf ball) is roughly 8×10^{13} J, the same energy as is contained in 19 000 tonnes of TNT.

Virtually all civilian nuclear power plants throughout the world operate on the same general principles. The heat of fission is used either directly or indirectly to increase the pressure of some gas that then drives an electric generator. The heart of a nuclear power plant is the reactor, where fission takes place in the fuel core. The nuclear fuel is generally uranium oxide, enriched to 2– 4% $^{235}_{92}$U and formed into glass-like pellets. These are housed in long, sealed metal tubes called cladding. Bunches of tubes are assembled in spacers that permit a coolant to circulate around the tubes. A reactor has several such assemblies in its fuel core. The coolant carries away the heat of fission.

There is no danger of a nuclear power plant undergoing a nuclear explosion as the concentration of fissile isotopes in a reactor (2 to 4%) is too low. However, if the coolant fails to carry away the heat of fission, the reactor core can melt down, and the molten mass might even go through the thick-walled containment vessel in which the reactor is kept. It is also possible that the heat can split molecules of coolant water into

hydrogen and oxygen, which, on recombining, could produce an immense explosion. This is what happened when the reactor at the Ukrainian energy park at Chernobyl failed in 1986 and when the Fukushima reactor in Japan was damaged by an earthquake in 2011.

To convert secondary neutrons to thermal neutrons, the fuel core has a moderator, which is the coolant water itself in nearly all civilian reactors. Collisions between secondary neutrons and moderator molecules heat up the moderator. This heat energy eventually generates steam that enables an electric turbine to run. Ordinary water is a good moderator, and so are heavy water (deuterium oxide, D_2O, a form of water in which all the protons have been replaced by deuterium atoms) and graphite. Two main types of reactors dominate civilian nuclear power, the boiling water reactor and the pressurised water reactor. Both use ordinary water as the moderator, and so are sometimes called light water reactors. A pressurised water reactor, such as that depicted in figure 27.21, has two loops, and water circulates in both.

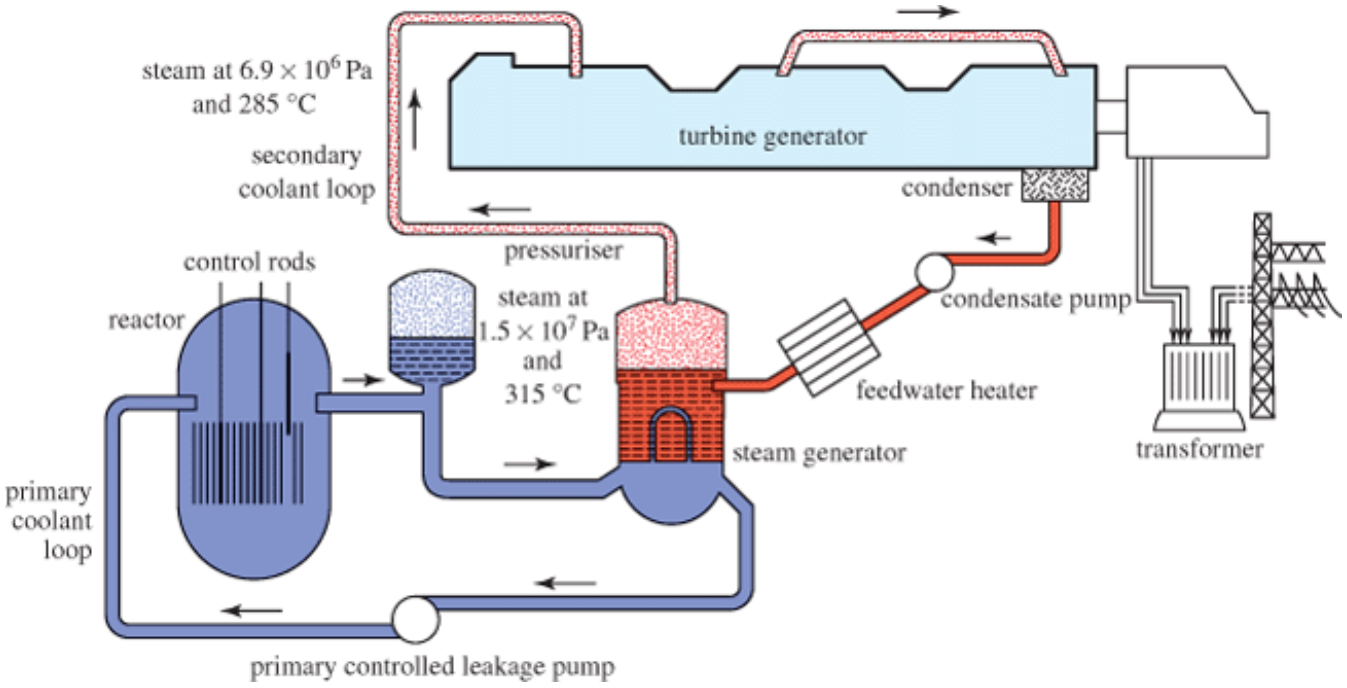


FIGURE 27.21 Pressurised water reactor. Water in the primary coolant loop is pumped around and through the fuel elements in the core, and it carries away heat produced by the nuclear chain reactions. The hot water delivers its heat to the cooler water in the secondary coolant loop, where steam is generated to drive the turbines. (Drawing from WASH-1261, U.S. Atomic Energy Commission, 1973)

The primary coolant loop moves water through the reactor core, where it picks up thermal energy from fission. The water is kept in the liquid state by being under high pressure (hence the name ‘pressurised water reactor’). The hot water in the primary loop transfers thermal energy to the secondary loop at the steam generator. This makes steam at high temperature and pressure, which is piped to the turbine. As the steam drives the turbine, the steam pressure drops. The condenser at the end of the turbine, cooled by water circulating from a river or lake or from huge cooling towers, forces a large pressure drop within the turbine by condensing the steam to liquid water. The returned water is then recycled to high-pressure steam. (In the boiling water reactor, there is only one coolant loop. The water heated in the reactor itself is changed to steam that drives the turbine.)

Currently, neither Australia nor New Zealand has a commercial fission reactor for electricity generation. However, Australia has the OPAL research reactor at Lucas Heights (figure 27.22), just outside Sydney. This is used for, among other things, the production of radioisotopes for both industrial and medical uses, and processing silicon chips. OPAL replaced the HIFAR reactor, which commenced operation in 1960 and began decommissioning in 2007, a process that will be completed in 2016.



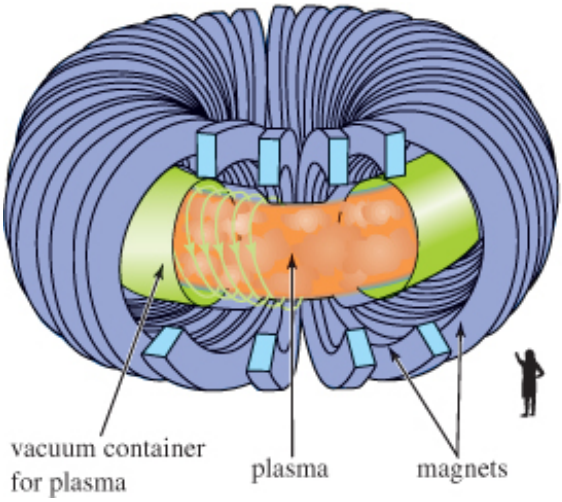
FIGURE 27.22 The Lucas Heights Research Reactor, on the outskirts of Sydney.Ian Waldie

The major problem with fission, and one that appears insurmountable, is that significant amounts of radioactive nuclear waste are produced. Such waste must be safely contained for at least 10 half-lives (0.098% of the original sample remains after this time) and this presents enormous practical difficulties. Radioactive wastes from nuclear power plants occur as gases, liquids and solids. The gases are mostly radionuclides of krypton and xenon but, with the exception of $^{85}_{54}\text{Xe}(t_{\frac{1}{2}} = 10.4\,\text{years})$, the gases have short half-lives and decay quickly. During decay, they must be contained, and this is one function of the cladding. Other dangerous radionuclides produced by fission include $^{131}_{53}\text{I}$, $^{90}_{38}\text{Sr}$ and $^{137}_{55}\text{Cs}$. $^{131}_{53}\text{I}$ must be contained because the human thyroid gland concentrates iodide ions to make the hormone thyroxine. Once the isotope is in the gland, beta radiation from $^{131}_{53}\text{I}$ could cause harm, possibly thyroid cancer or impaired thyroid function. An effective countermeasure to $^{131}_{53}\text{I}$ poisoning is to take doses of ordinary iodine (as sodium iodide). Statistically, this increases the likelihood that the thyroid will take up the stable iodide ion rather than the radioactive anion of $^{131}_{53}\text{I}$. $^{137}_{55}\text{Cs}$ and $^{90}_{38}\text{Sr}$ also pose problems to humans. Caesium is in group 1 together with sodium, so radiating $^{137}_{55}\text{Cs}$ cations can travel to some of the same places in the body where sodium ions are concentrated. Strontium is in group 2 with calcium, so $^{90}_{38}\text{Sr}$ cations can replace calcium ions in bone tissue, sending radiation into bone marrow and possibly causing leukaemia. The half-lives of $^{137}_{55}\text{Cs}$ and $^{38}_{90}\text{Sr}$, however, are relatively short. Some radionuclides in wastes are so long-lived that solid reactor wastes must be kept away from all human contact for tens of centuries, longer than any nation has ever yet endured. Probably the most intensively studied procedure for making solid radioactive wastes secure is to convert them to glass-like or rock-like solids and bury them deep within a rock stratum or in a mountain believed to be geologically stable with respect to earthquakes and volcanoes. There is no known way of making nuclear waste safe — we simply have to wait until it has undergone complete decay.

Nuclear Fusion

Fusion is a more attractive energy source than fission. Whereas fission occurs for only a few rare, extremely heavy nuclides, fusion is possible for abundant light nuclides such as ^{1}H. Moreover, some fusion reactions release more energy per unit mass than do fission reactions. For example, the fusion of two hydrogen isotopes, deuterium and tritium, releases 3.4×10^{8} kJ g^{-1}, compared with 8×10^{7} kJ g^{-1} released in the fission of ^{235}U. Another attractive feature of fusion reactions is that the product nuclides are usually stable, so smaller amounts of radioactive by-products result from fusion than from fission.

The major impediment to fusion reactions is that the reacting nuclei must have very high kinetic energies to overcome the electrical repulsion between positive particles. The fusion of two hydrogen nuclei has the lowest possible repulsion barrier because it involves two $Z = 1$ nuclei. Even so, this reaction requires kinetic energies equivalent to temperatures of 10^{7} K (the temperature at the core of the Sun) or greater. As Z increases, so does this energy requirement, and the fusion of two ^{12}C nuclei, for example, requires kinetic energies equivalent to a temperature of 10^{9} K. There are several ways to produce nuclei with enough kinetic energy to fuse. One method uses particle accelerators to generate small quantities of fast-moving nuclei. The characteristics of fusion reactions are studied with such accelerators, but the scale of fusion events in these experiments is too small to release useful amounts of energy. A second way to induce fusion uses the energy released in gravitational attraction to generate a temperature high enough to start the reaction. The Sun and other stars operate in this way. A third way is the fusion bomb, which uses a fission bomb to generate a temperature high enough for fusion. None of these provides a method for harnessing fusion as a practical source of power on Earth. However, much effort is currently being expended in initiating a useful fusion reaction by heating a plasma confined in a magnetic field. If successful, this method may harness fusion as a source of power. The technological problems are immense, however, because the fusing material must be confined to a volume small enough to generate high nuclear densities and many nuclear collisions. Because all materials vaporise at temperatures well below that required to sustain fusion reactions, containers that would withstand sustained fusion cannot be built. The approach most often taken to address these problems is to use a hot, ionised plasma that contains cations of ^{2}H, ^{3}H and ^{6}Li, along with enough electrons to maintain charge neutrality. This plasma is heated intensely, usually by powerful laser beams. To keep the plasma from flying apart, it is confined by a doughnut-shaped magnetic field in an apparatus called a tokamak. Figure 27.23 shows a diagram of such a magnetic field and a photo of a prototype that is in operation in the USA.



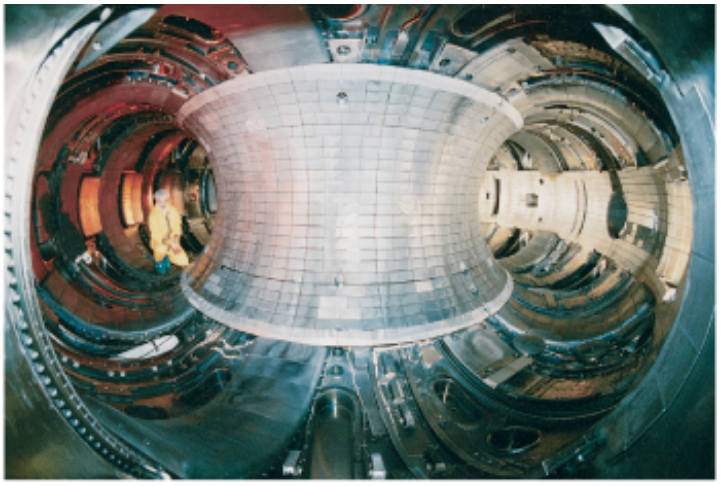


FIGURE 27.23 The tokamak is a version of a fusion reactor that has been the subject of intense development efforts. The design and an experimental prototype of the tokamak are shown here.US Department of Energy

Fusion cannot become a practical source of energy unless the energy released exceeds the energy used to heat and confine the plasma. Unfortunately, the energy input requirement is enormous, even in small-scale experimental studies. The best experiments conducted so far have managed to achieve fusion but not sustain it long enough to achieve any net production of energy. Assuming that a sustained fusion reaction is achieved, some way must be found to harness its energy output. Because the field confining the plasma prevents the escape of charged particles, most of the energy output of the reactor is expected to be photons, ranging in energy from infrared rays to γ rays. These photons will have to be absorbed by a suitable material that converts their energy, directly or indirectly, into electricity. Currently, a full-scale experimental fusion reactor called ITER (International Thermonuclear Experimental Reactor) is under construction in Cadarache, France, with completion expected in 2017 and the first plasma to be generated in 2019. This will use tokamak technology and will attempt to demonstrate the viability of commercial electricity production from fusion. There are enormous practical difficulties to be overcome before fusion can be used as an energy source, and, even if this experimental reactor proves to be successful, it is estimated that commercial fusion reactors would not become operational until at least the year 2050.

Nuclear Medicine

As we have seen, many radioisotopes are extremely hazardous to human health. Despite this, radioisotopes are now widely used in medicine, both as diagnostic aids and as treatments. As a diagnostic tool, nuclear decomposition allows doctors to examine internal organs by noninvasive procedures. Although X-rays are good for forming images of bones and teeth, most soft tissue organs are transparent to X-rays. For these organs, γ rays resulting from nuclear decay can be used to produce images. Like an X-ray film, a γ-ray image reveals abnormalities, allowing physicians to diagnose ailments of the heart, spleen, liver, brain and other vital organs.

Radioactive tracers for medical imaging are designed to concentrate in specific organs. For example, glucose can be labelled with ^{11}C, a positron emitter, for use in positron emission tomography (PET), a very useful technique for monitoring brain function. A PET scan detects situations where glucose is not taken up normally, e.g. in bipolar disorder, schizophrenia and Alzheimer's disease. After the ^{11}C-labelled glucose is ingested, radiation detectors outside the body pick up the annihilation radiation of positron emission specifically from those brain sites that use glucose. PET scan technology, for example, has shown that the uptake of glucose by a brain containing nicotine is less than that of a normal brain, suggesting that smokers cannot get as much glucose into the brain as nonsmokers (figure 27.24).

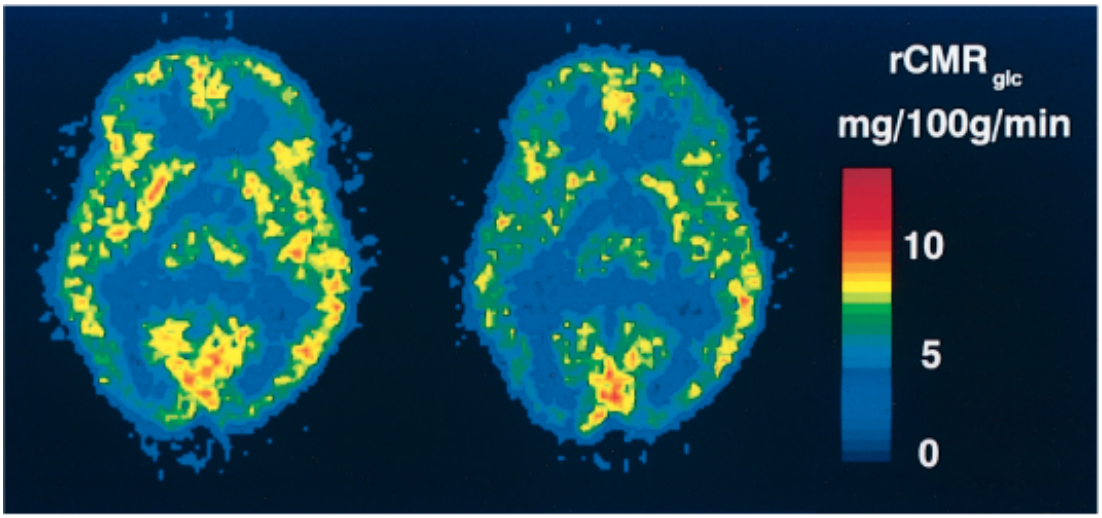


FIGURE 27.24 Positron emission tomography (PET) in the study of brain activity: (left) nonsmoker, (right) smoker. The colours are related to the degree of uptake of glucose, with red being the highest and blue the lowest. The PET scan reveals widespread reduction in the rate of glucose metabolism when nicotine is present. (Photos courtesy of E.D. London, National Institute of Drug Abuse); ED London, National Institute of Drug Abuse

Other examples of radionuclides that are useful for targeting specific organs include ^{52}Fe for bone marrow scans, ^{133}Xe for studying lung functions and ^{131}I for the thyroid gland. Probably the most important diagnostic radioisotope in use today is the technetium isotope ^{99m}Tc. This is a metastable isotope, meaning that the nucleus is in a high-energy state and decays by emission of a γ ray to give the ground state ^{99}Tc nuclide with a half-life of about 6 hours. ^{99m}Tc has near-perfect properties for medical imaging. First, it emits γ rays of moderate energy that are easy to detect but are not highly damaging to living tissue. Second, although technetium is not normally found in the body, the element can be bound to many chemical species called tracers that the body recognises and processes, thereby allowing targeting of specific organs. Third, the isotope decomposes at a rate that is slow enough to deliver tracers containing ^{99m}Tc to the body and generate an image, but fast enough to minimise long-term effects of γ radiation. About 95% of the ^{99m}Tc administered for a medical scan decomposes within the first 24 hours after introduction into the body.

Because exposure to radiation is a health risk, the administration of radioactive isotopes must be monitored and controlled carefully. Isotopes that emit alpha or beta particles are not used for imaging because these radiations cause substantial tissue damage. Specificity for a target organ is essential so that the amount of radioactive material can be kept as low as possible. In addition, an isotope for medical imaging must have a decay rate that is slow enough to allow time to make and administer the tracer compound yet fast enough to rid the body of radioactivity in as short a time as possible.

Radioactivity is also used to treat certain cancers that respond particularly well to radiation therapy. The key to radiation therapy is that cancer cells reproduce more rapidly than normal cells, and rapidly reproducing cells are more sensitive to radiation. If concentrated doses of radiation are focused on the malignant cells, a cancer may be destroyed with minimal damage to healthy tissue. Thyroid cancers are often treated with radioactive iodine because the thyroid gland preferentially absorbs iodine. If a patient is treated with ^{131}I, the β emissions from this isotope are concentrated in the gland, destroying cancerous cells more rapidly than normal cells. At the correct dosage, the cancer may be eliminated without destroying the healthy part of the thyroid gland. In an alternative approach, a metal wire of radioactive ^{197}Ir is implanted within the target area through a catheter. The wire implant is removed after the correct dose of radiation has been administered. The radioactive source need not always be introduced into the body. Inoperable brain tumours can be treated with γ rays from an external source, usually a sample of ^{60}Co, which can be focused on the tumour,

thereby minimising damage to surrounding healthy tissue.

Chemical Connections

Radiopharmaceuticals

Although we usually think of radioactive substances as being harmful to health, a number of radioactive isotopes have found extensive use in both the treatment and diagnosis of a variety of medical conditions. In therapeutic nuclear medicine, radiopharmaceuticals are introduced to the body to target tumour cells. The radiopharmaceuticals used usually emit beta particles, which can kill cancer cells.

In diagnostic nuclear medicine, the patient is injected with a small quantity of a radioisotope, and the pattern of radiation (gamma rays) emitted from within their body is then recorded by a gamma camera. To create the desired image, the injected isotope must be targeted to the organ of interest. This is often done by incorporating the isotope into a molecule that is taken up preferentially by that organ. For example, glucose, which is used by nerve cells for energy, is tagged with a radioisotope for studies of the brain. Two isotopes of iodine, ^{123}I and ^{131}I, can be incorporated by the thyroid gland simply as iodide ions, and so allow both imaging and treatment of thyroid disorders.

Nuclear medicine imaging creates an image of the activity of the organ of interest, rather than just the anatomy. Because of this, any unusual activity, such as that produced by the presence of cancer cells, can be detected by the presence of a ‘hot spot’ or ‘cold spot’ on the image produced (see figure 27.25). In fact, nuclear medicine imaging can detect cancer, heart disease and other medical conditions much earlier than some other imaging techniques such as CT scans. Most of the radioisotopes used in diagnostic imaging in Australia are produced by the Lucas Heights reactor. It is expected that, on average, most Australians will need at least one nuclear medicine procedure in their lifetime.

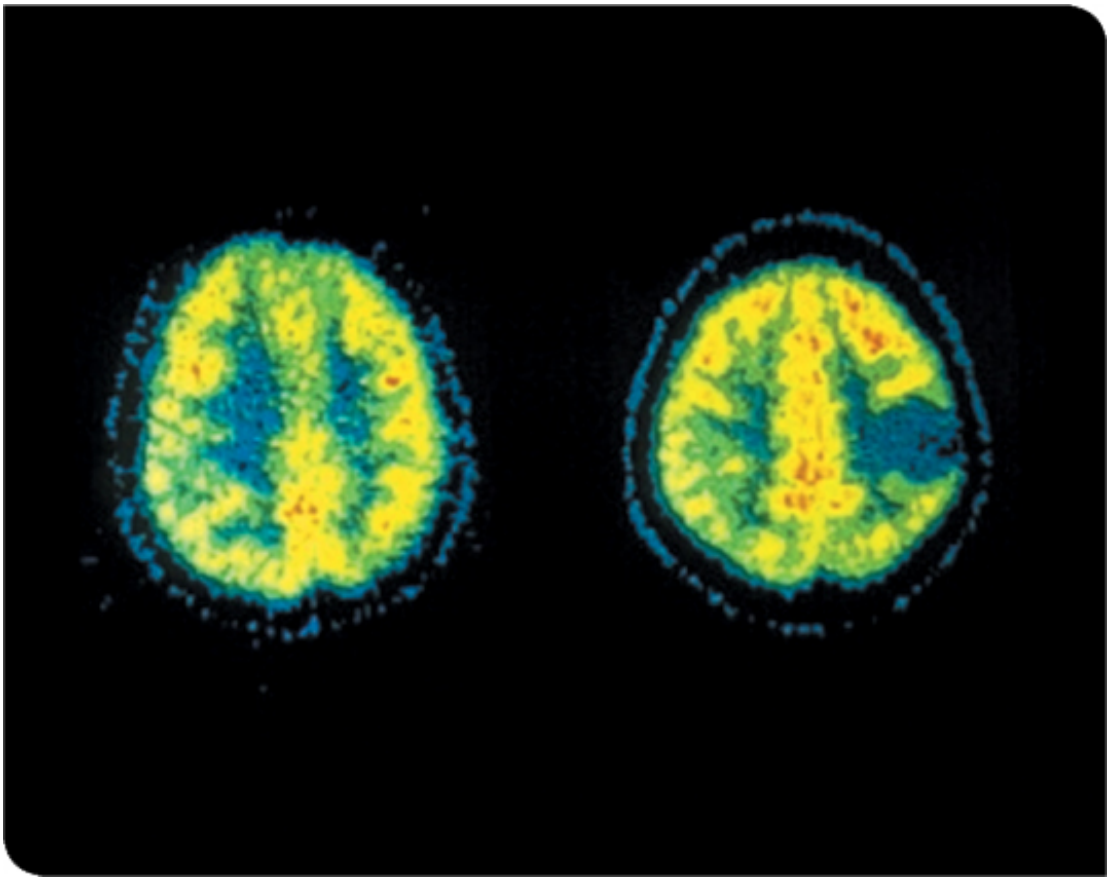


FIGURE 27.25 Coloured positron emission tomography (PET) scan of a healthy brain (left) and one affected by a tumour (right). The cerebral hemispheres of the healthy brain show a regular yellow band. The tumour appears blue ('cold spot') within the yellow band. It shows low blood supply because of tissue damage or tissue death at the tumour.SPL/National Cancer Institute

The most widely used radioisotope is the metastable technetium isotope ^{99m}Tc, which can be used to image the lungs, brain, kidneys, heart, lymph nodes and bones, on coordination to suitable ligands. It is also used in combination with an antimony–sulfur colloid in sentinel node imaging, a process that can identify the first lymph node that receives lymphatic flow from the breast, thereby reducing the need for the extensive removal of lymph nodes in cases of breast cancer.

The ^{13}N and ^{18}F isotopes are being used increasingly in positron emission tomography and ^{18}F is particularly useful in cancer diagnosis. Cancer cells rely on a process called glycolysis for their energy, rather than the Krebs cycle used by normal cells. ^{18}F-labelled deoxyglucose is incorporated into the Krebs cycle and can therefore be used as an index of cancer activity.

While many diagnostic procedures involving radioactive isotopes involve some type of imaging, Australian physician Barry Marshall developed a simple breath test for the presence of *Helicobacter pylori* (the bacterium that causes peptic ulcers) which uses ^{14}C-labelled urea. As the bacterium rapidly converts urea to carbon dioxide and ammonia, the carbon dioxide is labelled with radioactive ^{14}C. The patient is administered with the labelled urea and, shortly afterwards, blows up a balloon. The presence of ^{14}C in the exhaled air confirms infection by the bacterium. For this and other work with *Helicobacter pylori*, Dr Marshall was awarded the Nobel Prize in physiology or medicine in 2005, along with his Australian co-worker Robin Warren.

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SUMMARY

Nuclear Stability

The stability of a particular nucleus is determined by its neutron to proton ratio. On a plot of number of neutrons versus number of protons, the stable nuclei lie in a band of stability in which the ratio increases from $^{4}_{2}\mathrm{He}$ (1.00) to $^{208}_{82}\mathrm{Pb}$ (1.54). The nucleus is held together by the strong nuclear force, which acts between protons and neutrons at extremely short distances. However, proton–proton repulsion increases as Z increases, and there are no stable nuclei beyond lead ($Z = 82$).

The sum of the masses of the constituent nucleons in a nucleus is always greater than the actual mass of the nucleus, as some mass is converted to energy on formation of the nucleus in a process called nuclear fusion. This mass difference, the mass defect, allows the nuclear binding energy to be calculated, which shows the substantial energies involved in the atomic nucleus. The nuclear binding energy divided by the mass number A gives the binding energy per nucleon, which measures how tightly each nucleon is bound to the nucleus. Using this criterion, it can be shown that the $^{68}_{28}\mathrm{Ni}$ nucleus is the most stable of all nuclei. Nuclei of greater Z would be expected to undergo nuclear fission, a break-up of the nucleus into smaller parts, to become more stable.

Nuclei having even numbers of both protons and neutrons are more likely to be stable than those having both odd numbers. Magic numbers of 2, 8, 20, 28, 50, 82 and 126 protons and/or neutrons also impart stability to the nucleus.

Unstable Nuclei

Unstable nuclei undergo radioactive decay to give nuclei with more favourable neutron to proton ratios. The processes available for such decay are alpha decay, beta decay, gamma decay, positron emission, neutron emission and electron capture, and these processes can be depicted by use of nuclear equations. Beta decay involves emission of a beta particle from the nucleus, gamma decay gives rise to gamma radiation, and positron emission results from ejection of a positron, the antimatter counterpart of the electron. Neutron emission and electron capture involve ejection of a neutron and capture of an orbital electron, respectively. Decay processes occur at different rates, which we can quantify by measuring the change in activity (measured in becquerels) over time. The law of radioactive decay states that:

$$\text{activity} = -\frac{\Delta N}{\Delta t} = kN$$

where k is the decay constant and ΔN is the change in the number of radioactive nuclei ($N_{\text{final}} - N_{\text{initial}}$) over the time interval Δt. Radio active decay is a first-order process, meaning that the half-life of a radioactive nucleus is independent of the amount of the nucleus present. When the product nucleus of radioactive decay is itself radioactive, a radioactive disintegration series can be formed, and four of these occur naturally.

Synthesis of New Elements

Transmutation occurs when one element is converted to another. This can occur through natural decay processes or can be induced by bombardment of nuclei with high-energy particles. Such bombardment can give rise to a compound nucleus that is short-lived and decays to give the product nucleus. All the transuranium elements (elements 93–118) have been prepared using these techniques.

Radioactive Dating Methods

Naturally occurring radionuclides can be used in radiological dating, and the $^{40}_{19}\mathrm{K}$ / $^{40}_{18}\mathrm{Ar}$ pair in particular have been used to date the Earth. $^{14}\mathrm{C}$ dating is widely used to date organic remains and relies on comparison of the $^{14}\mathrm{C}$: $^{12}\mathrm{C}$ ratio in the object of interest with the ratio in living objects. The

equation:

$$\ln\frac{r_0}{r_t} = (1.21 \times 10^{-4}\,\mathrm{yr}^{-1})t$$

is used to determine the age of the sample, where r_0 is the ^{14}C : ^{12}C ratio at the time of death and r_t is the current ratio.

Applications of Nuclear Processes

Nuclear fission was discovered in the 1930s. In this case, a fissile isotope undergoes decay following capture of a neutron to give smaller nuclei and the release of significant amounts of energy. Use of a critical mass of a fissile nucleus results in a chain reaction that eventually leads to an explosion. Nuclear power plants operate using the heat derived from nuclear fission reactions to produce steam that spins turbines and generates electricity. Nuclear fusion is a cleaner process than nuclear fission and involves the fusion of small nuclei to give larger nuclei. In contrast to fission, fusion cannot be easily induced and currently requires very high temperatures to be initiated. Radioactive isotopes are useful in nuclear medicine and can be used as both therapeutic and diagnostic reagents.

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KEY CONCEPTS AND EQUATIONS

Band of stability *(section 27.1)*

The band ascertains the stability of nuclei, and identifies the likely decay type from the ratio of neutrons to protons.

Magnitude of the nuclear binding energy *(section 27.1)*

This property allows comparison of the stability of nuclei.

Nuclear equations *(section 27.2)*

These reactions quantitatively describe nuclear reactions and relate amounts of nuclear reactants and products.

Law of radioactive decay *(section 27.2)*

The equation:

$$\text{activity} = -\frac{\Delta N}{\Delta t} = kN$$

relates activities, decay constants and the number of disintegrating atoms in a sample.

Half-life *(section 27.2)*

This property quantitatively measures the stability of any nucleus.

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REVIEW QUESTIONS

Nuclear Stability

27.1 Why isn't the sum of the masses of all nucleons in one nucleus equal to the mass of the actual nucleus?

27.2 What data are plotted and what criterion is used to identify the actual band in the band of stability?

27.3 Both ^{123}Ba and ^{140}Ba are radioactive, but which is more likely to have the longer half-life? Explain your answer.

27.4 ^{112}Sn is a stable nuclide but ^{112}In is radioactive and has a very short half-life $(t_{\frac{1}{2}} = 15\,\text{min})$. What does ^{112}Sn have that ^{112}In does not to account for this difference in stability?

27.5 ^{139}La is a stable nuclide but ^{140}La is unstable $(t_{\frac{1}{2}} = 40\,\text{h})$. What rule of thumb concerning nuclear stability explains this?

27.6 As the atomic number increases, the neutron : proton ratio increases. What does this suggest is a factor in nuclear stability?

27.7 Although ^{164}Pb has two magic numbers, 82 protons and 82 neutrons, it is unknown. ^{208}Pb, however, is known and stable. What problem accounts for the nonexistence of ^{164}Pb?

Unstable Nuclei

27.8 Three kinds of radiation make up nearly all of the radiation observed from naturally occurring radionuclides. What are they?

27.9 Give the composition of each of the following.

(a) alpha particle

(b) beta particle

(c) positron

27.10 Why is the penetrating ability of alpha radiation less than that of beta or gamma radiation?

27.11 What decay particle is emitted from a nucleus of low to intermediate atomic number but a relatively high neutron : proton ratio? How does the emission of this particle benefit the nucleus?

27.12 What decay particle is emitted from a nucleus of low to intermediate atomic number but a relatively low neutron : proton ratio? How does the emission of this particle benefit the nucleus?

27.13 What does electron capture do to the neutron : proton ratio in a nucleus: increase it, decrease it or leave it unchanged? Which kinds of radionuclides are more likely to undergo electron capture: those above or those below the band of stability?

27.14 What is the most probable decay process for silicon-32? Write the balanced nuclear equation.

Synthesis of New Elements

27.15 Compound nuclei form and decay almost at once. What accounts for the instability of a compound nucleus?

27.16 Rutherford theorised that a compound nucleus forms when helium nuclei hit ^{14}N nuclei. If this compound nucleus decayed by the loss of a neutron instead of a proton, what would the other product be?

27.17 Why is it easier to use neutrons to form compound nuclei rather than alpha particles or other nuclei?

Radioactive Dating Methods

27.18

If a sample used for ^{14}C dating is contaminated by air, there is a potentially serious problem with the method. What is it?

27.19 An archaeologist discovers a new site where small pieces of charcoal are mixed with human remains. Burning a small sample of this charcoal gives gaseous CO_2 that, when placed in a counter, registers 1.75 decays per second. When an equal mass of CO_2 from fresh charcoal is placed in this counter, the count rate is 3.85 decays per second. How old is the archaeological site?

Applications of Nuclear Processes

27.20 Why should a radionuclide used in medical diagnostic work have a short half-life? If the half-life is too short, what problem arises?

27.21 An alpha emitter is not used in medical diagnostic work. Why?

27.22 Why is it easier for a nucleus to capture a neutron than a proton?

27.23 What does each of the following terms mean?

(a) thermal neutron

(b) nuclear fission

(c) fissile isotope

27.24 Which fissile isotope occurs in nature?

27.25 What fact about the fission of ^{235}U makes it possible for a chain reaction to occur?

27.26 Explain in general terms why fission generates more neutrons than needed to initiate it.

27.27 Why would there be a subcritical mass of a fissile isotope? (Why isn't any mass of ^{235}U critical?)

27.28 What purpose is served by a moderator in a nuclear reactor?

27.29 Why is there no possibility of an atomic bomb-like explosion from a nuclear power plant?

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REVIEW PROBLEMS

27.30 Calculate the binding energy in J of the following nuclei.

(a) deuterium nucleus (mass = 2.0135 u)

(b) tritium nucleus (mass = 3.015 50 u)

27.31 Complete the following nuclear equations by writing the symbols of the missing particles.

(a) $^{211}_{82}\text{Pb} \rightarrow {}^{0}_{-1}\text{e} + ____$

(b) $^{177}_{73}\text{Ta} \xrightarrow{\text{electron capture}} ____$

(c) $^{220}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + ____$

(d) $^{19}_{10}\text{Ne} \rightarrow {}^{0}_{1}\text{e} + ____$

(e) $^{245}_{96}\text{Cm} \rightarrow {}^{4}_{2}\text{He} + ____$

(f) $^{146}_{56}\text{Ba} \rightarrow {}^{0}_{-1}\text{e} + ____$

(g) $^{58}_{29}\text{Cu} \rightarrow {}^{0}_{1}\text{e} + ____$

(h) $^{68}_{32}\text{Ge} \xrightarrow{\text{electron capture}} ____$

27.32 Write a balanced nuclear equation for each of the following changes.

(a) alpha emission by ^{242}Pu

(b) beta emission by ^{28}Mg

(c) positron emission by ^{26}Si

(d) electron capture by ^{37}Ar

(e) electron capture by ^{55}Fe

(f) beta emission by ^{42}K

(g) positron emission by ^{93}Ru

(h) alpha emission by ^{251}Cf

27.33 Write the symbols, including the atomic and mass numbers, for the radionuclides that would give each of the following products.

(a) ^{257}Fm by alpha emission

(b) ^{211}Bi by beta emission

(c) ^{141}Nd by positron emission

(d) ^{179}Ta by electron capture

27.34 Each of the following nuclides forms by the decay mode described. Write the symbols of the parents, giving both atomic and mass numbers.

(a) ^{80}Rb formed by electron capture

(b) ^{121}Sb formed by beta emission

(c) ^{50}Cr formed by positron emission

(d) ^{253}Cf formed by alpha emission

27.35 ^{87}Kr decays to ^{86}Kr. What other particle forms?

27.36 Write the symbol of the nuclide that forms from ^{58}Co when it decays by electron capture.

27.37 If an atom of ^{38}K had the option of decaying by positron emission or beta emission, which route would it more likely take, and why? Write the nuclear equation.

27.38 Suppose that an atom of ^{37}Ar could decay by either beta emission or electron capture. Which route would it more likely take, and why? Write the nuclear equation.

27.39 If we begin with 3.00 mg of ^{131}I $(t_{\frac{1}{2}} = 8.03\,h)$, how much remains after six half-life periods?

27.40 Smoke detectors contain a small amount of ^{241}Am, which has a half-life of 432.6 years. If the detector contains 0.20 mg of ^{241}Am, what is the activity, in becquerels?

27.41 ^{90}Sr is a dangerous radioisotope present in fallout produced by nuclear weapons. It has a half-life of 28.9 years. What is the activity of 1.00 g of ^{90}Sr, in becquerels?

27.42 ^{131}I is a radioisotope present in radioactive fallout that targets the thyroid gland. If 1.00 mg of ^{131}I has an activity of 4.6×10^{12} Bq, what is the decay constant for ^{131}I? What is the half-life, in seconds?

27.43 A 10.0 mg sample of ^{201}Tl has an activity of 7.9×10^{13} Bq. What is the decay constant for ^{201}Tl? What is the half-life of ^{201}Tl, in seconds?

27.44 When ^{51}V captures a deuteron, $^{2}_{1}H$ what compound nucleus forms? (Write its symbol.) This particle expels a proton, $^{1}_{1}p$. Write the nuclear equation for the overall change from ^{51}V.

27.45 The alpha-particle bombardment of ^{19}F generates ^{22}Na and neutrons. Write the nuclear equation, including the intermediate compound nucleus.

27.46 Gamma-ray bombardment of ^{81}Br causes a transmutation in which neutrons are one product. Write the symbol of the other product.

27.47 Neutron bombardment of ^{115}Cd results in neutron capture and the release of gamma radiation. Write the nuclear equation.

27.48 When ^{55}Mn is bombarded by protons, neutrons are released. What else forms? Write the nuclear equation.

27.49 Which nuclide forms when ^{23}Na is bombarded by alpha particles and the compound nucleus emits a gamma-ray photon?

27.50 The nuclei of which isotope of zinc would be needed as bombardment particles to make nuclei of element 112 from ^{208}Pb if the intermediate compound nucleus loses a neutron?

27.51 A tree killed by being buried under volcanic ash was found to have a ratio of ^{14}C atoms to ^{12}C atoms of 4.8×10^{-14}. How long ago did the eruption occur?

27.52 A wooden door lintel from an archaeological excavation would be expected to have what ratio of ^{14}C to ^{12}C atoms if the lintel is 9.0×10^{3} years old?

27.53 Complete the following nuclear equation by supplying the symbol for the other product of the fission.

$$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{94}_{38}Sr + ___ + 2{}^{1}_{0}n$$

27.54 Both products of the fission in question 27.53 are unstable. According to figures 27.1 and 27.5, what is the most likely way for each of them to decay: by alpha emission, beta emission or positron emission? Explain. What are some of the possible fates of the extra neutrons produced by the fission shown in question 27.53?

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ADDITIONAL EXERCISES

27.55 What is the nuclear equation for each of the following changes?

(a) beta emission by ^{30}Al

(b) alpha emission by ^{252}Es

(c) electron capture by ^{93}Mo

(d) positron emission by ^{28}P

27.56 Calculate the binding energy (J per nucleon) of the nucleus of an atom of ^{56}Fe. The observed mass of one atom is 55.9349 u.

27.57 Calculate the binding energy (J per nucleon) of ^{235}U. The observed mass of one atom is 235.0439 u.

27.58 Give the nuclear equation for each of the following changes.

(a) positron emission by ^{10}C

(b) alpha emission by ^{243}Cm

(c) electron capture by ^{49}V

(d) beta emission by ^{20}O

27.59 If a positron is to be emitted spontaneously, how much more mass (as a minimum) must an atom of the parent have than an atom of the daughter nuclide? Explain.

27.60 There is a gain in binding energy per nucleon when light nuclei fuse to form heavier nuclei. Yet, a tritium atom and a deuterium atom, in a mixture of these isotopes, do not spontaneously fuse to give helium (and energy). Explain why not.

27.61 The ^{14}C content of an ancient piece of wood was found to be one-eighth of that in living trees. How many years old is this piece of wood $(t_{\frac{1}{2}} = 5730\,\text{yr for } ^{14}C)$?

27.62 Dinitrogen trioxide, N_2O_3, is largely dissociated into NO and NO_2 in the gas phase, where the following equilibrium exists:

$$N_2O_3 \rightleftharpoons NO + NO_2$$

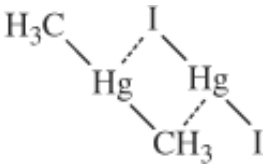
To determine the structure of N_2O_3, a mixture of NO and $*NO_2$ was prepared, containing isotopically labelled *N in the NO_2. After a period of time, the mixture was analysed and found to contain substantial amounts of both *NO and $*NO_2$. Explain how this is consistent with the structure for N_2O_3 being ONONO.

27.63 Which element has the largest binding energy per nucleon? What happens to the nuclei when the binding energy is too small?

27.64 Which is more dangerous: ingesting a radioactive compound with a short half-life or a radioactive compound with a long half-life if the compound can be eliminated from the body within a day?

27.65 The age of 'young' groundwater can be determined by measuring the ratio of tritium to ^3He in water. If 'young' groundwater is no more than 40 years old, what percent of tritium remains in water after 40 years? The amount of ^3He in the water is measured at the same time as the amount of tritium. What would the sum of the amounts of tritium and ^3He represent?

27.66 The reaction $(CH_3)_2Hg + HgI_2 \rightarrow 2CH_3HgI$ is believed to occur through a transition state with the structure:



If this is so, what should be observed if CH_3HgI and $*HgI_2$ are mixed, where the asterisk denotes a radioactive isotope of Hg? Explain your answer.

27.67 A large, complex piece of apparatus has a cooling system built into it containing an unknown volume of cooling liquid. It is desired to measure the volume of the coolant without draining the lines. To the coolant was added 10.0 mL of ^{14}C-labelled methanol. Its specific activity was 580 counts per minute per gram (cpm g^{-1}), as determined using a Geiger counter. The coolant was permitted to circulate to ensure complete mixing. A sample was then withdrawn and found to have a specific activity of 29 cpm g^{-1}. Calculate the volume of coolant in the system in millilitres. The density of methanol is 0.792 g mL^{-1}, and the density of the coolant is 0.884 g mL^{-1}.

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EPILOGUE

We have reached the end of our chemistry journey. We began this book by looking at the constituents of the atom and showing how we could order all 118 different types of atoms on the basis of their atomic number to give the periodic table. We have looked in depth at the structure of the atom, and how and why atoms come together to form molecules. We have shown that all matter exists as a solid, liquid or gas under defined conditions, and we have discussed the factors that determine which of these three phases a substance will adopt. The power of thermodynamics to predict the preferred direction of chemical change was discussed and we also looked at chemical equilibrium and the speed of chemical change. We then turned our attention to different areas of the periodic table, with particular emphasis on the transition metals and the *p*-block elements. We looked extensively at the chemistry of carbon, and organic chemistry in general, focusing on the reactivity of organic molecules, and some of the ways in which we could determine the structures of such molecules. After some discussion of important biological molecules, we eventually found ourselves back where we started, at the atom, and particularly its nucleus.

It is appropriate that the last section of the book concentrated on the applications of chemistry to human life. Our way of life owes an enormous amount to chemistry and the advances made in this science in the future will, to a significant extent, determine the nature of our world in years to come. Given the importance of chemistry, it is, in our view, vital that as many people as possible have at least a working knowledge of the subject, and we have aimed to impart just such a working knowledge to you over the past 27 chapters. Of course, what is contained within this textbook is by no means all of chemistry; those of you who will continue on in the subject will find a wealth of material that we have barely touched on, if at all. But we have presented you with the basics which underpin both this science, and many others.

All we can do within the context of a textbook is provide you with the material and explain it in (what we hope is) a comprehensible way. It's up to you to learn and understand it. In this, we wish you all the best.

Good luck!

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KEY TERMS

activity
alpha particle
antimatter
band of stability
becquerel (Bq)
beta particle
binding energy per nucleon
compound nucleus
critical mass
decay constant k
electron capture
fissile isotope
gamma radiation
half-life $(t_{\frac{1}{2}})$
law of radioactive decay
magic numbers
mass defect
neutron emission
nuclear binding energy
nuclear equation
nuclear fission
Nuclear fusion
positron
radioactive decay
radioactive disintegration series
radiological dating
strong nuclear force
transmutation
transuranium elements

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Appendix A
Thermodynamic Data for Selected Elements, Compounds and Ions (25 °C)

Substance	$\Delta_f H^\ominus \left(\mathrm{kJ\,mol^{-1}}\right)$	$S^\ominus \left(\mathrm{J\,mol^{-1}\,K^{-1}}\right)$	$\Delta_f G^\ominus \left(\mathrm{kJ\,mol^{-1}}\right)$
Aluminium			
Al(s)	0	28.3	0
Al^{3+}(aq)	-524.7		-481.2
$AlCl_3$(s)	-704	110.7	-629
Al_2O_3(s)	-1669.8	51.0	-1576.4
$Al_2(SO_4)_3$(s)	-3441	239	-3100
Arsenic			
As(s)	0	35.1	0
AsH_3(g)	+66.4	223	+68.9
As_4O_6(s)	-1314	214	-1153
As_2O_5(s)	-925	105	-782
H_3AsO_3(aq)	-742.2		
H_3AsO_4(aq)	-902.5		
Barium			
Ba(s)	0	66.9	0
Ba^{2+}(aq)	-537.6	9.6	-560.8
$BaCO_3$(s)	-1219	112	-1139
$BaCrO_4$(s)	-1428.0	159	-1345
$BaCl_2$(s)	-860.2	125	-810.8
BaO(s)	-553.5	70.4	-525.1
$Ba(OH)_2$(s)	-998.22	-8	-875.3
$Ba(NO_3)_2$(s)	-992	214	-795
$BaSO_4$(s)	-1465	132	-1353
Beryllium			
Be(s)	0	9.50	0
$BeCl_2$(s)	-468.6	89.9	-426.3
BeO(s)	-611	14	-582
Bismuth			
Bi(s)	0	56.9	0
$BiCl_3$(s)	-379	177	-315

$Bi_2O_3(s)$	-576	151	-497
Boron			
B(s)	0	5.87	0
$BCl_3(g)$	-404	290	-389
$B_2H_6(g)$	+36	232	+87
$B_2O_3(s)$	-1273	53.8	-1194
$B(OH)_3(s)$	-1094	88.8	-969
Bromine			
$Br_2(l)$	0	152.2	0
$Br_2(g)$	+30.9	245.4	3.11
HBr(g)	-36	198.5	53.1
$Br^-(aq)$	-121.55	82.4	-103.96
Cadmium			
Cd(s)	0	51.8	0
$Cd^{2+}(aq)$	-75.90	-73.2	-77.61
$CdCl_2(s)$	-392	115	-344
CdO(s)	-258.2	54.8	-228.4
CdS(s)	-162	64.9	-156
$CdSO_4(s)$	-933.5	123	-822.6
Calcium			
Ca(s)	0	41.4	0
$Ca^{2+}(aq)$	-542.83	-53.1	-553.58
$CaCO_3(s)$	-1207	92.9	-1128.8
$CaF_2(s)$	-741	80.3	-1166
$CaCl_2(s)$	-795.0	114	-750.2
$CaBr_2(s)$	-682.8	130	-663.6
$CaI_2(s)$	-535.9	143	-529
CaO(s)	-635.5	40	-604.2
$Ca(OH)_2(s)$	-986.59	76.1	-896.76
$Ca_3(PO_4)_2(s)$	-4119	241	-3852
$CaSO_3(s)$	-1156		
$CaSO_4(s)$	-1432.7	107	-1320.3
$CaSO_4 \cdot \frac{1}{2}H_2O(s)$	-1575.2	131	-1435.2
	-2021.1	194.0	-1795.7

$CaSO_4 \cdot 2H_2O(s)$			
Carbon			
C(*s*, graphite)	0	5.69	0
C(*s*, diamond)	+1.88	2.4	+2.9
$CCl_4(l)$	-134	214.4	-65.3
$CHCl_3(g)$	-82.0	234.2	-58.6
CO(g)	-110.5	197.9	-137.3
$CO_2(g)$	-394	213.6	-394.4
$CO_2(aq)$	-413.8	117.6	-385.98
$H_2CO_3(aq)$	-699.65	187.4	-623.08
$HCO_3^-(aq)$	-691.99	91.2	-586.77
$CO_3^{2-}(aq)$	-677.14	-56.9	-527.81
$CS_2(l)$	+89.5	151.3	+65.3
$CS_2(g)$	+115.3	237.7	+67.2
HCN(g)	+135.1	201.7	+124.7
$CN^-(aq)$	+150.6	94.1	+172.4
$CH_4(g)$	-74.848	186.2	-50.79
$C_2H_4(g)$	+226.75	200.8	+209
$C_2H_4(g)$	+51.9	219.8	+68.12
$C_2H_6(g)$	-84.667	229.5	-32.9
$C_2H_8(g)$	-104	269.9	-23
$C_4H_{10}(g)$	-126	310.2	-17.0
$C_6H_6(l)$	+49.0	173.3	+124.3
$CH_3OH(l)$	-238.6	126.8	-166.2
$C_2H_5OH(l)$	-277.63	161	-174.8
HCOOH(g)	-363	251	+335
$CH_3COOH(l)$	-487.0	160	-392.5
HCHO(g)	-108.6	218.8	-102.5
$CH_3CHO(g)$	-167	250	-129
$(CH_3)_2CO(l)$	-248.1	200.4	-155.4
$C_6H_5CO_2H(s)$	-385.1	167.6	-245.3
$CO(NH_2)_2(s)$	-333.19	104.6	-197.2
$CO(NH_2)_2(aq)$	-319.2	173.8	-203.8
	-532.9	103.5	-373.4

$CH_2(NH_2)CO_2H(s)$			
Chlorine			
$Cl_2(g)$	0	223.0	0
$Cl^-(aq)$	-167.2	56.5	-131.2
HCl(g)	-92.30	186.7	-95.27
HCl(aq)	-167.2	56.5	-131.2
HClO(aq)	-131.3	106.8	-80.21
Chromium			
Cr(s)	0	23.8	0
$Cr^{3+}(aq)$	-232		
$CrCl_2(s)$	-326	115	-282
$CrCl_3(s)$	-563.2	126	-493.7
$Cr_2O_3(s)$	-1141	81.2	-1059
$CrO_3(s)$	-585.8	72.0	-506.2
$(NH_4)_2Cr_2O_7(s)$	-1807		
$K_2Cr_2O_7(s)$	-2033.01	291	-1882
Cobalt			
Co(s)	0	30.0	0
$Co^{2+}(aq)$	-59.4	-110	-53.6
$CoCl_2(s)$	-325.5	106	-282.4
$Co(NO_3)_2(s)$	-422.2	192	-230.5
CoO(s)	-237.9	53.0	-214.2
CoS(s)	-80.8	67.4	-82.8
Copper			
Cu(s)	0	33.15	0
$Cu^{2+}(aq)$	+64.77	-99.6	+65.49
CuCl(s)	-137.2	86.2	-119.87
$CuCl_2(s)$	-172	119	-131
$Cu_2O(s)$	-168.6	93.1	-146.0
CuO(s)	-155.25	42.6	-127
$Cu_2S(s)$	-79.5	121	-86.2
CuS(s)	-53.1	66.5	-53.6
$CuSO_4(s)$	-771.4	109	-661.8
$CuSO_4 \cdot 5H_2O(s)$	-2279.7	300.4	-1879.7

Fluorine			
$F_2(g)$	0	202.7	0
$F^-(aq)$	-332.6	-13.8	-278.8
HF(g)	-271	173.5	-273
Gold			
Au(s)	0	47.7	0
$Au_2O_3(s)$	+80.8	125	+163
$AuCl_3(s)$	-118	148	-48.5
Hydrogen			
$H_2(g)$	0	130.6	0
$H_2O(l)$	-285.9	69.96	-237.2
$H_2O(g)$	-241.8	188.7	-228.6
$H_2O_2(l)$	-187.6	109.6	-120.3
$H_2Se(g)$	+76	219	+62.3
$H_2Te(g)$	+154	234	+138
Iodine			
$I_2(s)$	0	116.1	0
$I_2(g)$	+62.4	260.7	+19.3
HI(g)	+26.6	206	+1.30
Iron			
Fe(s)	0	27	0
$Fe^{2+}(aq)$	-89.1	-137.7	-78.9
$Fe^{3+}(aq)$	-48.5	-315.9	-4.7
$Fe_2O_3(s)$	-822.3	90.0	-741.0
$Fe_3O_4(s)$	-1118.4	146.4	-1015.4
FeS(s)	-100.0	60.3	-100.4
$FeS_2(s)$	-178.2	52.9	-166.9
Lead			
Pb(s)	0	64.8	0
$Pb^{2+}(aq)$	-1.7	10.5	-24.4
$PbCl_2(s)$	-359.4	136	-314.1
PbO(s)	-219.2	67.8	-189.3
$PbO_2(s)$	-277	68.6	-219
$Pb(OH)_2(s)$	-515.9	88	-420.9

$PbS(s)$	-100	91.2	-98.7
$PbSO_4(s)$	-920.1	149	-811.3
Lithium			
$Li(s)$	0	28.4	0
$Li^+(aq)$	-278.6	10.3	
$LiF(s)$	-611.7	35.7	-583.3
$LiCl(s)$	-407.5	59.29	-383.7
$LiBr(s)$	-350.3	66.9	-338.87
$Li_2O(s)$	-596.5	37.9	-560.5
$Li_3N(s)$	-199	37.7	-155.4
Magnesium			
$Mg(s)$	0	32.5	0
$Mg^{2+}(aq)$	-466.9	-138.1	-454.8
$MgCO_3(s)$	-1113	65.7	-1029
$MgF_2(s)$	-1124	79.9	-1056
$MgCl_2(s)$	-641.8	89.5	-592.5
$MgCl_2 \cdot 2H_2O(s)$	-1280	180	-1118
$Mg_3N_2(s)$	-463.2	87.9	-411
$MgO(s)$	-601.7	26.9	-569.4
$Mg(OH)_2(s)$	-924.7	63.1	-833.9
Manganese			
$Mn(s)$	0	32.0	0
$Mn^{2+}(aq)$	-223	-74.9	-228
$MnO_4^-(aq)$	-542.7	191	-449.4
$KMnO_4(s)$	-813.4	171.71	-713.8
$MnO(s)$	-385	60.2	-363
$Mn_2O_3(s)$	-959.8	110	-882.0
$MnO_2(s)$	-520.9	53.1	-466.1
$Mn_3O_4(s)$	-1387	149	-1280
$MnSO_4(s)$	-1064	112	-956
Mercury			
$Hg(l)$	0	76.1	0
$Hg(g)$	+60.84	175	+31.8
$Hg_2Cl_2(s)$	-265.2	192.5	-210.8

$HgCl_2(s)$	-224.3	146.0	-178.6
$HgO(s)$	-90.83	70.3	-58.54
$HgS(s, red)$	-58.2	82.4	-50.6
Nickel			
$Ni(s)$	0	30	0
$NiCl_2(s)$	-305	97.5	-259
$NiO(s)$	-244	38	-216
$NiO_2(s)$			-199
$NiSO_4(s)$	-891.2	77.8	-773.6
$NiCO_3(s)$	-664.0	91.6	-615.0
$Ni(CO)_4(g)$	-220	399	-567.4
Nitrogen			
$N_2(g)$	0	191.5	0
$NH_3(g)$	-46.0	192.5	-16.7
$NH_4^+(aq)$	-132.5	113	-79.37
$N_2H_4(g)$	+95.40	238.4	+159.3
$N_2H_4(l)$	+50.6	121.2	+149.4
$NH_4Cl(s)$	-315.4	94.6	-203.9
$NO(g)$	+90.37	210.6	+86.69
$NO_2(g)$	+33.8	240.5	+51.84
$N_2O(g)$	+81.57	220.0	+103.6
$N_2O_4(g)$	+9.67	304	+98.28
$N_2O_5(g)$	+11	356	+115
$HNO_3(l)$	-173.2	155.6	-79.91
$NO_3^-(aq)$	-205.0	146.4	-108.74
Oxygen			
$O_2(g)$	0	205.0	0
$O_3(g)$	+143	238.8	+163
$OH^-(aq)$	-230.0	-10.75	-157.24
Phosphorus			
$P(s, white)$	0	41.09	0
$P_4(g)$	+314.6	163.2	+278.3
$PCl_3(g)$	-287.0	311.8	-267.8
	-374.9	364.6	-305.0

$PCl_5(g)$			
$PH_3(g)$	+5.4	210.2	+12.9
$P_4O_6(s)$	-1640		
$POCl_3(g)$	-1109.7	646.5	-1019
$POCl_3(l)$	-1186	26.36	-1035
$P_4O_{10}(s)$	-3062	228.9	-2698
$H_3PO_4(s)$	-1279	110.5	-1119
Potassium			
K(s)	0	64.18	0
$K^+(aq)$	-252.4	102.5	-283.3
KF(s)	-567.3	66.6	-537.8
KCl(s)	-435.89	82.59	-408.3
KBr(s)	-393.8	95.9	-380.7
KI(s)	-327.9	106.3	-324.9
KOH(s)	-424.8	78.9	-379.1
$K_2O(s)$	-361	98.3	-322
$K_2SO_4(s)$	-1433.7	176	-1316.4
Silicon			
Si(s)	0	19	0
$SiH_4(g)$	+33	205	+52.3
SiO_2(s, alpha)	-910.0	41.8	-856
Silver			
Ag(s)	0	42.55	0
$Ag^+(aq)$	+105.58	72.68	+77.11
AgCl(s)	-127.1	96.2	-109.7
AgBr(s)	-100.4	107.1	-96.9
$AgNO_3(s)$	-124	141	-32
$Ag_2O(s)$	-31.1	121.3	-11.2
Sodium			
Na(s)	0	51.0	0
$Na^+(aq)$	-240.12	59.0	-261.91
NaF(s)	-571	51.5	-545
NaCl(s)	-411.0	72.38	-384.0
NaBr(s)	-360	83.7	-349
NaI(s)	-288	91.2	-286

$NaHCO_3(s)$	-947.7	102	-851.9
$Na_2CO_3(s)$	-1131	136	-1048
$Na_2O_2(s)$	-510.9	94.6	-447.7
$Na_2O_2(s)$	-510	72.8	-376
NaOH(s)	-426.8	64.18	-382
$Na_2SO_4(s)$	-1384.5	149.4	-1266.83
Sulfur			
S(s, rhombic)	0	31.9	0
$SO_2(g)$	-296.9	248.5	-300.4
$SO_3(g)$	-395.2	256.2	-370.4
$H_2S(g)$	-20.15	206	-33.6
$H_2SO_4(l)$	-811.32	157	-689.9
$H_2SO_4(aq)$	-909.3	20.1	-744.5
$SF_6(g)$	-1209	292	-1105
Tin			
Sn(s, white)	0	51.6	0
$Sn^{2+}(aq)$	-8.8	-17	-27.2
$SnCl_4(l)$	-511.3	258.6	-440.2
SnO(s)	-285.8	56.5	-256.9
$SnO_2(s)$	-580.7	52.3	-519.6
Zinc			
Zn(s)	0	41.6	0
$Zn^{2+}(aq)$	-153.9	-112.1	-147.06
$ZnCl_2(s)$	-415.1	111	-369.4
ZnO(s)	-348.3	43.6	-318.3
ZnS(s)	-205.6	57.7	-201.3
$ZnSO_4(s)$	-982.8	120	-874.5

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Appendix B
Average Bond Enthalpies (25 °C)

Bond	Bond enthalpy (kJ mol^{-1})
C—C	348
C═C	612
C—C	960
C—H	412
C—N	305
C═N	613
C—N	890
C—O	360
C═O	743
C—F	484
C—Cl	338
C—Br	276
C—I	238
H—H	436
H—F	565
H—Cl	431
H—Br	366
H—I	299
H—N	388
H—O	463
H—S	338
H—Si	376

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Appendix C
Solubility Products (25 °C)

Salt	Solubility equilibrium	K_{sp}
Fluorides		
MgF_2	$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$	6.6×10^{-9}
CaF_2	$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$	3.9×10^{-11}
SrF_2	$SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2F^-(aq)$	2.9×10^{-9}
BaF_2	$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$	1.7×10^{-6}
LiF	$LiF(s) \rightleftharpoons Li^+(aq) + F^-(aq)$	1.7×10^{-3}
PbF_2	$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$	3.6×10^{-8}
Chlorides		
$CuCl$	$CuCl(s) \rightleftharpoons Cu^+(aq) + Cl^-(aq)$	1.9×10^{-7}
$AgCl$	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.8×10^{-10}
Hg_2Cl_2	$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq)$	1.2×10^{-18}
$TlCl$	$TlCl(s) \rightleftharpoons Tl^+(aq) + Cl^-(aq)$	1.8×10^{-4}
$PbCl_2$	$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$	1.7×10^{-5}
$AuCl^3$	$AuCl^3(s) \rightleftharpoons Au^{3+}(aq) + 3Cl^-(aq)$	3.2×10^{-25}
Bromides		
$CuBr$	$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$	5×10^{-9}
$AgBr$	$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$	5.0×10^{-13}
Hg_2Br_2	$Hg_2Br_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Br^-(aq)$	5.6×10^{-23}
$HgBr_2$	$HgBr_2(s) \rightleftharpoons Hg^{2+}(aq) + 2Br^-(aq)$	1.3×10^{-19}
$PbBr_2$	$PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$	2.1×10^{-6}
Iodides		
CuI	$CuI(s) \rightleftharpoons Cu^+(aq) + I^-(aq)$	1×10^{-12}
AgI	$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$	8.3×10^{-17}
Hg_2I_2	$Hg_2I_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2I^-(aq)$	4.7×10^{-29}
HgI_2	$HgI_2(s) \rightleftharpoons Hg^{2+}(aq) + 2I^-(aq)$	1.1×10^{-28}
PbI_2	$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$	7.9×10^{-9}
Hydroxides		

$Mg(OH)_2$	$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$	7.1×10^{-12}
$Ca(OH)_2$	$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$	6.5×10^{-6}
$Mn(OH)_2$	$Mn(OH)_2(s) \rightleftharpoons Mn^{2+}(aq) + 2OH^-(aq)$	1.6×10^{-13}
$Fe(OH)_2$	$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$	7.9×10^{-16}
$Fe(OH)_3$	$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$	1.6×10^{-39}
$Co(OH)_2$	$Co(OH)_2(s) \rightleftharpoons Co^{2+}(aq) + 2OH^-(aq)$	1×10^{-15}
$Co(OH)_3$	$Co(OH)_3(s) \rightleftharpoons Co^{3+}(aq) + 3OH^-(aq)$	3×10^{-45}
$Ni(OH)_2$	$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$	6×10^{-16}
$Cu(OH)_2$	$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$	4.8×10^{-20}
$V(OH)_3$	$V(OH)_3(s) \rightleftharpoons V^{3+}(aq) + 3OH^-(aq)$	4×10^{-35}
$Cr(OH)_3$	$Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3OH^-(aq)$	2×10^{-30}
$Zn(OH)_2$	$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$	3.0×10^{-16}
$Cd(OH)_2$	$Cd(OH)_2(s) \rightleftharpoons Cd^{2+}(aq) + 2OH^-(aq)$	5.0×10^{-15}
$Al(OH)_3$ (alpha form)	$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$	3×10^{-34}
Cyanides		
$AgCN$	$AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$	2.2×10^{-16}
$Zn(CN)_2$	$Zn(CN)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2CN^-(aq)$	3×10^{-16}
Sulfites		
$CaSO_3$	$CaSO_3(s) \rightleftharpoons Ca^{2+}(aq) + SO_3^{2-}(aq)$	3×10^{-7}
Ag_2SO_3	$Ag_2SO_3(s) \rightleftharpoons 2Ag^+(aq) + SO_3^{2-}(aq)$	1.5×10^{-14}
$BaSO_3$	$BaSO_3(s) \rightleftharpoons Ba^{2+}(aq) + SO_3^{2-}(aq)$	8×10^{-7}
Sulfates		
$CaSO_4$	$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$	2.4×10^{-5}
$SrSO_4$	$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq)$	3.2×10^{-7}
$BaSO_4$	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	1.1×10^{-10}
$RaSO_4$	$RaSO_4(s) \rightleftharpoons Ra^{2+}(aq) + SO_4^{2-}(aq)$	4.3×10^{-11}
Ag_2SO_4	$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$	1.5×10^{-5}
Hg_2SO_4	$Hg_2SO_4(s) \rightleftharpoons Hg_2^{2+}(aq) + SO_4^{2-}(aq)$	7.4×10^{-7}
$PbSO_4$	$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$	6.3×10^{-7}
Chromates		

$BaCrO_4$	$BaCrO_4(s) \rightleftharpoons Ba^{2+}(aq) + CrO_4^{2-}(aq)$	2.1×10^{-10}
$CuCrO_4$	$CuCrO_4(s) \rightleftharpoons Cu^{2+}(aq) + CrO_4^{2-}(aq)$	3.6×10^{-6}
Ag_2CrO_4	$Ag_2CrO_4(s) \rightleftharpoons 2Ag^{+}(aq) + CrO_4^{2-}(aq)$	1.2×10^{-12}
Hg_2CrO_4	$Hg_2CrO_4(s) \rightleftharpoons Hg_2^{2+}(aq) + CrO_4^{2-}(aq)$	2.0×10^{-9}
$CaCrO_4$	$CaCrO_4(s) \rightleftharpoons Ca^{2+}(aq) + CrO_4^{2-}(aq)$	7.1×10^{-4}
$PbCrO_4$	$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$	1.8×10^{-14}
Carbonates		
$MgCO_3$	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	3.5×10^{-8}
$CaCO_3$	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	4.5×10^{-9}
$SrCO_3$	$SrCO_3(s) \rightleftharpoons Sr^{2+}(aq) + CO_3^{2-}(aq)$	9.3×10^{-10}
$BaCO_3$	$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$	5.0×10^{-9}
$MnCO_3$	$MnCO_3(s) \rightleftharpoons Mn^{2+}(aq) + CO_3^{2-}(aq)$	5.0×10^{-10}
$FeCO_3$	$FeCO_3(s) \rightleftharpoons Fe^{2+}(aq) + CO_3^{2-}(aq)$	2.1×10^{-11}
$CoCO_3$	$CoCO_3(s) \rightleftharpoons Co^{2+}(aq) + CO_3^{2-}(aq)$	1.0×10^{-10}
$NiCO_3$	$NiCO_3(s) \rightleftharpoons Ni^{2+}(aq) + CO_3^{2-}(aq)$	1.3×10^{-7}
$CuCO_3$	$CuCO_3(s) \rightleftharpoons Cu^{2+}(aq) + CO_3^{2-}(aq)$	2.3×10^{-10}
Ag_2CO_3	$Ag_2CO_3(s) \rightleftharpoons 2Ag^{+}(aq) + CO_3^{2-}(aq)$	8.1×10^{-12}
Hg_2CO_3	$Hg_2CO_3(s) \rightleftharpoons Hg_2^{2+}(aq) + CO_3^{2-}(aq)$	8.9×10^{-17}
$ZnCO_3$	$ZnCO_3(s) \rightleftharpoons Zn^{2+}(aq) + CO_3^{2-}(aq)$	1.0×10^{-10}
$CdCO_3$	$CdCO_3(s) \rightleftharpoons Cd^{2+}(aq) + CO_3^{2-}(aq)$	1.8×10^{-14}
$PbCO_3$	$PbCO_3(s) \rightleftharpoons Pb^{2+}(aq) + CO_3^{2-}(aq)$	7.4×10^{-14}
Phosphates		
$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$	2.0×10^{-29}
$Mg_3(PO_4)_2$	$Mg_3(PO_4)_2(s) \rightleftharpoons 3Mg^{2+}(aq) + 2PO_4^{3-}(aq)$	6.3×10^{-26}
$SrHPO_4$	$SrHPO_4(s) \rightleftharpoons Sr^{2+}(aq) + HPO_4^{2-}(aq)$	1.2×10^{-7}
$BaHPO_4$	$BaHPO_4(s) \rightleftharpoons Ba^{2+}(aq) + HPO_4^{2-}(aq)$	4.0×10^{-8}
$LaPO_4$	$LaPO_4(s) \rightleftharpoons La^{3+}(aq) + PO_4^{3-}(aq)$	3.7×10^{-23}
$Fe_3(PO_4)_2$	$Fe_3(PO_4)_2(s) \rightleftharpoons 3Fe^{2+}(aq) + 2PO_4^{3-}(aq)$	1×10^{-36}
Ag_3PO_4	$Ag_3PO_4(s) \rightleftharpoons 3Ag^{+}(aq) + PO_4^{3-}(aq)$	2.8×10^{-18}
$FePO_4$		4.0×10^{-27}

	$FePO_4(s) \rightleftharpoons Fe^{3+}(aq) + PO_4^{3-}(aq)$	
$Zn_3(PO_4)_2$	$Zn_3(PO_4)_2(s) \rightleftharpoons 3Zn^{2+}(aq) + 2PO_4^{3-}(aq)$	5×10^{-36}
$Pb_3(PO_4)_2$	$Pb_3(PO_4)_2(s) \rightleftharpoons 3Pb^{2+}(aq) + 2PO_4^{3-}(aq)$	3.0×10^{-44}
$Ba_3(PO_4)_2$	$Ba_3(PO_4)_2(s) \rightleftharpoons 3Ba^{2+}(aq) + 2PO_4^{3-}(aq)$	5.8×10^{-38}
Ferrocyanides		
$Zn_2[Fe(CN)_6]$	$Zn_2[Fe(CN)_6](s) \rightleftharpoons 2Zn^{2+}(aq) + [Fe(CN)_6]^{4-}(aq)$	2.1×10^{-16}
$Cd_2[Fe(CN)_6]$	$Cd_2[Fe(CN)_6](s) \rightleftharpoons 2Cd^{2+}(aq) + [Fe(CN)_6]^{4-}(aq)$	4.2×10^{-18}
$Pb_2[Fe(CN)_6]$	$Pb_2[Fe(CN)_6](s) \rightleftharpoons 2Pb^{2+}(aq) + [Fe(CN)_6]^{4-}(aq)$	9.5×10^{-19}

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Appendix D
Cumulative Formation Constants of Complexes (25 °C)

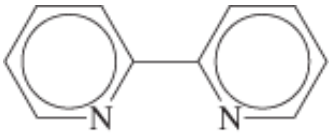
Equilibrium	β_n	*n*
Halide complexes		
$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	2.5×10^4	6
$Al^{3+} + 4F^- \rightleftharpoons [AlF_4]^-$	2.0×10^8	4
$Be^{2+} + 4F^- \rightleftharpoons [BeF_4]^{2-}$	1.3×10^{13}	4
$Sn^{4+} + 6F^- \rightleftharpoons [SnF_6]^{2-}$	1×10^{25}	6
$Cu^+ + 2Cl^- \rightleftharpoons [CuCl_2]^-$	3×10^5	2
$Ag^+ + 2Cl^- \rightleftharpoons [AgCl_2]^-$	1.8×10^5	2
$Pb^{2+} + 4Cl^- \rightleftharpoons [PbCl_4]^{2-}$	2.5×10^{15}	4
$Zn^{2+} + 4Cl^- \rightleftharpoons [ZnCl_4]^{2-}$	1.6	4
$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	5.0×10^{15}	4
$Cu^+ + 2Br^- \rightleftharpoons [CuBr_2]^-$	8×10^5	2
$Ag^+ + 2Br^- \rightleftharpoons [AgBr_2]^-$	1.7×10^7	2
$Hg^{2+} + 4Br^- \rightleftharpoons [HgBr_4]^{2-}$	1×10^{21}	4
$Cu^+ + 2I^- \rightleftharpoons [CuI_2]^-$	8×10^8	2
$Ag^+ + 2I^- \rightleftharpoons [AgI_2]^-$	1×10^{11}	2
$Pb^{2+} + 4I^- \rightleftharpoons [PbI_4]^{2-}$	3×10^4	4
$Hg^{2+} + 4I^- \rightleftharpoons [HgI_4]^{2-}$	1.9×10^{30}	4
Ammonia complexes		
$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.6×10^7	2
$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$	7.8×10^8	4
$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.1×10^{13}	4
$Hg^{2+} + 4NH_3 \rightleftharpoons [Hg(NH_3)_4]^{2+}$	1.8×10^{19}	4
$Co^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	5.0×10^4	6
$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	4.6×10^{33}	6
$Cd^{2+} + 6NH_3 \rightleftharpoons [Cd(NH_3)_6]^{2+}$	2.6×10^5	6
	2.0×10^8	6

$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$		
Cyanide complexes		
$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$	1.0×10^{24}	6
$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1.0×10^{31}	6
$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	5.3×10^{18}	2
$Cu^+ + 2CN^- \rightleftharpoons [Cu(CN)_2]^-$	1.0×10^{16}	2
$Cd^{2+} + 4CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$	7.7×10^{16}	4
$Au^+ + 2CN^- \rightleftharpoons [Au(CN)_2]^-$	2×10^{38}	2
Complexes with other monodentate ligands		
methylamine (CH_3NH_2)		
$Ag^+ + 2CH_3NH_2 \rightleftharpoons [Ag(CH_3NH_2)_2]^+$ thiocyanate ion (SCN^-)	7.8×10^6	2
$Cd^{2+} + 4SCN^- \rightleftharpoons [Cd(SCN)_4]^{2-}$	1×10^3	4
$Cu^{2+} + 2SCN^- \rightleftharpoons [Cu(SCN)_2]$	5.6×10^3	2
$Fe^{3+} + 3SCN^- \rightleftharpoons [Fe(SCN)_3]$	2×10^6	3
$Hg^{2+} + 4SCN^- \rightleftharpoons [Hg(SCN)_4]^{2-}$ hydroxide ion (OH^-)	5.0×10^{21}	4
$Cu^{2+} + 4OH^- \rightleftharpoons [Cu(OH)_4]^{2-}$	1.3×10^{16}	4
$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	2×10^{20}	4
Complexes with bidentate ligands[(a)]		
$Mn^{2+} + 3$ en $\rightleftharpoons [Mn(en)_3]^{2+}$	6.5×10^5	3
$Fe^{2+} + 3$ en $\rightleftharpoons [Fe(en)_3]^{2+}$	5.2×10^9	3
$Co^{2+} + 3$ en $\rightleftharpoons [Co(en)_3]^{2+}$	1.0×10^{14}	3
$Co^{3+} + 3$ en $\rightleftharpoons [Co(en)_3]^{3+}$	5.0×10^{48}	3
$Ni^{2+} + 3$ en $\rightleftharpoons [Ni(en)_3]^{2+}$	4.1×10^{17}	3
$Cu^{2+} + 2$ en $\rightleftharpoons [Cu(en)_2]^{2+}$	4.0×10^{19}	2
$Mn^{2+} + 3$ bipy $\rightleftharpoons [Mn(bipy)_3]^{2+}$	1×10^6	3
$Fe^{2+} + 3$ bipy $\rightleftharpoons [Fe(bipy)^3]^{2+}$	1.6×10^{17}	3
$Ni^{2+} + 3$ bipy $\rightleftharpoons [Ni(bipy)_3]^{2+}$	3.0×10^{20}	3
$Co^{2+} + 3$ bipy $\rightleftharpoons [Co(bipy)^3]^{2+}$	8×10^{15}	3
$Mn^{2+} + 3$ phen $\rightleftharpoons [Mn(phen)^3]^{2+}$	2×10^{10}	3
$Fe^{2+} + 3$ phen $\rightleftharpoons [Fe(phen)_3]^{2+}$	1×10^{21}	3

$Co^{2+} + 3\ phen \rightleftharpoons [Co(phen)_3]^{2+}$	6×10^{19}	3
$Ni^{2+} + 3\ phen \rightleftharpoons [Ni(phen)_3]^{2+}$	2×10^{24}	3
$Co^{2+} + 3C_2O_4^{2-} \rightleftharpoons [Co(C_2O_4)_3]^{4-}$	4.5×10^{6}	3
$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	3.3×10^{20}	3
Complexes of other ligands		
$Zn^{2+} + EDTA^{4-} \rightleftharpoons [Zn(EDTA)]^{2-}$	3.8×10^{16}	1
$Mg^{2+} + 2NTA^{3-} \rightleftharpoons [Mg(NTA)_2]^{4-}$	1.6×10^{10}	2
$Ca^{2+} + 2NTA^{3-} \rightleftharpoons [Ca(NTA)_2]^{4-}$	3.2×10^{11}	2

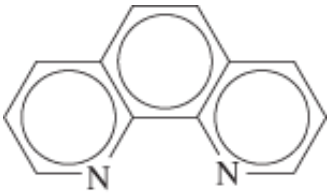
(a) en = ethylenediamine

bipy = bipyridine



bipyridine

phen = 1,10-phenanthroline



1,10-phenanthroline

$EDTA^{4-}$ = ethylenediaminetetraacetate ion

NTA^{3-} = nitrilotriacetate ion

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Appendix E
Acidity and Basicity Constants for Weak Acids and Bases (25 °C)

Monoprotic acids	Name	K_a
Cl_3CCOOH	trichloroacetic acid	2.2×10^{-1}
HIO_3	iodic acid	1.7×10^{-1}
$Cl_2CHCOOH$	dichloroacetic acid	5.0×10^{-2}
$ClCH_2COOH$	chloroacetic acid	1.4×10^{-3}
HNO_2	nitrous acid	7.1×10^{-4}
HF	hydrofluoric acid	6.8×10^{-4}
HOCN	cyanic acid	3.5×10^{-4}
HCOOH	formic acid	1.8×10^{-4}
$CH_3CH(OH)COOH$	lactic acid	1.4×10^{-4}
$C_4H_4N_2O_3$	barbituric acid	9.8×10^{-5}
C_6H_5COOH	benzoic acid	6.3×10^{-5}
$CH_3CH_2CH_2COOH$	butanoic acid	1.5×10^{-5}
HN_3	hydrazoic acid	1.8×10^{-5}
CH_3COOH	acetic acid	1.8×10^{-5}
CH_3CH_2COOH	propanoic acid	1.4×10^{-5}
HOCl	hypochlorous acid	3.0×10^{-8}
HOBr	hypobromous acid	2.1×10^{-9}
HCN	hydrocyanic acid	6.2×10^{-10}
C_6H_5OH	phenol	1.3×10^{-10}
HOI	hypoiodous acid	2.3×10^{-11}
H_2O_2	hydrogen peroxide	1.8×10^{-12}

Polyprotic acids	Name	K_{a1}	K_{a2}	K_{a3}
H_2SO_4	sulfuric acid	large	1.0×10^{-2}	
H_2CrO_4	chromic acid	5.0	1.5×10^{-6}	
$H_2C_2O_4$	oxalic acid	5.6×10^{-2}	5.4×10^{-5}	
H_3PO_3	phosphorous acid	3×10^{-2}	1.6×10^{-7}	
H_2SO_3 [SO_2(aq)]	sulfurous acid	1.2×10^{-2}	6.6×10^{-8}	
H_2SeO_3	selenous acid	4.5×10^{-3}	1.1×10^{-8}	

H_2TeO_3	tellurous acid	3.3×10^{-3}	2.0×10^{-8}	
$HOOCCH_2COOH$	malonic acid	1.4×10^{-3}	2.0×10^{-6}	
$C_6H_4(COOH)_2$	phthalic acid	1.1×10^{-3}	3.9×10^{-6}	
$HOOCCH(OH)CH(OH)COOH$	tartaric acid	9.2×10^{-4}	4.3×10^{-5}	
$C_6H_8O_6$	ascorbic acid	6.8×10^{-5}	2.7×10^{-12}	
H_2CO_3	carbonic acid	4.5×10^{-7}	4.7×10^{-11}	
H_3PO_4	phosphoric acid	7.1×10^{-3}	6.3×10^{-8}	4.5×10^{-13}
H_3AsO_4	arsenic acid	5.6×10^{-3}	1.7×10^{-7}	4.0×10^{-12}
$C_6H_8O_7$	citric acid	7.1×10^{-4}	1.7×10^{-5}	6.3×10^{-6}

Weak bases	**Name**	K_b
$(CH_3)_2NH$	dimethylamine	9.6×10^{-4}
CH_3NH_2	methylamine	4.4×10^{-4}
$CH_3CH_2NH_2$	ethylamine	4.3×10^{-4}
$(CH_3)_3N$	trimethylamine	7.4×10^{-5}
NH_3	ammonia	1.8×10^{-5}
N_2H_4	hydrazine	1.7×10^{-6}
NH_2OH	hydroxylamine	6.6×10^{-9}
C_5H_5N	pyridine	1.7×10^{-9}
$C_6H_5NH_2$	aniline	4.1×10^{-10}

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Appendix F
Standard Reduction Potentials (25 °C)

Half-reaction	E° (volts)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	+2.08
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	+2.01
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.69
$2HOCl(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$	+1.63
$Mn^{3+}(aq) + e^- \rightleftharpoons Mn^{2+}(aq)$	+1.51
$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O(l)$	+1.51
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.49
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	+1.47
$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightleftharpoons Br^-(aq) + 3H_2O(l)$	+1.46
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.42
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$O_3(g) + H_2O(l) + 2e^- \rightleftharpoons O_2(g) + 2OH^-(aq)$	+1.24
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Pt^{2+}(aq) + 2e^- \rightleftharpoons Pt(s)$	+1.20
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons HNO_2(aq) + H_2O(l)$	+0.94
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	+0.91
$HO_2^-(aq) + H_2O(l) + 2e^- \rightleftharpoons 3OH^-(aq)$	+0.87
$NO_3^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons 2NO_2(g) + 2H_2O(l)$	+0.80
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.69
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$NiO_2(s) + 2H_2O(l) + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$SO_2(aq) + 4H^+(aq) + 4e^- \rightleftharpoons S(s) + 2H_2O(l)$	+0.45
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.401
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$	+0.27
$PbO_2(s) + H_2O(l) + 2e^- \rightleftharpoons PbO(s) + 2OH^-(aq)$	+0.25
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	+0.23
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.17
$S_4O_6^{2-}(aq) + 2e^- \rightleftharpoons 2S_2O_3^{2-}(aq)$	+0.169
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.16
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(g)$	+0.14
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$	+0.07
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-(aq)$	-0.15
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	-0.28
$In^{3+}(aq) + 3e^- \rightleftharpoons In(s)$	-0.34
$Tl^+(aq) + e^- \rightleftharpoons Tl(s)$	-0.34
$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$	-0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Ga^{3+}(aq) + 3e^- \rightleftharpoons Ga(s)$	-0.56
$PbO(s) + H_2O(l) + 2e^- \rightleftharpoons Pb(s) + 2OH^-(aq)$	-0.58
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76

$Cd(OH)_2(s) + 2e^- \rightleftharpoons Cd(s) + 2OH^-(aq)$	-0.81
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Fe(OH)_2(s) + 2e^- \rightleftharpoons Fe(s) + 2OH^-(aq)$	-0.88
$Cr^{2+}(aq) + 2e^- \rightleftharpoons Cr(s)$	-0.91
$N_2(g) + 4H_2O(l) + 4e^- \rightleftharpoons N_2O_4(aq) + 4OH^-(aq)$	-1.16
$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	-1.18
$ZnO_2^{2-}(aq) + 2H_2O(l) + 2e^- \rightleftharpoons Zn(s) + 4OH^-(aq)$	-1.216
$Ti^{2+}(aq) + 2e^- \rightleftharpoons Ti(s)$	-1.63
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66
$U^{3+}(aq) + 3e^- \rightleftharpoons U(s)$	-1.79
$Sc^{3+}(aq) + 3e^- \rightleftharpoons Sc(s)$	-2.02
$La^{3+}(aq) + 3e^- \rightleftharpoons La(s)$	-2.36
$Y^{3+}(aq) + 3e^- \rightleftharpoons Y(s)$	-2.37
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.76
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	-2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	-2.90
$Cs^+(aq) + e^- \rightleftharpoons Cs(s)$	-2.92
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.92
$Rb^+(aq) + e^- \rightleftharpoons Rb(s)$	-2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.05

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Appendix G
Ionisation Energies and Electron Affinities of the First 36 Elements at 25 °C

Z	Symbol	EA	IE_1	IE_2	IE_3
1	H	-72.8	1312	-	-
2	He	>0	2372	5250	-
3	Li	-59.7	520.2	7298	11 815
4	Be	>0	899.4	1757	14 848
5	B	-26.8	800.6	2427	3660
6	C	-121.9	1086	2353	4620
7	N	>0	1402	2856	4578
8	0	-141.1	1314	3388	5300
9	F	-322.0	1681	3374	6050
10	Ne	>0	2080	3952	6122
11	Na	-52.9	495.6	4560	6912
12	Mg	>0	737.7	1450	7730
13	Al	-42.7	577	1817	2745
14	Si	-133.6	786.4	1577	3232
15	P	-72.0	1012	1908	2912
16	S	-200.4	999.6	2251	3357
17	Cl	-348.8	1256	2297	3822
18	Ar	>0	1520	2666	3931
19	K	-48.4	418.8	3051	4420
20	Ca	-2.4	589.8	1145	4912
21	Sc	-18.2	633	1235	2389
22	Ti	-7.7	658	1310	2653
23	V	-50.8	650	1414	2828
24	Cr	-64.4	652.8	1591	2987
25	Mn	>0	717.4	1509	3248
26	Fe	-14.6	763	1561	2957
27	Co	-63.9	758	1646	3232
28	Ni	-111.6	736.7	1753	3396
29	Cu	-119.2	745.4	1958	3554
30	Zn	>0	906.4	1733	3833
31	Ga	-28.9	578.8	1979	2963
32	Ge	-119	761	1537	3302

33	As	-78	947	1798	2736
34	Se	-195.0	940.9	2045	2974
35	Br	-324.6	1143	2103	3500
36	Kr	>0	1351	2350	3565

All values are in kJ mol^{-1}. A value of >0 means that the anion is unstable, so its electron affinity cannot be determined experimentally. Colour shading indicates the principal quantum number, *n*, of the electron whose ionisation energy is listed: blue, $n = 1$; green, $n = 2$; orange, $n = 3$; purple, $n = 4$; yellow, $n = 5$.

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Appendix H
Characteristic Infrared Absorption Frequencies

Bonding		Frequency (cm^{-1})	Intensity[(a)]
C—H	alkane	2850–3000	s
	—CH_3	1375 and 1450	w–m
	—CH_2—	1450	m
	alkene	3000–3100	w–m
		650–1000	s
	alkyne	3300	m–s
		1600–1680	w–m
	aromatic	3000–3100	s
		690–900	s
	aldehyde	2700–2800	w
		2800–2900	w
C═C	alkene	1600–1680	w–m
	aromatic	1450 and 1600	w–m
C—O	alcohol, ether, ester, carboxylic acid, anhydride	1050–1100 (sp^3 C—O)	s
			s
		1200–1250 (sp^2 C—O)	s
C═O	amide	1630–1680	s
	carboxylic acid	1700–1725	s
	ketone	1705–1780	s
	aldehyde	1705–1740	s
	ester	1735–1750	s
	anhydride	1760 and 1800	s
O—H	alcohol, phenol		
	free	3600–3650	m
	H-bonded	3200–3500	m
	carboxylic acid	2400–3400	m
N—H	amine and amide	3100–3500	m–s

(a) m = medium, s = strong, w = weak

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GLOSSARY OF EQUATIONS

acidity constant for the acid–base reaction: HA(aq) + $H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

Arrhenius equation

$$k = Ae^{-E_a/RT}$$

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Avogadro's Law

$$V_{gas} = k'' n_{gas} \quad \text{(fixed pressure and temperature)}$$

basicity constant for the acid–base reaction: B(aq) + $H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$pK_b = -\log K_b$$

boiling point elevation

$$\Delta T_b = K_b b$$

bond order

bond order $= \frac{1}{2}$ (number of electrons in bonding molecular orbitals– number of electrons in antibonding molecular orbitals)

Boyle's Law

$$p_{gas} V_{gas} = k \quad \text{(fixed temperature and amount)}$$

Bragg equation

$$n\lambda = 2d \sin\theta$$

cell potential

$$E_{cell} = E_R - E_L$$

$$E^{\ominus}_{cell} = E^{\ominus}_R - E^{\ominus}_L$$

$$E^{\ominus}_{cell} = \frac{RT}{zF}\ln K_c$$

Charles' Law

$$V_{gas} = k' T_{gas} \quad \text{(fixed pressure and amount)}$$

concentration molality

$$b = \frac{\text{amount of solute (mol)}}{\text{mass of solvent (kg)}}$$

molarity

$$c = \frac{n}{V}$$

cumulative formation constant for the formation reaction: $M^{x+}(aq) + nL(aq) \rightleftharpoons [ML_n]^{x+}(aq)$

$$\beta_n = \frac{[ML_n{}^{x+}(aq)]}{[M^{x+}(aq)][L(aq)]^n}$$

Dalton's law of partial pressures

$$p_{total} = p_1 + p_2 + p_3 + \ldots + p_i$$

de Broglie equation

$$\lambda_{particle} = \frac{h}{mu}$$

electrostatic potential energy

$$E_{\text{electrostatic}} = k\frac{q_1 q_2}{r}$$

energy of a photon

$$\begin{aligned} E &= h\nu \\ &= \frac{hc}{\lambda} \end{aligned}$$

enthalpy

$$H = U + pV$$

entropy of reaction, standard for the general reaction: *aA* + *bB* → *cC* + *dD*

$$\Delta_r S^\ominus = cS^\ominus_C + dS^\ominus_D - (aS^\ominus_A + bS^\ominus_B)$$

entropy and enthalpy, relationship

$$\Delta S_{\text{surroundings}} = \frac{-\Delta H_{\text{system}}}{T}$$

equilibrium constant expression for the solution-phase reaction: *aA* + *bB* ⇌ *cC* + *dD*

$$K_c = \frac{\left(\frac{[C]_e}{c^\ominus}\right)^c \left(\frac{[D]_e}{c^\ominus}\right)^d}{\left(\frac{[A]_e}{c^\ominus}\right)^a \left(\frac{[B]_e}{c^\ominus}\right)^b}$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}, \qquad \text{when } c^\ominus = 1\ \text{mol L}^{-1}$$

equilibrium constant for the gas-phase reaction: *aA* + *bB* ⇌ *cC* + *dD*

$$K_p = \frac{\left(\frac{p_C}{p^\ominus}\right)^c \left(\frac{p_D}{p^\ominus}\right)^d}{\left(\frac{p_A}{p^\ominus}\right)^a \left(\frac{p_B}{p^\ominus}\right)^b}$$

Faraday's law

$$\text{amount of product} = \frac{It}{zF}$$

first law of thermodynamics

$$\Delta U = q + w$$

freezing point depression

$$\Delta T_f = K_f b$$

gas density

$$\rho_{\text{gas}} = \frac{m}{V} = \frac{pM}{RT}$$

Gibbs free energy

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -zFE_{\text{cell}}$$

$$\Delta G^\ominus = -zFE^\ominus_{\text{cell}}$$

$$\Delta_r G^\ominus = -RT\ln K$$

$$\Delta_r G = \Delta_r G^\ominus + RT\ln Q$$

change in standard Gibbs free energy

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

for: $aA + bB + cC + dD$

$$\Delta_r G^\ominus = c\Delta_f G^\ominus_C + d\Delta_f G^\ominus_D - \left(a\Delta_f G^\ominus_A + b\Delta_f G^\ominus_B\right)$$

half-life for a first-order reaction

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

half-life for a second-order reaction

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

half-life for a zero-order reaction

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$

heat

$$q = C\Delta T$$

$$q = cm\Delta T$$

heat of reaction

$$\Delta H = q_p \quad \text{(constant pressure)}$$

$$\Delta_r U = q_v \quad \text{(constant volume)}$$

Henderson–Hasselbalch equation

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

Henry's law

$$c_{gas} = k_H p_{gas} \text{ (constant } T\text{)}$$

$$\frac{c_1}{p_1} = \frac{c_2}{p_2}$$

Hess's law equation for the general reaction: *aA* + *bB* → *cC* + *dD*

$$\Delta_r H^\ominus = c\Delta_f H^\ominus_C + d\Delta_f H^\ominus_D - \left(a\Delta_f H^\ominus_A + b\Delta_f H^\ominus_B\right)$$

hydrogen atom emission energies

$$E_n = -\frac{2.18 \times 10^{-18}\ \mathrm{J}}{n^2}$$

hydrogen atom emission frequencies

$$\nu_{\text{emission}} = (3.29 \times 10^{15}\ \mathrm{s}^{-1})\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

ideal gas equation

$$pV = nRT$$

$$p_i V_i = p_f V_f \quad \text{(constat } n \text{ and } T\text{)}$$

index of hydrogen deficiency (IHD)

$$\mathrm{IHD} = \frac{(\mathrm{H}_{\text{reference}} - \mathrm{H}_{\text{molecule}})}{2}$$

integrated rate law for a first-order reaction

$$\ln[A]_t = -kt + \ln[A]_0$$

$$[A]_t = [A]_0 e^{-kt}$$

integrated rate law for a second-order reaction

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

integrated rate law for a zero-order reaction

$$[A]_t = -kt + [A]_0$$

isoelectric point of an amino

acid

$$\mathrm{pI} = \frac{1}{2}(\mathrm{p}K_\mathrm{a}\text{ of }\alpha\text{-COOH} + \mathrm{p}K_\mathrm{a}\text{ fo }\alpha\text{-}{NH_3}^+)$$

kinetic energy

$$E_\mathrm{kinetic} = \frac{1}{2}mu^2$$

$$E_\mathrm{kinetic,molar} = \frac{3}{2}RT, \quad \text{for 1 mole of gas molecules}$$

$$\bar{E}_\mathrm{kinetic} = \frac{3RT}{2N_A}, \quad \text{average of gas molecules}$$

K_p abd K_c, relationship

$$K_P = K_c\left(\frac{RT}{p^\ominus}\right)^{\Delta n_g}$$

law of radioactive decay

$$\text{activity} = -\frac{\Delta N}{\Delta t} = kN$$

magnetic moment of a transition metal complex

$$\mu = \sqrt{n(n+2)}\,\mu_\mathrm{B}$$

Michaelis–Menten equation

$$\frac{\mathrm{d}[P]}{\mathrm{d}t} = \frac{k_2[E]_0[S]}{\mathrm{K_M} + [S]}, \quad \text{where } \mathrm{K_M} = \frac{k_2 + k_{-1}}{k_1}$$

molar mass

$$M = \frac{m}{n}$$

mole fraction

$$\text{mole fraction of A} = x_A = \frac{n_A}{n_\mathrm{total}}$$

momentum of a particle

$$p = \frac{h}{\lambda}$$

Nernst equation

$$E_\mathrm{cell} = E^\ominus_\mathrm{cell} - \frac{RT}{zF}\ln Q$$

NMR chemical shift

$$\delta = \frac{\text{shift in frequency of a signal from TMS in (Hz)}}{\text{operating frequency of the spectrometer (MHz)}}$$

partial pressure of a component of a gas mixture

$$p_A = x_A p_\mathrm{total}$$

percentage by mass

$$\%\text{ by mass of element} = \frac{\text{mass of element present in the sample}}{\text{mass of whole sample}} \times 100\%$$

percentage yield

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

pH

$$\mathrm{pH} = -\log\left[\mathrm{H_3O^+}\right]$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}]$$

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_\mathrm{w} = 14.00(\text{at } 25.0\,^\circ\mathrm{C})$$

pK_a and pK_b, relationship

$$\mathrm{p}K_\mathrm{a} + \mathrm{p}K_\mathrm{b} = \mathrm{p}K_\mathrm{w} = 14.00(\text{at } 25.0\,^\circ\mathrm{C})$$

radiocarbon dating

$$\ln\frac{r_0}{r_t} = \left(1.21 \times 10^{-4}\,\mathrm{yr}^{-1}\right)t$$

Raoult's law

$$p_{\text{solution}} = X_{\text{solvent}} P^*_{\text{solvent}}$$

$$p_{\text{solution}} = \left(1 - X_{\text{solute}}\right) P^*_{\text{solvent}}$$

$$= P^*_{\text{solvent}} - X_{\text{solute}} P^*_{\text{solvent}}$$

Raoult's law for a two-component system:

$$p_{\text{total}} = X_A P^*_A + X_B p^*_B$$

rate laws for organic reactions

S_N1 reaction

$$\text{rate of reaction} = k[\text{haloalkane}]$$

S_N2 reaction

$$\text{rate of reaction} = k[\text{haloalkane}]\,[\text{nucleophile}]$$

E1 reaction

$$\text{rate of reaction} = k[\text{haloalkane}]$$

E2 reaction

$$\text{rate of reaction} = k[\text{haloalkane}]\,[\text{base}]$$

rate of reaction for the general reaction: *aA* + *bB* → *cC* + *dD*

$$\text{rate of reaction} = -\frac{1}{a}\frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{1}{c}\frac{\mathrm{d}[C]}{\mathrm{d}t} = \frac{1}{d}\frac{\mathrm{d}[D]}{\mathrm{d}t}$$

reaction quotient for the solution-phase reaction: *aA* + *bB* ⇌ *cC* + *dD*

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

root-mean-square speed of gas atoms/molecules

$$\overline{u}_{\text{RMS}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

Schrödinger equation

$$\hat{H}\psi = E\psi$$

solubility product of a salt for: M_aX_b(s) ⇌ aM^{b+}(aq) + bX^{a-}(aq)

$$K_{\text{sp}} = \left[\mathrm{M}^{b+}\right]^a \left[X^{a-}\right]^b$$

specific heat

$$C = \frac{c}{m}$$

specific rotation

$$\text{specific rotation} = [\alpha]^T_\lambda$$

$$= \frac{\text{observed rotation (degrees)}}{\text{length (dm)} \times \text{concentration (g/mL)}}$$

speed of a light wave

$$c = \nu\lambda$$

van der Waals equation

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

van't Hoff equation

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H^\ominus}{RT^2}$$

$$\ln K_{T_2} - \ln K_{T_1} = \frac{-\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

van't Hoff equation for osmotic pressure

$$\Pi V = nRT$$

van't Hoff factor

$$i = \frac{(\Delta T_f)_{\text{measured}}}{(\Delta T_f)_{\text{calculated as a nonelectrolyte}}}$$

work done in the expansion/compression of a gas

$$w = -p\Delta V$$

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GLOSSARY

A

absolute uncertainty An uncertainty which has the same units as the quantity being measured. (p. 31)

absorbance (*A*) A measure of the light absorbed by a solution of a compound; defined by the equation $A = \log\frac{I_0}{I}$. (p. 571)

absorption spectrum The distribution of wavelengths of light absorbed by a species. (p. 117)

acid anhydride A compound in which two acyl groups are bonded to the same oxygen atom. (p. 1002)

acceptor stem The part of the tRNA molecule that carries the amino acid and in which nucleotide sequences from the 5′ and 3′ ends are paired to form duplex RNA. (p. 1101)

accuracy A measurement is of high accuracy if it is close to the correct value. (p. 34)

acetal A molecule containing two —OR or —OAr groups bonded to the same carbon atom. (p. 946)

achiral Describes an object that lacks chirality, that is, it is superimposable on its mirror image. (p. 747)

acid Arrhenius theory — a substance that produces H^+ ions in water (p. 428); Brønsted–Lowry theory — a proton donor (p. 428); Lewis theory — an electron-pair acceptor. (p. 476)

acid–base indicator A dye having one colour in acid and another colour in base. (p. 467)

acid–base reaction A reaction that involves the transfer of a single proton from one species to another. (Note that this is the Brønsted–Lowry definition.) (p. 428)

acid–base titration An analytical procedure involving the gradual addition of a solution of an acid or base of known concentration to a specified volume of a solution of a base or acid of unknown concentration. (p. 467)

acid halide A derivative of a carboxylic acid in which the —OH of the carboxyl group is replaced by a halogen, most commonly chlorine. (p. 1002)

acidic Describes an aqueous solution in which $[H_3O^+] > [OH^-]$. (p. 433)

acidity constant (K_a) The equilibrium constant for the dissociation of an acid in aqueous solution. For the general equilibrium:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a \text{ has the form } K_a = \frac{[H_3O^+][A^-]}{[HA]}.$$

(p. 443)

actinoids Elements 89 to 103 of the periodic table. (p. 14)

activation energy (E_a) The minimum kinetic energy that must be possessed by the reactants in order to give an effective collision leading to products. (p. 652)

activities Effective concentrations that give rise to thermodynamic equilibrium constants when substituted into an equilibrium constant expression. (p. 353)

activity The number of disintegrations per second of a radioactive substance. (p. 1168)

actual yield The mass of a product obtained from a reaction. (p. 88)

acyclic alkanes Alkane molecules that consist solely of chains of carbon atoms. (p. 54)

acylation The process of introducing an acyl group into a compound. (p. 734)

acyl group A carbonyl group bonded to an alkyl or aryl group. (p. 1002)

addition polymerisation See *chain-growth polymerisation*. (p. 1123)

addition to the carbon–carbon double bond A characteristic reaction of alkenes in which the π bond is broken and, in its place, σ bonds are formed to two new atoms or groups of atoms. (p. 712)

adduct The product of a reaction between a Lewis acid and a Lewis base. (p. 476)

A-DNA A thicker form of DNA than B-DNA. The base pairs are 0.25 nm apart, and 11 base pairs form one complete turn of the helix. (p. 1095)

alcohol A compound containing an —OH (hydroxyl) group bonded to an sp^3 hybridised carbon atom. (p. 810)

aldehyde A compound in which a carbonyl group is bonded to a hydrogen atom plus a hydrocarbon group (or a second hydrogen atom). (p. 934)

alditol The product formed when the C═O group of a monosaccharide is reduced to a CHOH group. (p. 986)

aldoses Monosaccharides containing an aldehyde group. (p. 978)

aliphatic amine An amine in which the nitrogen atom is bonded only to alkyl groups. (p. 834)

aliphatic hydrocarbon See *alkane*. (p. 686)

alkali metals The elements in group 1 (except hydrogen) of the periodic table. (p. 15)

alkaline battery A type of power cell dependent on the reaction between zinc and manganese dioxide (Zn/MnO_2). (p. 530)

alkaline dry cell See *alkaline battery*. (p. 530)

alkaline An alternative word for basic. (p. 433)

alkaline earth metals The elements in group 2 of the periodic table. (p. 15)

alkane A molecule composed only of carbon and hydrogen atoms in which all carbon–carbon bonds are single. (pp. 54, 686)

alkene An unsaturated hydrocarbon with a carbon–carbon double bond. (p. 686)

alkoxy An —OR group, where R is an alkyl group. (p. 829)

alkylamines Amines in which the nitrogen atom is bonded only to alkyl groups. (p. 835)

alkylation The transfer of an alkyl group from one compound to another. (p. 733)

alkyl group A group derived from an alkane by the removal of a hydrogen atom, commonly represented by the symbol R. (p. 55)

alkyne An unsaturated hydrocarbon with a carbon–carbon triple bond. (p. 686)

α-amino acid An amino acid in which the amino group is attached to the carbon atom adjacent to the carboxyl group. (p. 1056)

α-carbon A carbon atom adjacent to a functional group. (p. 962)

α-helix A type of secondary structure in which a section of polypeptide chain coils into a

	spiral, most commonly a right-handed spiral (p. 1070)
α-hydrogen	A hydrogen atom bonded to an α-carbon atom. (p. 962)
alpha particle	The nucleus of a helium atom ($^4_2\mathrm{He}$). (pp. 7, 1163)
alternating	Describes a polymer with regularly alternating A and B units. (p. 1122)
ambidentate	Describes ligands with two or more different potential donor atoms. (p. 555)
amide	An acyl group bonded to a trivalent nitrogen atom. (p. 1003)
amino acid	A compound that contains both a carboxyl group and an amino group. (p. 1056)
amorphous	Without any organised regular repeating pattern. (p. 281)
amorphous domain	A disordered, noncrystalline region in the solid state of a polymer. (p. 1119)
amount of substance	A base quantity in the SI system, with the unit of mole. (p. 75)
ampere (A)	The SI unit of electric current; 1 A = 1 C s^{-1}. (pp. 25, 527)
amphiprotic	A solvent that can act either as a proton donor or a proton acceptor. (p. 430)
amplitude	The maximum displacement of a wave from its centre. (p. 110)
angle strain	The strain induced in a molecule as a result of bond angles that are distorted from the ideal values. (p. 691)
anhydrous	Describes a chemical substance that contains no water. (p. 37)
aniline	The common name for the monosubstituted benzene $C_6H_5NH_2$. (pp. 728, 836)
anion	A negatively charged ion (p. 2)
anisole	The common name for the monosubstituted benzene $C_6H_5OCH_3$. (p. 728)
anode	The positive electrode in a gas discharge tube; the electrode at which oxidation occurs during an electrochemical change. (p. 503)
anomeric carbon	The hemiacetal carbon atom of the cyclic form of a monosaccharide. (p. 982)
anomers	Monosaccharides that differ in configuration only at their anomeric carbon atoms. (p. 982)
***anti* addition**	The addition of atoms or groups of atoms from opposite sides or faces of a carbon–carbon double bond. (p. 720)
antibonding molecular orbital	A molecular orbital that has electron density concentrated outside the bonding region, making it less stable than the atomic orbitals from which it forms. (p. 199)
anticodon	A triplet of bases on tRNA that pairs to a matching triplet (a codon) on an mRNA molecule during mRNA-directed polypeptide synthesis. (p. 1101)
antimatter	Any particle annihilated by a particle of ordinary matter. (p. 1166)
antioxidant	Usually an added substance or compound which has a lower oxidation potential than its surroundings so that it is preferentially oxidised instead of the material it is protecting. (p. 1148)
***anti* selectivity**	The characteristic that bromine and chlorine always add *trans* to each other in cycloalkenes. (p. 720)
antisense strand	The strand of DNA that is transcribed into mRNA during transcription. The resulting RNA transcript is the same as the sense strand except that the nucleotides are RNA and the base thymine is substituted by uracil. (p. 1102)
aprotic solvents	Solvents that do not contain —OH groups and, therefore, cannot function as hydrogen-bond donors. (p. 791)

aramid A polymer in which the monomer units are an aromatic diamine and an aromatic dicarboxylic acid. (p. 1125)

arene A compound containing one or more benzene rings. (p. 686)

aromatic Describes a compound containing one or more benzene rings. (p. 723)

aromatic amine An amine in which the nitrogen atom is bonded to at least one aromatic ring. (p. 834)

Arrhenius equation An equation that relates the rate constant of a reaction to the reaction's activation energy. (p. 655)

aryl group A group derived from an aromatic compound by the removal of a hydrogen atom. (p. 723)

association The clustering of molecular species in solution. (p. 421)

asymmetric synthesis A synthetic procedure that gives rise to predominantly one enantiomer. (p. 767)

atactic polypropylene One diastereomeric form of polypropylene in which the methyl groups take random positions in the front and back of the carbon chain. (p. 1138)

atom A neutral particle having one nucleus; the smallest representative sample of an element. (p. 2)

atomic mass The average mass (in u) of the atoms of the isotopes of a given element as they occur naturally. (p. 10)

atomic mass unit (u) The mass ($1.660\ 54 \times 10^{-27}$ kg) equal to $\frac{1}{12}$ of the mass of one atom of ^{12}C. (p. 10)

atomic number (Z) The number of protons in a nucleus. (p. 9)

atomic radius The distance from the nucleus of an atom at which electron–electron repulsion prevents closer approach of another atom. (p. 148)

atomisation enthalpy ($\Delta_{at}H$) The enthalpy change on rupturing all of the bonds in 1 mole of a substance in the gas phase to produce its atoms, also in the gas phase. (p. 314)

Aufbau principle The statement that the most stable arrangement of electrons in an atom results from placing each successive electron in the most stable (lowest energy) available atomic orbital. (p. 138)

autoprotolysis A process involving the transfer of a proton between two identical molecules. (p. 432)

autoprotolysis constant of water (K_w) The equilibrium constant for the reaction:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

It has the form $K_w = [H_3O^+][OH^-$, where $K_w = 1.0 \times 10^{-14}$ at 25.0 °C. (p. 433)

average rate The rate of a reaction over a particular time period. (p. 631)

Avogadro constant (N_A) 6.022×10^{23}; the number of specified entities in 1 mole. (p. 75)

axial Describes the two ligands in an octahedral or trigonal bipyramidal complex that, by convention, point above and below the plane defined by the equatorial ligands; also describes the orientation of the groups bound to a cycloalkane that are above or below the plane of the ring (p. 553)

axial bonds The bonds connecting axial groups. For instance, in an octahedral or trigonal bipyramidal complex, axial bonds point above and below the plane defined by the equatorial ligands. For organic conformers, the axial bonds are those that are

oriented perpendicular to the plane of the chair, boat or envelope. (p. 692)

azimuthal quantum number (*l*) The quantum number, restricted to integers from 0 to (*n* - 1), that indexes the electron distribution of an atomic orbital. (p. 128)

azo compounds Compounds of the form Ar—N═N—Ar, commonly used as dyes. (p. 848)

B

balanced chemical equation A chemical equation that has the same number of each type of atom and the same net charge on opposite sides of the arrow. (p. 72)

ball-and-stick model A three-dimensional representation of a molecule in which atoms are shown as balls and bonds between atoms as sticks. (p. 43)

band of stability The envelope that encloses just the stable nuclides in a plot of all nuclides constructed according to their numbers of neutrons versus their numbers of protons. (p. 1161)

barometer An instrument for measuring atmospheric pressure. (p. 214)

base Arrhenius theory — a substance that releases OH^- ions in water (p. 410); Brønsted–Lowry theory — a proton acceptor (p. 428); Lewis theory — an electron-pair donor. (p. 476)

basic Describes an aqueous solution in which $[H_3O^+] < [OH^-]$. (p. 433)

basicity constant (K_b) The equilibrium constant for the reaction of a base with water. For the general equilibrium:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}.$$

(p. 443)

battery A group of galvanic cells usually connected in series. (p. 528)

B-DNA The predominant form of DNA in dilute aqueous solution and the most common form in nature. The base pairs are stacked on top of each other, with a distance of 0.34 nm between the base pairs and with 10 base pairs in one complete turn of the helix. (p. 1093)

becquerel (Bq) The SI unit for the activity of a radioactive source; 1 Bq = 1 disintegration s^{-1}. (p. 1168)

Beer–Lambert law This relates the absorbance (*A*) of a solution to the molar absorption coefficient (ε) of the absorbing species, the concentration (*c*) of the absorbing species, and the pathlength of the cell (*l*), via the equation $A = \varepsilon cl$. (pp. 574, 905)

Beer's law See *Beer–Lambert law*. (p. 574)

β-elimination An elimination reaction where atoms or groups are removed from two adjacent carbon atoms. (p. 783)

bending A type of vibration that changes bond angles. (p. 872)

benzaldehyde The common name for the monosubstituted benzene C_6H_5CHO. (p. 728)

benzoic acid The common name for the monosubstituted benzene C_6H_5COOH. (p. 728)

benzyl group

	The $C_6H_5CH_2$— group. (p. 728)
benzylic carbon	An sp^3 carbon atom bonded to a benzene ring. (p. 1011)
benzylic hydrogen	A hydrogen atom bonded to a benzylic carbon atom. (p. 1011)
beta particle	An electron emitted by radioactive decay. (p. 1164)
β-pleated sheet	A type of secondary structure in which two sections of polypeptide chain are aligned parallel or antiparallel to one another. (p. 1072)
bidentate	Describes ligands with two donor atoms that can be simultaneously attached to the same metal ion. (p. 547)
bimolecular reaction	A reaction in which two species are involved in the transition state of the rate-determining step. (p. 786)
binary compound	A compound that contains only two elements. (p. 36)
binding energy per nucleon	The nuclear binding energy divided by the mass number, *A*; a measure of how tightly each nucleon is bound to the nucleus. (p. 1162)
biodegradable polymer	A polymer designed to degrade as a result of enzymecatalysed hydrolysis of the polymer chain into smaller, biologically acceptable units. (p. 1151)
biopolymer	A polymer found in nature, such as starch, proteins and peptides, DNA and RNA. (p. 1118)
block	Describes a polymer with two or more homopolymer subunits joined together by covalent bonds. (p. 1123)
boat conformation	The conformation of cyclohexane that roughly resembles a ‘boat’. (p. 692)
body-centred cubic lattice (bcc)	The crystal structure whose unit cell is a cube with lattice points at its corners and its centre. (p. 273)
boiling point elevation (ΔT_b)	A colligative property of a solution by which the solution's boiling point is higher than that of the pure solvent. (p. 412)
bomb calorimeter	Apparatus used in the determination of the heat of a reaction under constant volume conditions. (p. 302)
bond energy	The energy difference between two atoms at their bond distance and the infinitely separated atoms. (p. 167)
bond enthalpy	The enthalpy change on breaking 1 mole of a particular bond to give electrically neutral fragments. (p. 313)
bonding molecular orbital	An orbital formed from atomic orbitals in which electron density is maximised between the bonded atoms. (p. 198)
bonding orbital	An orbital with high electron density between atoms, formed by constructive interaction between atomic orbitals. (p. 189)
bond length	The separation distance between two atoms that gives the maximum possible energetic advantage over infinitely separated atoms. (p. 167)
bond order	$\frac{1}{2}$ (number of electrons in bonding molecular orbitals–number of electrons in antibonding molecular orbitals). (p. 199)
boundary	The interface between a system and its surroundings across which energy or matter

might pass. (p. 296)

Bragg equation $n\lambda = 2d \sin \theta$. (p. 278)

bridged halonium ion A cyclic structure containing a halonium ion. (p. 720)

Brønsted–Lowry A definition of acids and bases in which an acid is a proton donor and a base is a proton acceptor. (p. 428)

buffer capacity A measure of the amount of H_3O^+ or OH^- that can be added to a buffer solution without significant change in its pH. (p. 467)

buffer solution A solution containing appreciable amounts of either a weak acid and its conjugate base, or a weak base and its conjugate acid. (p. 462)

burette A device used for the addition of accurately measured volumes of solution in a titration. (p. 467)

by-product Substances formed by side reactions. (p. 88)

C

^{13}C-NMR spectroscopy Nuclear magnetic resonance spectroscopy of carbon atoms within molecules. It provides information about the carbon–hydrogen framework of a molecule. (p. 883)

***C*-terminal amino acid** The amino acid of a polypeptide with the free —COO^-group. (p. 1066)

calorimeter A device for measuring the heat evolved or absorbed in a chemical reaction. (p. 302)

candela The SI unit of luminous intensity. (p. 25)

capillary action The upward movement of a liquid in a narrow tube against the force of gravity. (p. 254)

carbanion An anion in which carbon has an unshared pair of electrons and bears a negative charge. (p. 943)

carbocation A species containing a positively charged carbon atom with only three bonds to it. (p. 714)

carbohydrates Polyhydroxyaldehydes, polyhydroxyketones or substances that give either of these compounds after hydrolysis. (p. 978)

carboxylic acid group See *carboxyl group*. (p. 1002)

carboxyl group A —COOH group. (p. 1002)

catalysis Rate enhancement caused by a catalyst. (p. 668)

catalyst A substance that in relatively small proportions accelerates the rate of a reaction without being chemically changed. (p. 668)

catalytic hydrogenation Reduction by hydrogen in the presence of a catalyst. (p. 720)

catalytic reduction Reduction in the presence of a catalyst. (p. 720)

catenation The linking of atoms of the same element (particularly carbon) to form chains. (p. 38)

cathode The negative electrode in a gas discharge tube; the electrode at which reduction

	occurs during an electrochemical change. (p. 503)
cathodic protection	The process in which a structural metal, such as iron, is protected from corrosion by connecting it to a metal that has a more negative reduction half-cell potential. (p. 523)
cation	A positively charged ion. (p. 2)
cationic polymerisation	Ionic polymerisation in which the chain carriers are cations. (p. 1138)
cell diagram	A shorthand way of describing the make-up of a galvanic cell. (p. 505)
cell potential (E_{cell})	The maximum potential that a given cell can generate. (p. 507)
cell reaction	The overall chemical change that takes place in an electrolytic cell or a galvanic cell. (p. 502)
ceramics	Materials composed of inorganic components that have been heat treated. (p. 282)
chain-growth polymerisation	Polymerisation that involves sequential addition reactions, either to unsaturated monomers or to monomers with other functional groups. (p. 1123)
chain initiation	In radical or cationic polymerisation, the formation of radicals or carbocations from molecules containing only paired electrons. (p. 1134)
chain length	In polymerisation, the number of times a cycle of chainpropagation steps repeats. (p. 1135)
chain propagation	In radical or cationic polymerisation, the reaction of a radical or carbocation with a molecule to give a new radical or carbocation. (p. 1134)
chain termination	In radical polymerisation, the reaction between two radicals to form a covalent bond or to undergo disproportionation into a saturated and an unsaturated compound; in cationic polymerisation, the reaction between a carbocation and an anion to give an uncharged stable compound. (p. 1134)
chain-transfer reaction	In radical polymerisation, the transfer of reactivity of an end-group from one chain to another during polymerisation. (p. 1136)
chair conformation	The most stable puckered conformation of a cyclohexane ring. (pp. 691, 983)
chalcogens	The elements in group 16 of the periodic table. (p. 15)
chelate complex	A complex ion containing one or more chelate rings. (p. 547)
chelate effect	The larger value of the cumulative formation constant (β_n) found for complexes containing chelate rings when compared with analogous complexes containing monodentate ligands. (p. 562)
chelate ring	The ring formed when a polydentate ligand coordinates to a transition metal ion. (p. 547)
chemical equation	A form of notation used to describe chemical reactions, in which the reactants and products of the reaction are separated by a directional arrow, with the reactants appearing on the left-hand side. (pp. 4, 72)
chemical equilibrium	A situation in which the chemical composition of a system does not change with time. (p. 346)
chemical formula	A formula written using chemical symbols and subscripts that describes the composition of a chemical compound or element. (p. 36)
chemical kinetics	The study of the rates of chemical reactions. (p. 630)
chemical reaction	A process involving transformation of chemical species into different chemical species, usually involving the making and/or breaking of chemical bonds. (pp. 2, 72)

chemical shift (δ)	The quantity used in NMR spectroscopy to identify the positions of signals produced by the nuclei of a sample. The unit of chemical shift (δ) is parts per million (ppm). (p. 885)
chemical symbol	The formula of an element. (p. 9)
chemical thermodynamics	The study of the role of energy in chemical change and in determining the behaviour of materials. (p. 295)
chiral	Describes an object that is not superimposable on its mirror image. (p. 746)
chromatin	A complex formed between negatively charged DNA molecules and positively charged histones. (p. 1096)
circular DNA	A type of double-stranded DNA in which the 5′ and the 3′ ends of each strand are joined by phosphodiester groups. (p. 1095)
***cis* isomer**	A stereoisomer in which two groups lie on the same side of a reference plane. (p. 555)
***cis–trans* isomers**	Stereoisomers that differ in the positioning of two groups with respect to a reference plane. (pp. 555, 695)
close-packed structures	The most efficient arrangement for packing atoms, molecules or ions in a regular crystal. (p. 270)
coding strand	The DNA strand which has the same base sequence as the mRNA transcript produced during DNA transcription, except that the thymine base is replaced by uracil. (p. 1102)
codon	A triplet of nucleotides on mRNA that directs the incorporation of a specific amino acid into a polypeptide sequence. (p. 1103)
colligative property	A property, such as vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure, that depends only on the ratio of the numbers of moles of solute and solvent particles and not on their chemical identities. (p. 408)
collision theory	A theory that assumes that for a reaction to occur, reactant molecules must collide with proper orientation and with an energy larger than a threshold value. (p. 651)
combustion	A rapid reaction with oxygen accompanied by a flame and the evolution of heat and light. (p. 82)
combustion reaction	The reaction of a chemical substance with oxygen. (p. 302)
common ion	An ion in a mixture of ionic substances that is common to the formulae of at least two of those substances. (p. 404)
common ion effect	The effect by which the solubility of one salt is reduced by the presence of another having a common ion. (p. 404)
competing reaction	A reaction that reduces the yield of the main product by forming by-products. (p. 88)
complementary colour	The colour of the reflected or transmitted light when one component of white light is removed by absorption. (p. 571)
complex	The combination of one or more anions or neutral molecules (ligands) with a transition metal ion. (p. 544)
complex splitting pattern	A splitting pattern resulting from more than one set of equivalent hydrogen atoms. Signals of this type are called multiplets. (p. 892)
compound	A chemical substance containing two or more elements in a definite and unchanging proportion. (p. 2)
compound	An atomic nucleus carrying excess energy following its capture of some

nucleus	bombarding particle. (p. 1171)
concentration	The ratio of the quantity of solute to the quantity of solution (or the quantity of solvent); see also *molal concentration; molar concentration; mole fraction*. (p. 90)
concentration cell	An electrolytic cell in which the potential difference is caused by a difference in concentration of some component in the electrolyte. (p. 521)
concentration table	A table that outlines the changes in concentration that occur as a chemical system comes to equilibrium. (p. 371)
condensation	Conversion of a vapour into its liquid. (p. 240)
condensation polymerisation	See *stepgrowth polymerisation*. (p. 1123)
condensed structural formula	A shorthand method of representing molecules in which bonds between atoms are not drawn explicitly. (p. 39)
configurational isomers	Isomers that cannot be interconverted by rotation around a single bond. (p. 701)
conformation	The representation of the position of atoms in a conformer. (p. 688)
conformer	Any three-dimensional arrangement of atoms that results from rotation around a single bond. (p. 688)
conjugate acid	The species in a conjugate acid–base pair that has the greater number of protons. (p. 430)
conjugate acid–base pair	Two species that differ only by a proton. (p. 430)
conjugate base	The species in a conjugate acid–base pair that has the fewer number of protons. (p. 430)
constitutional isomers	Isomers with different sequences of atom connectivity. (pp. 58, 746)
coordinate bond	A covalent bond between a Lewis acidic metal ion and a Lewis basic ligand in which both electrons originate from the ligand. (p. 552)
coordination chemistry	The study of transition metal complexes. (p. 552)
coordination compound	A transition metal complex. (p. 552)
coordination isomers	Isomers that result when ligands are exchanged between a complex cation and a complex anion of the same coordination compound, e.g. $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6]\,[Co(CN)_6]$. (p. 555)
coordination number	The number of donor atoms coordinated to a metal ion. (p. 553)
core electrons	The inner atomic electrons with principal quantum number less than that of the valence electrons. (p. 140)
correlation table	A table of data on spectroscopic absorption patterns of selected functional groups. (p. 872)
coulomb (C)	The SI unit of electric charge. (p. 501)
counterion	An ion that balances the charge on a cationic or anionic complex ion. (p. 552)
covalent bond	A chemical bond in which two atoms share one or more pairs of electrons. (pp. 2, 166)
critical mass	The mass of a fissile isotope above which a self-sustaining chain reaction occurs. (p. 1176)

critical point The temperature and pressure above which the distinction between the liquid and vapour phases disappears.(p. 263)

critical pressure The pressure associated with the critical point. (p. 263)

critical temperature (T_c) The temperature associated with the critical point. (p. 263)

cross-links A bridge formed between polymer strands. (p. 1147)

crystal field splitting energy (Δ_0) The difference in energy between the two sets of *d* orbitals in an octahedral or tetrahedral complex ion. (p. 567)

crystal field theory A theory that considers the effects of the polarities or the charges of the ligands in a complex ion on the energies of the *d* orbitals of the central metal ion. (p. 566)

crystal lattice The lattice of a crystalline solid. (p. 273)

crystalline defects Imperfections in a regular solid. (p. 281)

crystalline domain An ordered crystalline region in the solid state of a polymer; also called crystallites. (p. 1119)

crystalline solid A solid that has a regular arrangement of unit cells and diffracts X-rays. (p. 273)

cubic close-packed (ccp) The arrangement in which close-packed layers are stacked in an ABCABC … pattern. (p. 270)

cumulative formation constant (β_n) The equilibrium constant for the process:

$$M^{x+}(aq) + nL(aq) \rightleftharpoons [ML_n]^{x+}(aq)$$

given by the expression $\beta_n = \dfrac{[ML_n]^{x+}}{[M^{x+}][L]^n}$ (p. 561)

cyanohydrins A compound in which both an —OH and a —CN group are bonded to the same carbon atom. (p. 946)

cyclic ether An ether in which the oxygen atom is one of the atoms of a ring. (p. 829)

cycloalkane A saturated hydrocarbon with carbon atoms joined together to form a ring. (pp. 54, 690)

cycloalkene An unsaturated hydrocarbon with carbon atoms joined together to form a ring that contains a carbon–carbon double bond. (p. 707)

D

***d*-block elements** Collective name for the elements in groups 3 to 12 of the periodic table. (p. 14)

***d–d* transition** An electronic transition between the t_{2g} and e_g sets of orbitals in an octahedral complex. (p. 570)

Dalton's atomic theory Matter consists of tiny, indestructible particles called atoms. All atoms of one element are identical. The atoms of different elements have different masses. Atoms combine in definite ratios of atoms when they form compounds. (p. 4)

Dalton's law of partial pressures The law stating that in a gas mixture, each gas exerts a pressure equal to the pressure that it would exert if present by itself under otherwise identical conditions. (p. 227)

dative bond A coordinate bond. (p. 552)

decay constant (*k*)	The first-order rate constant for radioactive decay. (p. 1168)
degenerate	Describes orbitals with the same energy. (pp. 135, 566)
degradation	Any change in properties of a polymer relative to their initial desired properties. (p. 1147)
dehydration	Elimination of a molecule of water from a compound. (p. 819)
dehydrohalogenation	A process in which a halogen is removed from one carbon atom of a haloalkane and a hydrogen atom is removed from the adjacent carbon atom to form a carbon–carbon double bond. (p. 794)
delocalised bond	A bond in which electron density is distributed over more than two atoms. (p. 189)
denaturation	Interference with the secondary, tertiary and quaternary structures of a protein, changing its conformation and often removing its functionality. (p. 1078)
deposition	The phase change in which a vapour converts directly to a solid without passing through the liquid phase. (p. 261)
deshielded	Describes the situation in NMR spectroscopy in which resonance or inductive effects reduce the electron density around a nucleus, thus increasing the ability of an applied magnetic field to bring the nucleus into resonance. (p. 885)
dextrorotatory	Describes the clockwise rotation of a plane of polarised light in a polarimeter. (p. 762)
dialysis	The passage of solvent and small molecules and ions through a semipermeable membrane. (p. 414)
diamagnetic	The quality of not being attracted to a magnetic field. Substances with no unpaired electrons are diamagnetic. (pp. 146, 544)
diastereomers	A pair of stereoisomers that are not mirror images of each other. (p. 747)
differential rate law	A rate law that expresses the rate of a reaction as a function of concentration. (p. 637)
diffraction pattern	The pattern formed from X-rays diffracted by a crystal. (p. 278)
diffusion	The movement of one type of gas molecule through molecules of another type. (p. 223)
dimensional analysis	The use of units of a physical quantity to derive the equation used to determine its value. (p. 28)
dimer	A close association of two similar molecules. (p. 421)
diol	A compound with two alcohol groups. (p. 811)
dipeptide	A molecule containing two amino acid units joined by a peptide bond. (p. 1066)
dipole–dipole force	The attractive force between polar molecules that results from the negative end of one molecule aligning with the positive end of its neighbour. (p. 241)
dipole-induced dipole force	The force resulting from the induction of a dipole in a molecule by a neighbouring molecule having a permanent dipole. (p. 241)
dipole moment	The net electrical character arising from an asymmetric charge distribution. (p. 183)
diprotic acid	An acid that can potentially donate two equivalents of protons to water. (p. 429)
disaccharides	Carbohydrates containing two monosaccharide units joined by a glycosidic bond. (p. 991)
dispersion force	The attraction between the negatively charged electron cloud of one molecule and the positively charged nuclei of neighbouring molecules. (p. 241)

diprotic base A base which is able to accept two protons. (p. 430)

disproportionation An electrochemical process in which a species is simultaneously oxidised and reduced to form two different products. (pp. 529, 565)

dissociation The breaking apart of a molecule or ionic solid into ions when dissolved in a solvent (usually water). (pp. 96, 418)

dissolution The process of dissolving a solute in a solvent. (p. 390)

disulfide A compound of the form RS—SR, where the R groups are either alkyl or aryl groups. (p. 834)

disulfide bond A covalent bond between two sulfur atoms, i.e. an —S—S— bond. (p. 1072)

D-monosaccharide A monosaccharide that, when written as a Fischer projection, has the —OH on its penultimate carbon atom to the right. (p. 979)

DNA Deoxyribonucleic acid, a nucleic acid that hydrolyses to 2′-deoxyribose, phosphate ions, adenine, thymine, guanine and cytosine, and that carries genes. (p. 1088)

DNA ligase An enzyme that repairs singlestranded discontinuities in double-stranded DNA. (p. 1097)

DNA polymerase An enzyme that catalyses the polymerisation of deoxyribonucleotides to form DNA. (p. 1097)

donor atom An atom of a ligand in a complex that is directly coordinated to the transition metal ion. (p. 547)

donor covalent bond A coordinate bond. (p. 552)

double bond A chemical bond containing two pairs of bonding electrons. (p. 171)

double bond equivalent See *index of hydrogen deficiency*. (p. 864)

double helix A type of secondary structure of DNA molecules in which two antiparallel polynucleotide strands are coiled in a right-handed manner around the same axis. (p. 1092)

doublet A signal in ^{1}H-NMR spectroscopy that has been split into two peaks in a ratio of 1 : 1. (p. 892)

downfield Describes a signal in NMR spectroscopy that is towards the left of the spectrum or of another signal. (p. 886)

dry cell battery A cell with an immobilised electrolyte, such as the Leclanché cell. (p. 529)

dynamic equilibrium An equilibrium in which the rates of the forward and reverse reactions are equal. (p. 346)

E

E1 A process in which the bond to the leaving group is completely broken before the hydrogen atom is removed and the carbon–carbon double bond is formed. (p. 795)

E2 A process in which the β-hydrogen is lost at the same time as the bond to the leaving group is broken and the carbon–carbon double bond is formed. (p. 796)

effective nuclear charge (Z_{eff}) The net positive charge, equal to the nuclear charge minus the effects of screening, that an electron in an atomic orbital experiences. (p. 136)

effusion The escape of a gas through a pinhole from a container into a vacuum. (p. 223)

elastomer A material that, when stretched or otherwise distorted, returns to its original shape

	when the distorting force is released. (p. 1120)
electrochemical changes	A chemical change that is caused by, or that produces, electricity. (p. 503)
electrochemical potential	The potential difference between the electrodes in a galvanic cell. (p. 502)
electrochemistry	The study of electrochemical changes. (p. 503)
electrolysis	The production of a chemical change by the passage of electricity through a solution that contains ions or through a molten ionic compound. (p. 524)
electrolysis cell	An apparatus for electrolysis. (p. 524)
electrolytic cell	See *electrolysis cell.* (p. 524)
electrolytic conduction	The transport of electric charge by ions. (p. 524)
electromagnetic radiation	Energy propagated through space in the form of oscillating electric and magnetic fields. (pp. 110, 870)
electron	A subatomic particle $\left(e, {}^{0}_{-1}e\right)$ with a charge of -1 and mass of 5.4858×10^{-4} u (9.1094×10^{-31} kg), that is outside an atomic nucleus; the particle that moves when an electric current flows. (p. 2)
electron affinity (E_{EA})	The energy change accompanying the attachment of an electron to an atom or anion. (p. 151)
electron capture	The capture by a nucleus of an orbital electron that changes a proton into a neutron in the nucleus. (p. 1166)
electron configuration	The distribution of electrons among the various orbitals of an atom, molecule or ion. (p. 141)
electron density picture	A twodimensional dot drawing representing the distribution of electron density in an orbital. (p. 131)
electron density plot	A plot of the distribution of electron probability in space around an atom or molecule. (p. 131)
electronegativity	A measure of the ability of an atom in a molecule to attract the shared electrons in a chemical bond. (p. 168)
electronic conduction	The conduction of electric charge by the movement of electrons. (p. 504)
electron paramagnetic resonance (EPR)	See *electron spin resonance (ESR).* (p. 906)
electron spin resonance (ESR)	A type of magnetic resonance used to study free radicals, paramagnetic species and other substances containing unpaired electrons; also known as electron paramagnetic resonance (EPR). (p. 906)
electronic transition	The movement of electrons between states of different energies. (pp. 17, 570)
electrophile	Any molecule or ion that can accept a pair of electrons to form a new covalent bond; a Lewis acid. (pp. 477, 712)
electrophilic aromatic substitution	A reaction in which an electrophile, E^+, substitutes for a hydrogen on an aromatic ring. (p. 730)
electrophoresis	The process of separating compounds on the basis of their electric charge. (p. 1063)
element	A chemical species consisting of atoms of a single type. (p. 2)

elemental analysis	A method of chemical analysis by which a given amount of a compound is decomposed chemically to find the masses of elements within it. (p. 80)
elementary reaction	One of the individual steps in the mechanism of a reaction. (p. 658)
emission spectrum	The distribution of wavelengths of light given off by a species in an excited state. (p. 117)
empirical formula	A chemical formula that uses the smallest whole-number subscripts to give the proportions of atoms of the different elements present. (p. 77)
enantiomers	A pair of stereoisomers that are nonsuperimposable mirror images of each other. (p. 746)
endothermic	Describes a change in which energy enters a system from the surroundings. (p. 304)
endpoint	The point in a titration when the indicator changes colour. (p. 467)
energy level diagram	A diagram of the specific energy levels of a species, showing increasing energy on the *y*-axis. (p. 122)
enol	A molecule containing an —OH group bonded to a carbon atom of a carbon–carbon double bond. (p. 962)
enthalpy (*H*)	The heat content of a system measured under constant pressure conditions. (p. 296)
enthalpy of hydrogenation	The enthalpy of reaction, $\Delta H^{\ominus}$, with hydrogen. (p. 721)
enthalpy of solution ($\Delta_{sol}H$)	The enthalpy change that accompanies the formation of a solution from a solute and a solvent. (p. 398)
entropy (*S*)	A thermodynamic quantity related to the number of equivalent ways the energy of a system can be distributed. The greater this number, the more probable is the state and the higher is the entropy. (p. 296)
epoxy resin	Material prepared by a polymerisation in which one monomer contains at least two epoxy groups. (p. 1132)
equatorial	Describes a covalent bond located in the plane perpendicular to the axial ligands of an octahedral or trigonal bipyramidal molecule. (p. 553)
equatorial bonds	Bonds oriented in a chair conformation of a cyclic structure in the general plane of the seat of the chair. (p. 692)
equilibrium constant (*K*)	The value of the equilibrium constant expression when the system is at equilibrium. (p. 347)
equilibrium constant expression	A fraction in which the numerator is the product of the equilibrium molar concentrations of the products, each raised to a power equal to its coefficient in the equilibrium equation, and the denominator is the product of the equilibrium molar concentrations of the reactants, each raised to a power equal to its coefficient in the equation. (For gaseous reactions, partial pressures can be used in place of molar concentrations.) (p. 347)
equivalence point	The point in a titration when the stoichiometry of the reaction is satisfied. (p. 467)
equivalent hydrogen atoms	Hydrogen atoms that are chemically equivalent. (p. 886)
ester	A functional group generated by combining a carboxylic acid and an alcohol with the elimination of water to give a carbonyl carbon atom that is also further bound to a different saturated carbon atom via an oxygen atom linkage. (p. 1003)
ether	A compound of the form ROR, where the R groups are either alkyl or aryl groups,

	such that an oxygen atom is bonded to two carbon atoms that are not also bonded to a heteroatom. (p. 829)
excess reagent	The reagent left over when the limiting reagent has been used up. (p. 87)
excited state	Any state in which a chemical system is not in its lowest possible energy state. (pp. 16, 116)
exothermic	Describes a change in which energy leaves a system and enters the surroundings. (p. 304)
extensive property	A property of an object that is described by a physical quantity (such as mass and volume) that is proportional to the size or amount of the object. (p. 300)
***E*, *Z* system**	A system used to specify the configuration of groups about a carbon–carbon double bond. (p. 706)

F

***f*-block elements**	A collective name for the lanthanoid and actinoid elements. (p. 14)
face-centred cubic structure (fcc)	A crystalline structure whose unit cell has lattice points at each corner of a cube plus one additional lattice point in the centre of each face of the cube. (p. 274)
facial (*fac*)	An isomer of an octahedral complex $[ML_3X_3]^{n+}$ in which the two sets of ligands occupy the face of an octahedron. (p. 557)
Faraday constant	1 F = 96 485 C mol^{-1}. (p. 516)
Faraday's law	Allows the calculation of the amount of product formed during electrolysis; amount of product $= \frac{It}{nF}$. (p. 527)
fat	A triglyceride that is semisolid or solid at room temperature. (p. 1039)
fatty acid	A long, unbranched carboxylic acid, most commonly of 12 to 20 carbon atoms, derived from the hydrolysis of animal fats, vegetable oils or the phospholipids of biological membranes. (p. 1038)
ferromagnetism	A property of species containing unpaired electrons where all of the electron spins are oriented in the same direction in the absence of a magnetic field. (p. 576)
fingerprint region	In infrared spectroscopy, the region of the spectrum from 1000 to 400 cm^{-1}. (p. 872)
first law of thermodynamics	A formal statement of the law of conservation of energy; $U = q + w$. (p. 298)
Fischer esterification	The process of forming an ester by refluxing a carboxylic acid and an alcohol in the presence of an acid catalyst, commonly sulfuric acid. (p. 1019)
Fischer projections	Two-dimensional representations that show the configuration of a stereocentre; horizontal lines represent bonds projecting forward from the stereocentre, vertical lines represent bonds projecting to the rear. (p. 979)
fishhook arrow	A single-barbed, curved arrow used to show the change in position of a single electron. (p. 1134)
fissile isotope	An isotope capable of undergoing fission following neutron capture. (p. 1176)
5′ end	The end of a polynucleotide at which the 5′ —OH group of the terminal 2′-deoxyribose/ribose unit is free. (p. 1090)
formal charge	The charge that an atom in a molecule would have if each of its bonding electrons were equally shared with its bonding partner(s). (p. 173)

freezing point depression (ΔT_f) A colligative property of a liquid solution by which the freezing point of the solution is lower than that of the pure solvent. (p. 412)

frequency (ν) The number of full cycles of a wave that pass a given point in a second. (pp. 110, 870)

frequency factor The proportionality constant A in the Arrhenius equation. (p. 655)

Friedel–Crafts acylation The acylation of aromatic rings with an acyl chloride using anhydrous aluminium chloride as a catalyst. (p. 734)

Friedel–Crafts alkylation The alkylation of an aromatic ring and an alkyl halide using anhydrous aluminium chloride as a catalyst. (p. 733)

fuel cell An electrochemical cell that converts the chemical energy of a reaction between fuels, such as liquid hydrogen and liquid oxygen, directly and continuously into electrical energy. (p. 533)

functional group A group of atoms within an organic molecule that determines the molecule's chemical reactivity. (p. 50)

furanose a five-membered cyclic hemiacetal form of a monosaccharide. (p. 982)

G

galvanic cell An electrochemical cell in which a spontaneous redox reaction produces electricity. (p. 502)

galvanisation The coating of a metal, such as iron, with another, such as zinc, to protect against corrosion. (p. 523)

gamma radiation Electromagnetic radiation with wavelengths in the range of 1×10^{-10} m or less. (p. 1165)

gas constant (R) The proportionality constant used in the ideal gas equation. (p. 216)

genetic code The correlation of codons with amino acids. (p. 1103)

Gibbs energy (G) A thermodynamic quantity that relates enthalpy (H), entropy (S) and temperature (T) by the equation $G = H - TS$. (p. 296)

Gibbs energy diagram A plot of the changes in Gibbs energy for a system versus its composition. (p. 357)

glass An amorphous solid that has cooled to a solid state without crystallising. (p. 281)

glycol A diol in which the —OH groups are on adjacent carbon atoms. (p. 811)

glycoside A carbohydrate in which the —OH on its anomeric carbon atom is replaced by —OR. (p. 985)

glycosidic bond The bond from the anomeric carbon atom of a glycoside to an —OR group. (p. 985)

Grignard reagent An organomagnesium compound of the type RMgX or ArMgX. (p. 942)

ground state The lowest possible energy state of a chemical system. (pp. 16, 116)

ground-state configuration The most stable orbital arrangement of electrons in an atom or molecule. (p. 137)

group A vertical column of elements in the periodic table. (p. 14)

H

^{1}H-NMR Nuclear magnetic resonance spectroscopy of hydrogen atoms within molecules. It

spectroscopy provides information about the carbon–hydrogen framework of a molecule. (p. 883)

half-cell That part of a galvanic cell in which either oxidation or reduction takes place. (p. 502)

half-equation A chemical equation describing either the oxidation or reduction process in a redox reaction. (p. 496)

half-life $\left(t\frac{1}{2}\right)$ The time required for a reactant concentration or the mass of a radionuclide to be reduced by half. (pp. 634, 1168)

haloalkanes Compounds containing a halogen atom covalently bonded to an sp^3 hybridised carbon atom. (p. 778)

haloform A substituted methane molecule containing three halogen atoms of the same type. (p. 779)

halogenation A reaction in which some of the hydrogen atoms are substituted by halogen atoms. (p. 780)

halogens The elements in group 17 of the periodic table. (p. 15)

halonium ion An ion in which a halogen atom bears a positive charge. (p. 720)

hardening The process of converting oils to fats by catalytic hydrogenation of the double bonds. (p. 1040)

hard Lewis acid A Lewis acid containing an acceptor atom of low polarisibility. (p. 479)

hard Lewis base A Lewis base containing one or more electron pairs of low polarisibility. (p. 479)

hashed wedge A hashed wedge denotes a bond going into the plane of the page away from the observer. (pp. 40, 43)

Haworth projection A way of viewing furanose and pyranose forms of monosaccharides. The ring is drawn flat and viewed through its edge, with the anomeric carbon atom on the right and the oxygen atom of the ring at the rear to the right. (p. 982)

heat (q) A transfer of energy due to a temperature difference. (p. 295)

heat capacity (C) The quantity of heat needed to raise the temperature of an object by 1 K. (p. 299)

heat of reaction at constant pressure (q_p) The heat of a reaction in an open system. (p. 304)

heat of reaction at constant volume (q_v) The heat of a reaction in a sealed vessel, such as a bomb calorimeter. (p. 302)

hemiacetal A molecule containing an —OH and an —OR or —OAr group bonded to the same carbon atom. (pp. 946, 981)

Henderson–Hasselbalch equation An equation that relates the pH of a buffer solution to the pK_a of the weak acid and the ratio of the conjugate base to the acid;

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}.$$

(p. 464)

Henry's law The concentration of a gas dissolved in a liquid at any given temperature is directly proportional to the partial pressure of the gas above the solution. (p. 394)

Hertz (Hz) The SI unit of frequency. One hertz equals one wave cycle per second. (p. 870)

Hess's law For any reaction that can be written in steps, the standard enthalpy of reaction is the same as the sum of the standard enthalpies of reaction for the steps. (p. 308)

heteroatom	Any atom in an organic molecule other than carbon or hydrogen. (p. 829)
heterocyclic amine	An amine in which nitrogen is one of the atoms of a ring. (p. 834)
heterocyclic aromatic amine	An amine in which nitrogen is one of the atoms of an aromatic ring. (p. 834)
heterocyclic compound	An organic compound with one or more atoms other than carbon in its ring. (p. 726)
heterogeneous catalyst	A catalyst that is in a different phase from the reactants. (p. 668)
heterogeneous equilibrium	An equilibrium system involving more than one phase. (p. 356)
heterogeneous reaction	A reaction in which not all of the chemical species are in the same phase. (pp. 356, 635)
heterolytic	Describes a bond-breaking process in which both electrons of a single bond end up on one of the atoms of the bond. (p. 45)
heterolytic cleavage	See *heterolytic*. (p. 457)
hexagonal close-packed (hcp)	The close packing arrangement in which closepacked layers are stacked in an ABAB pattern. (p. 270)
high-density polyethylene (HDPE or PE-HD)	Polyethylene with a density of 0.96 g cm^{-3} and a melt transition temperature (T_m) of 133 °C. (p. 1137)
high resolution mass spectrometry	A technique that allows the precise measurement of the mass to charge ratio of ions. (p. 868)
high-spin	Describes a complex ion or coordination compound with the maximum number of unpaired electrons. (p. 568)
histone	A protein that is particularly rich in the basic amino acids lysine and arginine and that is found associated with DNA molecules; see also *chromatin*. (p. 1096)
homogeneous catalyst	A catalyst that is in the same phase as the reactants. (p. 668)
homogeneous equilibrium	An equilibrium system in which all components are in the same phase. (p. 356)
homogeneous reaction	A chemical reaction in which all participating species are in the same phase. (pp. 356, 635)
homolytic	Describes a bond-breaking process in which each of the bonded atoms receives one electron. (p. 46)
homolytic cleavage	See *homolytic*. (p. 457)
Hund's rule	The observation that the lowest energy arrangement of electrons among orbitals of equal energy is the one that maximises the number of unpaired electron spins. (p. 144)
hybridisation of atomic orbitals	The formation of a set of hybrid orbitals with favourable directional characteristics by mixing together two or more valence orbitals of the same atom. (pp. 190, 724)
hybrid orbital	An atomic orbital obtained by combining two or more valence orbitals on the same atom. (p. 190)

hydrate A solid that contains a definite number of waters of crystallisation. (p. 37)

hydration The addition of water; the development in an aqueous solution of a ‘cage’ of water molecules around ions or polar molecules of the solute. (pp. 396, 717)

hydration enthalpy The enthalpy change when gaseous solute particles (obtained from 1 mole of solute) are dissolved in water. (p. 397)

hydrate isomers Isomers of complex ions in which water is either coordinated to the transition metal ion or acts as water of crystallisation. (p. 555)

hydride ion A hydrogen atom with two electrons in its valence shell; $H:^-$. (p. 957)

hydrocarbon A molecule composed only of carbon and hydrogen atoms. (pp. 54, 686)

hydrogen bonding A moderately strong intermolecular attraction caused by the partial sharing of electrons between a highly electronegative atom of F, O or N and the polar hydrogen atom in a F—H, O—H or N—H bond. (pp. 241, 813, 1074)

hydrometer An instrument used for measuring the density of a liquid. (p. 529)

hydronium ion (H_3O^+) The product of the reaction of a proton with water. It can also be thought of as a hydrated proton. (p. 428)

hydrophilic Describes a polar compound that dissolves readily in water. (p. 1010)

hydrophobic Describes a nonpolar compound that tends to be insoluble in water. (p. 1010)

hydrophobic interaction The force of attraction between nonpolar parts of a molecule or molecules. (p. 1074)

hydroxide ion (OH^-) The product of deprotonation of water. (p. 428)

hydroxyl group An —OH group. (p. 810)

hypertonic Describes a solution that has a higher osmotic pressure than cellular fluids. (p. 417)

hypotonic Describes a solution that has a lower osmotic pressure than cellular fluids. (p. 417)

I

ideal gas A gas in which molecular volumes and intermolecular forces are both negligible. (p. 216)

ideal gas equation The equation describing the behaviour of an ideal gas, $pV = nRT$. (p. 216)

ideal solution A hypothetical solution that obeys Raoult's law exactly. (p. 410)

immiscible Describes liquids that do not mix; see also *insoluble*. (p. 394)

index of hydrogen deficiency (IHD) The sum of the number of rings and π bonds in a molecule. (p. 864)

inductive effect The polarisation of electron density transmitted through covalent bonds caused by a nearby atom of higher electronegativity. (p. 716)

inert complex A transition metal complex in which ligand exchange is slow. (p. 565)

infrared active Any vibration that results in the absorption of infrared radiation. For a molecule to absorb infrared radiation, the bond undergoing vibration must be polar and its vibration must cause a periodic change in the bond dipole; the greater the polarity of the bond, the more intense the absorption. (p. 872)

infrared The portion of the electromagnetic spectrum with wavelengths in the range 7.8×10^{-7}

radiation	m to 2.0×10^{-3} m. (p. 870)
initial rate	The rate of a chemical reaction immediately after mixing the reactants. (p. 636)
insoluble	Describes a solute that does not dissolve in a solvent. (p. 397)
instantaneous rate of change of concentration	The rate of change of concentration of a reactant or product in a chemical reaction at a particular time. (p. 632)
integral membrane protein	A protein incorporated into a cell membrane. (p. 1078)
integrated rate law	A rate law that expresses the rate of a reaction as a function of time. (p. 637)
integration	A mathematical process used for determining the area under a signal in an NMR spectrum. (p. 888)
intensity	The brightness (number of photons) of light. (p. 110)
intensive property	A property of an object that is described by a physical quantity (such as density and temperature) that is independent of the size of the sample. (p. 300)
intercalation	The reversible inclusion of a molecule or atom into the crystal lattice of another compound. (p. 532)
intermolecular forces	Forces that exist between molecules. (p. 236)
internal energy (U)	The sum of all of the kinetic energies and potential energies of the particles within a system. (p. 296)
interstitial hole	The space between spheres/atoms. (p. 276)
ion	A charged chemical species. (p. 2)
ionic compound	A compound formed between two elements with different electronegativities. (p. 168)
ionic product	An alternative name for the reaction quotient (Q_{sp}). (p. 404)
ionic solid	A solid containing cations and anions that are attracted to each other by electrical interactions rather than covalent bonds. (p. 257)
ionisation energy (E_i)	The energy required to remove an electron from an isolated species. (p. 135)
ionisation isomers	Isomers in which a coordinated ligand is exchanged with a counterion, e.g. $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$. (p. 555)
ion pair	A more or less loosely associated pair of ions in a solution. (p. 419)
isoelectric point (pI)	The pH at which an amino acid, a polypeptide or a protein has no net charge. (p. 1063)
isoelectronic	Having the same number of electrons. (p. 146)
isomers	Molecules with the same molecular formula but different structures. (pp. 39, 746)
isotactic polypropylene	One diastereomeric form of polypropylene, in which all methyl groups are arranged on the same side of the carbon chain. (p. 1138)
isotonic	Describes a solution that has the same osmotic pressure as cellular fluids. (p. 417)
isotopes	Atoms of the same element having different numbers of neutrons in their nuclei. (p. 9)

J

joule (J) The SI unit of energy; 1 J = 1 kg m^2 s^{-2}. (pp. 296, 501)

K

Kekulé structure One of the two contributing structures of benzene proposed by August Kekulé. (p. 723)

kelvin The SI unit of temperature. (p. 25)

ketal A version of an acetal formed from a ketone rather than an aldehyde. (p. 947)

ketone A compound in which the carbon atom of the C═O group is bonded to two hydrocarbon groups. (p. 934)

ketoses Monosaccharides containing a ketone group. (p. 978)

kilogram The SI unit of mass. (p. 25)

kilojoule (kJ) 1000 J. (p. 296)

L

labile Describes a transition metal complex in which ligand exchange is rapid. (p. 564)

lactam A cyclic amide. (p. 1003)

lactone A cyclic ester. (p. 1003)

lanthanoids Elements 57 to 71 of the periodic table. (p. 14)

lattice A set of points with identical environments that describes a pattern. (p. 271)

lattice energy The energy change on converting 1 mole of an ionic solid into its constituent gaseous ions. (p. 170)

lattice enthalpy The enthalpy required to separate 1 mole of a crystalline compound into its gaseous constituent particles. (p. 397)

lattice point A point within a lattice. (p. 271)

law of conservation of mass No detectable gain or loss in mass occurs in chemical reactions. Mass is conserved. (p. 2)

law of definite proportions In a given chemical compound, the constituent elements are always combined in the same proportion by mass. (p. 2)

law of multiple proportions Whenever two elements form more than one compound, the different masses of one element that combine with the same mass of the other are in a ratio of small whole numbers. (p. 5)

law of radioactive decay Activity $= -\frac{\Delta N}{\Delta t} = KN$, where ΔN is the change in the number of radioactive nuclei during the time span Δt, and k is the decay constant. (p. 1168)

lead storage battery A lead–sulfuric acid storage battery in a motor vehicle; usually a 12-volt battery of six cells. (p. 528)

Le Châtelier's principle If an outside influence upsets an equilibrium, the system undergoes a change in a direction that counteracts the disturbing influence and, if possible, returns the system to equilibrium. (p. 364)

Leclanché cell A primary battery dependent on the reaction between zinc and manganese dioxide (Zn/MnO_2); see also *dry cell battery*. (p. 529)

levorotatory Describes the anticlockwise rotation of a plane of polarised light in a polarimeter. (p. 762)

Lewis acid An electron-pair acceptor. (p. 476)

Lewis base An electron-pair donor. (p. 476)

Lewis structure A representation of covalent bonding that uses symbols for the elements, dots for nonbonding valence electrons, and lines for pairs of bonding valence electrons. (p. 171)

ligand A molecule or an anion that can coordinate to a transition metal ion to form a complex. (p. 544)

ligand-to-metal charge transfer (LMCT) transitions Electronic transitions that involve formal transfer of an electron from a ligand to a transition metal ion. (p. 573)

light Electromagnetic radiation in the visible portion of the spectrum, between λ = 380 nm and λ = 780 nm. (p. 110)

like-dissolves-like rule Strongly polar and ionic solutes tend to dissolve in polar solvents, and nonpolar solutes tend to dissolve in nonpolar solvents. (p. 395)

limiting reagent The reagent that determines how much product can form when non-stoichiometric amounts of reagents are used. (p. 87)

linear Lying along a straight line. (p. 177)

line of integration A curved line at a signal on a ^{1}H-NMR spectrum that allows the determination of the relative number of hydrogen atoms giving rise to that signal. (p. 888)

line structure A shorthand method of drawing structural formulae in which each vertex and line ending represents a carbon atom. (p. 39)

linkage isomers Isomers that result from the different ways in which an ambidentate ligand can bind to a metal ion. (p. 555)

lipid A biomolecule isolated from plant or animal sources by extraction with nonpolar organic solvents, such as diethyl ether and acetone. (p. 1034)

lithium ion cell Rechargeable battery with twice the energy capacity of a nickel–cadmium (nicad) battery. (p. 532)

L-monosaccharide A monosaccharide that, when written as a Fischer projection, has the —OH on its penultimate carbon atom to the left. (p. 979)

local magnetic field The magnetic field generated by electrons surrounding a nucleus. (p. 884)

localised bond A chemical bond that involves only two atoms. (p. 189)

lone pair A pair of valence electrons that is localised on an atom rather than involved in bonding. (p. 172)

low-density polyethylene (LDPE or PE-LD) Polyethylene with a density between 0.91 and 0.94 g cm^{-3} and a melt transition temperature (T_m) of about 115 °C. (p. 1136)

low-spin Describes a complex ion or coordination compound with the minimum number of unpaired electrons. (p. 568)

M

macromolecule A molecule with a very large molecular mass. (p. 1118)

magic numbers The numbers 2, 8, 20, 28, 50, 82 and 126. The significance of these numbers in nuclear science is that a nuclide in which the number of protons or neutrons equals a magic number has nuclei that are relatively more stable than those of other nuclides nearby in the band of stability. (p. 1163)

magnetic moment (μ) A property related to the number of unpaired electrons in a transition metal complex through the equation $\mu = \sqrt{n(n+2)}\mu_B$. (p. 574)

magnetic quantum number (m_l) The quantum number, restricted to integers between $+l$ and $-l$, that indexes the orientation in space of an atomic orbital. (p. 129)

main-group metals A collective term for the metals in groups 1, 2 and 13–16 of the periodic table. (p. 544)

main reaction The desired reaction between the reagents rather than competing reactions that give by-products. (p. 88)

manometer A bent tube, containing a liquid and open at both ends, used to measure differences in pressure. (p. 214)

Markovnikov's rule In the addition of HX or H_2O to an alkene, hydrogen adds to the carbon atom of the double bond having the greater number of hydrogen atoms. (p. 713)

mass defect For a given isotope, the mass that changed into energy as the nucleons gathered to form the nucleus, this energy being released from the system. (p. 1161)

mass number (*A*) The numerical sum of the protons and neutrons in an atom of a given isotope. (p. 9)

mass percentage composition A list of the percentages by mass of the elements in a compound. (p. 80)

mass spectrometry A technique used to determine the mass of molecules and fragments of molecules. (p. 865)

matter Anything that has mass and occupies space. (p. 2)

mechanistic arrows Arrows which show the movement of electrons in bondbreaking and bond-making processes. (p. 45)

melt transition temperature (T_m) The temperature at which crystalline regions of a polymer melt. (p. 1120)

meniscus The curved surface of a liquid contained in a narrow tube. (p. 254)

mercaptan An alternative name for a thiol. (p. 832)

meridional (*mer*) An isomer of an octahedral complex $[ML_3X_3]^{n+}$ in which the donor atoms of each set of identical ligands are coplanar. (p. 557)

***meso* compound** An achiral compound with two or more stereocentres. (p. 758)

messenger RNA (mRNA) A ribonucleic acid that carries coded genetic information from DNA to ribosomes for the synthesis of proteins. (p. 1101)

meta Describes groups occupying positions 1 and 3 on a benzene ring. (p. 728)

metallic solid An elemental solid whose atoms are held together by valence electrons occupying delocalised orbitals spread across the entire solid. (p. 257)

metalloids Elements with properties that lie between those of metals and nonmetals, and that are found in the periodic table around the diagonal line running from boron, B, to astatine, At. (p. 15)

metallurgy The science and technology of metals, the procedures and reactions that separate metals from their ores, and the operations that create practical uses for metals. (p. 580)

metals	Elements that are good conductors of heat and electricity, are malleable (can be beaten into a thin sheet) and ductile (can be drawn out into a wire), and have the usual metallic lustre. (p. 15)
metal-to-ligand charge transfer transition	An electronic transition in a transition metal complex in which an electron is transferred from the metal to the ligand. (p. 573)
metre	The SI unit of length. (p. 25)
micelle	A spherical arrangement of organic molecules in aqueous solution, clustered so that their hydrophobic parts are buried inside the sphere and their hydrophilic parts are on the surface of the sphere and in contact with water. (p. 1041)
Michaelis constant	In enzyme reactions, the substrate concentration at half of the maximum reaction rate. (p. 673)
Michaelis–Menten equation	An equation that describes the reaction rate of many enzyme-catalysed reactions. (p. 673)
Michaelis–Menten mechanism	The reaction mechanism, by which many enzymecatalysed reactions proceed. (p. 672)
miscible	Describes liquids that mix completely; see also *soluble*. (p. 394)
molal boiling point elevation constant (K_b)	The number of degrees (°C) per unit of the molal concentration boiling point elevation of a solution relative to the pure solvent. (p. 412)
molal concentration (*b*)	The number of moles of solute in 1000 g of solvent; also called molality. (p. 408)
molal freezing point depression constant (K_f)	The number of degrees (°C) per unit of the molal concentration freezing point depression of a solution relative to the pure solvent. (p. 412)
molality (*b*)	Molal concentration. (p. 408)
molar concentration (*c*)	The concentration of a solution in units of mol L^{-1}; also called molarity. (p. 408)
molar enthalpy of fusion ($\Delta_{fus}H$)	The enthalpy change on melting 1 mole of a substance at its normal melting point. (p. 261)
molar enthalpy of sublimation ($\Delta_{sub}H$)	The enthalpy change on sublimation of 1 mole of a substance at its normal sublimation point. (p. 261)
molar enthalpy of vaporisation ($\Delta_{vap}H$)	The enthalpy change on vaporisation of 1 mole of a substance at its normal boiling point. (p. 261)
molar heat capacity	The heat capacity of 1 mole of a substance. (p. 301)
molarity (*c*)	Molar concentration. (pp. 90, 408)
molar mass (*M*)	The mass of 1 mole of the specified substance. (p. 75)
molar solubility (*s*)	The number of moles of solute required to prepare 1 L of a saturated solution of the solute. (p. 402)
mole	SI unit of amount of substance. One mole is the amount of substance that contains the same number of elementary entities (6.022×10^{23}) as there are atoms in exactly 12 g of ^{12}C. (pp. 25, 75)
molecular	A formula that shows the actual numbers of different types of atoms present in a

formula molecule. (pp. 36, 81)

molecular ion An ionised molecule that produces a peak in a mass spectrum. This is usually the peak with the highest *m*/*z* value. (p. 866)

molecular orbital (MO) A threedimensional wave that encompasses an entire molecule and describes a bound electron. (p. 198)

molecular orbital diagram An energy level diagram displaying the molecular orbitals of a particular molecule. (p. 199)

molecular orbital theory A bonding theory that considers all possible overlaps between atomic orbitals in a molecule. The overlap of two atomic orbitals leads to the formation of one bonding molecular orbital and one antibonding molecular orbital. Molecular orbitals are generally delocalised and can be spread over the entire molecule. (p. 198)

molecular solid A solid containing discrete molecules that do not have chemical bonds between them. (p. 257)

molecularity The number of colliding molecules involved in an elementary step. (p. 659)

molecule An uncharged collection of atoms bonded together in a definite structure. (p. 2)

mole fraction (*x*) The number of moles of a component in a solution divided by the total number of moles of material in the solution. (pp. 227, 409)

monodentate Describes a ligand that can coordinate to a metal ion using only one donor atom. (p. 547)

monomer The simplest nonredundant unit from which a polymer is formed. (p. 1118)

monoprotic acid An acid that can donate only a single proton to water. (p. 429)

monosaccharides Carbohydrates that cannot be hydrolysed to simpler compounds. (p. 978)

multiplet The splitting pattern of a complex signal in ^{1}H-NMR spectroscopy. (p. 892)

multiplicity The splitting pattern of a signal in ^{1}H-NMR spectroscopy, which can be described as, singlet, doublet, triplet, quartet, multiplet etc. (p. 893)

mutarotation The change in optical activity that occurs when an α or β form of a carbohydrate is converted to an equilibrium mixture of the two forms. (p. 984)

N

(*n* + 1) rule A rule for determining splitting patterns in NMR spectroscopy. If a hydrogen atom has *n* other hydrogen atoms that are not equivalent to it, but are equivalent to each other, on the same or adjacent atom(s), its ^{1}H-NMR signal is split into (*n* + 1) peaks. (p. 893)

***N*-terminal amino acid** The amino acid of a polypeptide with the free —NH_3^+ group. (p. 1066)

natural rubber An elastic material obtained from the latex sap of trees (especially trees of the species *Hevea brasiliensis*) that can be vulcanised and made into a variety of products. (p. 1146)

Nernst equation $E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{zF}\ln Q$ (p. 519)

net ionic equation An ionic equation from which spectator ions have been omitted. It is balanced when both atoms and electrical charge balance. (p. 97)

network solid A solid containing an array of covalent bonds linking every atom to its neighbours. (p. 257)

neutral	Describes a solution in which $[H_3O^+] = [OH^-]$. (p. 433)
neutron	A subatomic particle (n, ^1_0n), with a charge of 0 and a mass of 1.0086 u (1.6749×10^{-27} kg), that exists in all atomic nuclei except those of the ^1H isotope. (p. 8)
neutron emission	A nuclear reaction in which a neutron is ejected. (p. 1166)
Newman projection.	A way to view a molecule by looking along a carbon–carbon bond. (p. 688)
nicad battery	A nickel–cadmium battery, commonly used in laptop computers. (p. 531)
nickel–cadmium storage cell	See *nicad battery*. (p. 531)
nitrile	a —C≡N group. (p. 1012)
nitronium ion	NO_2^+. (p. 732)
noble gas configuration	The portion of the distribution of electrons among the orbitals of an atom that matches that of one of the noble gases. (p. 143)
noble gases	The elements in group 18 of the periodic table. (p. 15)
node	A point, line or surface where the electron density of an orbital is zero. (pp. 132, 198)
nomenclature	A system of naming. (p. 46)
nonmetals	Nonductile, nonmalleable, nonconducting elements. (p. 15)
nonoxidising acid	An acid in which the anion is a poorer oxidising agent than the hydrogen ion (e.g. HCl, H_3PO_4). (p. 513)
nonvolatile	Describes a substance with a high boiling point and a low vapour pressure that, consequently, does not evaporate. (p. 408)
normal boiling point	The boiling point of a substance under one atmosphere ($1.013\ 25 \times 10^5$ Pa) of pressure. (p. 240)
normal freezing point	The freezing point of a substance under $1.013\ 25 \times 10^5$ Pa pressure. (p. 240)
nuclear binding energy	The energy equivalent of the difference in mass between an atomic nucleus and the sum of the masses of its nucleons. (p. 1161)
nuclear equation	A description of a nuclear reaction that uses the special symbols of isotopes, that describes some kind of nuclear transformation or disintegration and that is balanced when the sums of the atomic numbers on either side of the arrow are equal and the sums of the mass numbers are also equal. (p. 1163)
nuclear fission	The breaking apart of atomic nuclei into smaller nuclei accompanied by the release of energy; the source of energy in nuclear reactors. (p. 1162)
nuclear fusion	The formation of atomic nuclei by the joining together of the nuclei of lighter atoms. (p. 1162)
nuclear magnetic resonance (NMR) spectroscopy	A spectroscopic technique that measures the absorption of energy by nuclei in the presence of a magnetic field. (p. 883)
nucleic acid	A biopolymer containing three types of monomer units: heterocyclic aromatic amine bases derived from purine or pyrimidine, the monosaccaride d-ribose or 2′-deoxy-d-ribose and phosphate. (p. 1088)

nucleon A proton or a neutron. (p. 8)

nucleophile Any reagent with an unshared pair of electrons that can be donated to another atom or ion to form a new covalent bond; a Lewis base. (pp. 477, 783)

nucleophilic acyl substitution A reaction in which a nucleophile bonded to a carbonyl carbon atom is replaced by another nucleophile. (p. 1017)

nucleophilicity A term for the relative rate at which a reagent undertakes nucleophilic substitution. (p. 788)

nucleophilic substitution Any reaction in which one nucleophile is substituted for another. (p. 783)

nucleoside The building block of nucleic acids, consisting of d-ribose or 2′-deoxy-d-ribose bonded to a heterocyclic aromatic amine base by a β-*N*-glycosidic bond. (p. 1088)

nucleosome The fundamental unit of the chromatin structure consisting of DNA wrapped around histones. (p. 1096)

nucleotide A nucleoside in which a molecule of phosphoric acid is esterified with an —OH group of d-ribose or 2′-deoxy-d-ribose, most commonly the 3′ or 5′ —OH group. (p. 1089)

nucleus The dense core of an atom that comprises protons and neutrons. (p. 7)

nuclide A particular atom of specified atomic number and mass number. (p. 9)

O

observed rotation The angle through which a compound rotates a plane of polarised light. (p. 762)

octahedral Describes a molecule in which a central atom is surrounded by six atoms located at the vertices of an imaginary octahedron. (pp. 181, 553)

oil A triglyceride that is liquid at room temperature. (p. 1039)

Okazaki fragments Short molecules of single-stranded DNA formed during DNA replication on the lagging strand. (p. 1097)

oligopeptide A peptide containing more than 10 but fewer than 20 amino acids. (p. 1066)

oligosaccharides Carbohydrates containing from 4 to 10 monosaccharide units joined by glycosidic bonds. (p. 991)

optical activity The ability to rotate a plane of polarised light. (p. 761)

orbital A three-dimensional wave describing a bound electron. (pp. 16, 128)

orbital mixing Interactions among *s* and *p* atomic orbitals that change the relative energies of the molecular orbitals resulting from these atomic orbitals. (p. 203)

orbital overlap The extent to which two orbitals on different atoms interact. (p. 189)

order In a reaction, the sum of the exponents in the rate law is the *overall* order. Each exponent gives the order with respect to the individual reactant. (p. 636)

order of precedence of functional groups A system for ranking functional groups in order of priority for the purposes of IUPAC nomenclature. (p. 937)

organometallic compound A compound containing a carbon–metal bond. (pp. 551, 942)

ortho Describes groups occupying positions 1 and 2 on a benzene ring. (p. 728)

osmosis The passage of solvent molecules, but not those of solutes, through a semipermeable membrane (more limiting than dialysis). (p. 414)

osmotic membrane A membrane that allows passage of solvent, but not solute particles. (p. 414)

osmotic pressure (*Π*) The back pressure that has to be applied to prevent osmosis; one of the colligative properties. (p. 414)

oxidation A change in which an oxidation number increases (becomes more positive or less negative); a loss of electrons. (p. 490)

oxidation number The charge that an atom in a molecule or ion would have if all of the electrons in its bonds belonged entirely to the more electronegative atoms; the oxidation state of an atom. (p. 491)

oxidation state See *oxidation number*. (p. 491)

oxidising acid An acid in which the anion is a stronger oxidising agent than H^+ (e.g. $HClO_4$, HNO_3). (p. 514)

oxidising agent The substance that causes oxidation and that is itself reduced. (p. 490)

oximes Compounds containing a C═NOH group. (p. 953)

oxoanion A negatively charged ion containing two or more elements, one of which is oxygen. (p. 50)

oxonium ion An ion in which oxygen is bonded to three other atoms and bears a positive charge. (p. 718)

P

***p*-block elements** A collective name for the elements in groups 13 to 18 of the periodic table. (pp. 14, 598)

pairing energy (*P*) The energy required to force two electrons to become paired and occupy the same orbital. (p. 568)

para Describes groups occupying positions 1 and 4 on a benzene ring. (p. 728)

paramagnetic Describes substances that are attracted into a magnetic field as a result of the presence of one or more unpaired electrons. (pp. 146, 544)

parent chain The longest straight carbon chain in an organic molecule. (p. 54)

partial pressure The pressure exerted by one component of a gaseous mixture. (p. 226)

parts per billion (ppb) The number of entities of one particular component present in one billion objects. (p. 228)

parts per million (ppm) The number of entities of one particular component present in one million objects. (p. 228)

pascal (Pa) The SI unit of pressure, one newton per square metre. (p. 215)

passivation The stabilisation of a substance (usually a metal) by the formation of a thin oxide layer on its surface (p. 523)

Pauli exclusion principle The requirement that no two electrons in a chemical species can be described by the same set of four quantum numbers. (p. 130)

pentapeptide A molecule containing five amino acid units joined by peptide bonds. (p. 1066)

penultimate carbon The stereocentre of a monosaccharide furthest from the carbonyl group; for example, C(5) of glucose. (p. 979)

peptide A short polymer of amino acids. (p. 1066)

peptide bond The name given to the amide bond formed between the α-amino group of one amino acid and the α-carboxyl group of another amino acid. (p. 1066)

percentage by The number of grams of an element present in 100 g of a compound. (p. 80)

mass	
percentage uncertainty	An uncertainty expressed as a percentage. (p. 31)
percentage yield	The ratio, given as a percentage, between the quantity of product actually obtained in a reaction and the theoretical yield. (p. 88)
period	A horizontal row of elements in the periodic table. (p. 14)
periodic table of the elements	A table in which symbols for the elements are displayed in order of increasing atomic number and arranged so that elements with similar properties lie in the same column. (p. 13)
pH	$-\log[H_3O^+]$. (p. 434)
phase	The starting position of a wave with respect to one wavelength. (p. 111)
phase change	The transition of a substance from one phase to another. (p. 260)
phase diagram	A pressure–temperature graph showing the conditions under which a substance exists as solid, liquid and gas. (p. 263)
phenol	A compound that contains an —OH group bonded to a benzene ring. (pp. 728, 823)
phenyl group	The C_6H_5 — group. (p. 728)
photoelectric effect	The ejection of electrons from a metal surface by light. (p. 112)
photodegradation	Degradation of a material or compound caused by exposure to light. (p. 1147)
photons	Particles of light, characterised by energy $E = h\nu$. (p. 113)
pi (π) bond	A chemical bond formed by side-by-side orbital overlap so that electron density is concentrated above and below the bond axis. (p. 196)
pK_a	$-\log K_a$. (p. 443)
pK_b	$-\log K_b$. (p. 443)
pK_w	$-\log K_w$. (p. 435)
Planck's constant (h)	The physical constant, 6.626×10^{-34} J s, that relates the energy of a photon to its frequency. (p. 113)
plane of symmetry	An imaginary plane passing through an object and dividing it so that one half is the mirror image of the other half. (p. 751)
plane polarised	Vibrating only in parallel planes. (p. 761)
plastic	A polymer that can be moulded when hot and retains its shape when cooled. (p. 1119)
pnictogens	The elements in group 15 of the periodic table. (p. 15)
pOH	$-\log[OH^-]$. (p. 434)
polar covalent bond	A bond that possesses an asymmetric distribution of electrons. (p. 167)
polarimeter	An instrument for measuring the ability of a compound to rotate a plane of polarised light. (p. 762)
polarisability	The ease with which the electron density about an atom or molecule can be distorted. (p. 241)
polyamide	A polymer in which each monomer unit is joined to the next by an amide bond. (p. 1124)
polycarbonate	A polyester in which the carboxyl groups are derived from carbonic acid. (p. 1130)

polycyclic aromatic hydrocarbon (PAH) A hydrocarbon with two or more fused aromatic rings. (p. 729)

polydentate Describes a ligand containing two or more atoms that can coordinate simultaneously to a metal ion. (p. 547)

polyester A polymer in which each monomer unit is joined to the next by an ester bond. (p. 1128)

polymer Any long-chained molecule synthesised by linking many single parts called monomers. (pp. 1056, 1118)

polymerisation A chemical reaction in which two or more small molecules (monomers) combine to form larger molecules (polymers) that contain repeating structural units of the monomers. (p. 1118)

polypeptide A macromolecule containing more than 20 amino acid units, each joined to the next by a peptide bond. (p. 1066)

polyprotic acid An acid which can donate more than one proton. (p. 429)

polyprotic base A base which can accept more than one proton. (p. 430)

polysaccharides Carbohydrates containing a large number of monosaccharide units joined together by one or more glycosidic bonds. (p. 991)

polyurethane A polymer containing the —NHC(O)O— group as the repeating unit. (p. 1131)

positron A positively charged particle with the mass of an electron. (p. 1165)

potential difference Voltage, which is a measure of the amount of energy that can be delivered as a current moves through a circuit. (p. 501)

precision A group of measurements is of high precision if all the values lie close together. (pp. 32, 34)

pre-exponential factor See *frequency factor*. (p. 655)

pressure Force per unit area. (p. 214)

primary carbon atom A carbon atom attached to only one other carbon atom. (p. 51)

primary cell A nonrechargeable battery. (p. 528)

primary (1°) structure The sequence of smaller molecular components that are assembled to make a biopolymer; thus for proteins and peptides it is the specific amino acids in a polypeptide chain read from the *N*-terminal amino acid to the *C*-terminal amino acid (p. 1067), and for DNA and RNA it is the sequence of bases along the 2′-deoxyribose/ribose–phosphodiester backbone of a DNA or RNA molecule read from the 5′ end to the 3′ end. (p. 1090)

primase An enzyme that catalyses the synthesis of small RNA molecules used as primers for DNA polymerases. (p. 1097)

primitive cubic structure The crystal form with a unit cell containing one lattice point at each corner of a cube only. (p. 273)

principal quantum number (*n*) The quantum number, restricted to positive integers, that indexes the energy and size of an atomic orbital. (p. 128)

product The chemical species obtained as the result of a chemical reaction. (pp. 2, 72)

protein A biological macromolecule with a molar mass of 5000 u or more and consisting of one or more polypeptide chains. (p. 1066)

protic solvents Solvents that contain —OH groups and are hydrogen-bond donors. (p. 790)

proton A subatomic particle $\left({}^{1}_{1}\mathrm{p}\right)$, with a charge of +1 and a mass of 1.0073 u (1.6726×10^{-27} kg), that is found in atomic nuclei. (p. 8)

pyranose A six-membered cyclic hemiacetal form of a monosaccharide. (p. 982)

pyridinium chlorochromate (PCC) A mild oxidising agent, commonly used to prepare aldehydes from primary alcohols. (p. 822)

Q

qualitative analysis The use of experimental procedures to determine what elements are present in a substance. (p. 72)

quantisation A phenomenon whereby the energy of a chemical system is not continuous but is restricted to certain definite values. (p. 17)

quantised Having discrete allowed values. (p. 121)

quantitative analysis The use of experimental procedures to determine the percentage composition of a compound or the percentage of a component of a mixture. (p. 72)

quantum number An integer or halfinteger describing the allowed values of some quantised property. (p. 128)

quartet A signal in ^{1}H-NMR spectroscopy that has been split into four peaks in a ratio of 1 : 3 : 3 : 1. (p. 892)

quaternary (4°) structure The arrangement of polypeptide monomers into a noncovalently bonded aggregation. (p. 1075)

R

R Used in the *R,S* system to show that the order of priority of groups on a stereocentre is clockwise; from the Latin word *rectus* meaning ‘right’. (p. 755)

racemic mixture A mixture of equal amounts of two enantiomers. (p. 764)

radical A nonmetal species containing an odd number of electrons in its outer electron shell. (pp. 780, 1133)

radical cation A species with a positive charge and an unpaired electron. (p. 866)

radical chain-growth polymerisation A type of polymerisation in which the chain carrier is a radical. (p. 1134)

radical substitution A substitution reaction that involves a radical in the mechanism of substitution. (p. 780)

radioactive Able to emit various atomic radiations or gamma rays. (p. 9)

radioactive decay The change of a nucleus into another nucleus (or into a more stable form of the same nucleus) by the loss of a small particle or a gamma-ray photon. (p. 1163)

radioactive disintegration series A sequence of nuclear reactions beginning with a very long-lived radionuclide and ending with a stable isotope of lower atomic number. (p. 1170)

radio-frequency radiation	The portion of the electromagnetic spectrum with wavelengths greater than a metre. (p. 884)
radiological dating	A technique for measuring the age of a geological formation or an ancient artefact by determining the ratio of the concentrations of two isotopes, one radioactive and the other a stable decay product. (p. 1172)
radionuclide	A radioactive isotope. (p. 9)
Raoult's law	The vapour pressure of one component above a mixture of molecular compounds equals the product of its mole fraction and its vapour pressure when pure. (p. 409)
rare earth elements	An alternative name for the lanthanoid elements. (p. 14)
rate coefficient	An alternative name for the rate constant, the proportionality constant in the rate law. (p. 636)
rate constant	The proportionality constant in the rate law. (p. 636)
rate-determining step	The slowest step in a reaction mechanism. (p. 659)
rate law	An equation that relates the rate of a reaction to the molar concentration of the reactants raised to powers. (p. 636)
rate of reaction	The amount (in moles or mass units) per volume per unit time of products formed or reactants consumed in a particular reaction. (p. 632)
reactant	A chemical species that is transformed in a chemical reaction. (pp. 2, 72)
reaction coordinate	The horizontal axis of a potential energy diagram for a reaction. (p. 652)
reaction intermediate	A species produced during a reaction that does not appear in the reaction equation because it is consumed in a subsequent step in the mechanism. (p. 653)
reaction mechanism	The series of individual steps (elementary processes) in a chemical reaction that gives the net, overall change. (p. 638)
reaction quotient (Q)	The numerical value of the equilibrium constant expression under any conditions; see also *equilibrium constant expression*. (p. 349)
reaction quotient expression	A fraction in which the numerator is the product of the molar concentrations of the products, each raised to a power equal to its coefficient in the equilibrium equation, and the denominator is the product of the molar concentrations of the reactants, each raised to a power equal to its coefficient in the equation. (For gaseous reactions, partial pressures can be used in place of molar concentrations.) (p. 349)
redox reaction	A reaction involving the transfer of one or more electrons between chemical species. (pp. 17, 490)
reducing agent	A substance that causes reduction and is itself oxidised. (p. 490)
reducing sugar	A carbohydrate that reacts with an oxidising agent to form an aldonic acid. (p. 988)
reduction	A change in which an oxidation number decreases (becomes less positive or more negative); a gain of electrons. (p. 490)
reduction–oxidation reaction	See *redox reaction*. (p. 490)
reduction potential (E_{red})	A measure of the tendency of a given half-reaction to occur as a reduction. (p. 507)

reductive amination The formation of an imine from an aldehyde or ketone, followed by its reduction to an amine. (p. 953)

reference compound A compound added to a sample to be studied by NMR spectroscopy, usually tetramethylsilane (TMS). The positions of the signals in the spectrum are then compared with those of the reference compound. (p. 864)

refractory A heat-resistant ceramic material. (p. 282)

regioselective reaction A reaction in which one direction of bond-breaking or bond-forming occurs in preference to all other directions. (p. 713)

repeating unit The smallest molecular fragment that contains all the nonrepeating structural features of a polymer chain. (p. 1119)

replication fork A structure that forms within DNA during replication; it has two branches of single-stranded DNA splitting from a single point such that it resembles a fork. (p. 1097)

resolution The separation of a racemic mixture into its enantiomers. (p. 766)

resonance The absorption of electromagnetic radiation by a spinning nucleus and the resulting flip of its nuclear spin state. (p. 884)

resonance energy The difference in energy between a resonance hybrid and the most stable of its hypothetical contributing structures. (p. 725)

resonance stabilisation The energetic stabilisation that occurs on delocalisation of negative charge over two or more atoms. (p. 460)

resonance structure One of two or more Lewis structures that are equivalent to one another. (p. 174)

retrovirus An RNA virus that propagates using the host cell's DNA replication chemistry by using a reverse transcriptase enzyme to produce DNA from its RNA genome. (p. 1108)

reverse transcriptase A DNA polymerase enzyme that transcribes single-stranded RNA into single-stranded DNA; this is the ‘reverse’ of normal transcription, which involves the synthesis of RNA from DNA. (p. 1108)

reverse transcriptase inhibitor An inhibitor of the reverse transcriptase enzyme. (p. 1108)

reversible reaction A reaction capable of proceeding in either the forward or reverse direction. (p. 72)

ribosomal RNA (rRNA) Ribonucleic acid found in ribosomes, the sites of protein synthesis. (p. 1101)

ribosome A component of a biological cell which assembles the specific amino acids to form proteins as determined by the nucleotide sequence of an RNA molecule. (p. 1101)

RNA Ribonucleic acid, a nucleic acid that hydrolyses to ribose, phosphate ions, adenine, uracil, guanine and cytosine. (p. 1088)

root-mean-square speed Average speed obtained by taking the square root of the mean value of the squares of the individual speeds. (p. 223)

***R, S* system** A set of rules for specifying the configuration of groups around a stereocentre. (p. 754)

S

S Used in the *R*, *S* system to show that the order of priority of groups on a

	stereocentre is anticlockwise; from the Latin word *sinister* meaning 'left'. (p. 755)
s-block elements	A collective name for the elements in groups 1 and 2 of the periodic table. (p. 14)
salt bridge	A tube containing an electrolyte, that connects the two half-cells of a galvanic cell. (p. 504)
salt linkage	An ionic bonding interaction between charged functional groups in a peptide. (p. 1074)
saponification	The hydrolysis of an ester in aqueous NaOH or KOH to an alcohol and the sodium or potassium salt of a carboxylic acid. (p. 1024)
saturated calomel electrode	A reference electrode that consists of elemental mercury, mercury(I) chloride and Hg_2Cl_2 (calomel) in saturated KCl solution. (p. 511)
saturated hydrocarbon	A compound composed solely of carbon and hydrogen atoms in which all C—C bonds are single; see also *alkane*. (pp. 54, 686)
saturated solution	A solution in which no more solute will dissolve at a specified temperature. (p. 390)
scientific notation	A method of expressing numbers in terms of powers of 10. For example, the number 3613 becomes 3.613×10^3 in scientific notation. (p. 30)
second	The SI unit of time. (p. 25)
secondary carbon atom	A carbon atom attached to two other carbon atoms. (p. 51)
secondary cell	A battery that can be recharged. (p. 528)
secondary (2°) structure	The ordered arrangement (conformation) of a biopolymer; thus the organised shape of the chain of amino acids in localised regions of a polypeptide or protein, seen as sheets or coils (p. 1069), and the ordered arrangement of DNA and RNA strands (p. 1091), to form a defined threedimensional shape.
second law of thermodynamics	Whenever a spontaneous event takes place in our universe, the total entropy of the universe increases ($\Delta S_{total} > 0$). (p. 322)
seesaw shape	The molecular shape that resembles a seesaw. (p. 180)
sense strand	Complimentary to the antisense strand, the sense strand has exactly same base sequence as the mRNA transcript produced (except with thymine replaced by uracil) such that the ultimate peptide generated from the process has an amino acid sequence defined by the bases present on this strand. (p. 1102)
shielded	Describes the situation in NMR spectroscopy in which local magnetic fields from electrons surrounding a nucleus decrease the ability of an applied magnetic field to bring the nucleus into resonance. (p. 884)
shielding	The partial cancellation of the electrostatic attraction between the nucleus and an electron within an atom, caused by one or more electrons of lower principal quantum number. (p. 136)
sigma (σ) bond	A bond that is totally symmetric with respect to rotation about the internuclear axis. (p. 167)
signal splitting	A phenomenon in NMR spectroscopy in which the ^{1}H-NMR signal from one set of hydrogen atoms is split by the influence of neighbouring nonequivalent hydrogen atoms. (p. 893)
significant figures	The figures in a physical measurement that are known to be certain plus the first figure that contains uncertainty. (p. 30)
silicone	See *silicon polymer*. (p. 1149)

silicon polymer	Inorganic polymer with a silicon–oxygen backbone. (p. 1149)
silver/silver chloride electrode	A reference electrode where an Ag rod is dipped into a mixture of AgCl and KCl of different concentrations. (p. 511)
silver-mirror test	A qualitative test for an aldehyde using Tollens' reagent ; the aldehyde is oxidised to a carboxylate anion, and Ag^+ is reduced to metallic silver. (p. 959)
single bond	A chemical bond formed by one pair of electrons shared between two atoms. (p. 171)
singlet	A signal in ^{1}H-NMR spectroscopy that has not been split. (p. 892)
SI (Système International) units	A system of units based on seven base units from which all others can be derived. (p. 24)
S_N1	A type of nucleophilic substitution reaction in which only one molecule is involved in the rate-determining step. (p. 787)
S_N2	A type of nucleophilic substitution reaction in which two molecules or ions are involved in the rate-determining step. (p. 786)
soap	The sodium or potassium salt of a fatty acid. (p. 1041)
soft Lewis acid	A Lewis acid having an acceptor atom of high polarisibility. (p. 479)
soft Lewis base	A Lewis base having a large donor atom of high polarisability and low electronegativity. (p. 479)
solid wedge	A solid wedge denotes a bond coming out of the page towards the observer. (p. 43)
solubility	The maximum amount of a solute that dissolves completely in a given mass or volume of solvent at a particular temperature. (p. 390)
solubility product (K_{sp})	The equilibrium constant for the dissolution of an ionic salt. (p. 400)
soluble	Describes a solid or a gas that dissolves in a solvent. (p. 390)
solute	The dissolved substance contained in a solution. (pp. 90, 390)
solution	A homogeneous mixture in which all particles are of the size of atoms, small molecules or small ions. (pp. 90, 390)
solvation	The development of a cage-like network of a solution's solvent molecules around a molecule or ion of the solute. (p. 396)
solvation enthalpy	The enthalpy change due to the interaction of gaseous molecules or ions of solute with solvent molecules during the formation of a solution. (p. 397)
solvent	The liquid component of a solution. (pp. 90, 390)
solvolysis	A reaction in which the solvent plays the role of the nucleophile in the substitution reaction. (p. 787)
space-filling model	A three-dimensional representation of a molecule that attempts to show the actual relative sizes of atoms within a molecule. (p. 43)
specific heat (*c*)	See *specific heat capacity*. (p. 301)
specific heat capacity (*c*)	The quantity of heat that will raise the temperature of 1 g of a substance by 1 K, usually in units of 1 J g^{-1} K^{-1}; also called specific heat. (p. 301)
specific rotation [α]	The observed rotation of a plane of polarised light when a sample is placed in a tube 1.0 dm long and at a concentration of 1.0 g/100 mL; if a pure sample is used, its concentration is given in g/mL (i.e. its density). (p. 763)
spectator ion	An ion whose formula is identical on both sides of an ionic equation, that does not participate in the reaction and that is excluded from the net ionic equation. (p. 97)

spectrochemical series	A list of ligands ordered in terms of their ability to produce a crystal field splitting. (p. 572)
sp hybrid orbitals	Two atomic orbitals constructed by the interaction between an *s* orbital and a *p* orbital on the same atom. (p. 194)
sp^2 hybrid orbitals	Three atomic orbitals constructed by the interactions between an *s* orbital and two *p* orbitals on the same atom. (p. 193)
sp^3 hybrid orbitals	Four atomic orbitals constructed by the interactions between an *s* orbital and three *p* orbitals on the same atom. (p. 190)
spin	The intrinsic angular momentum of electrons and protons that gives them magnetism. (pp. 17, 129)
spin quantum number (m_s)	The quantum number, restricted to either $+\frac{1}{2}$ or $-\frac{1}{2}$, which indexes the orientation of electron spin. (p. 130)
splitting pattern	The pattern obtained when a signal in a ^{1}H-NMR spectrum is split by the influence of neighbouring nonequivalent hydrogen atoms. These can be described as multiplets, singlets, doublets, triplets, quartets etc. (p. 892)
spontaneous	Describes a change that occurs by itself without outside assistance. (p. 294)
square planar	A geometry adopted by 4-coordinate complexes in which the four M—L bonds point to the corners of a square (p. 554)
square pyramidal	A geometry adopted by 5-coordinate complexes, consisting of a pyramid with four triangular sides and a square base. (p. 554)
standard cell notation	A way of describing the anode and cathode half-cells in a galvanic cell. The anode half-cell is specified on the left, with the electrode material of the anode given first and a vertical bar representing the phase boundary between the electrode and the solution. Dashed double bars represent the salt bridge between the half-cells. The cathode half-cell is specified on the right, with the material of the cathode given last. Once again, a single vertical bar represents the phase boundary between the solution and the electrode. (p. 505)
standard cell potential $\left(E^{\ominus}_{\text{cell}}\right)$	The potential of a galvanic cell at 25 °C, when all ionic concentrations are exactly 1 m and the partial pressures of all gases are 10^5 Pa. (p. 507)
standard enthalpy of combustion $\left(\Delta_c H^{\ominus}\right)$	The enthalpy change for the combustion of 1 mole of a compound under standard conditions. (p. 313)
standard enthalpy of formation $\left(\Delta_f H^{\ominus}\right)$	The enthalpy change when 1 mole of a compound is formed from its elements in their standard states. (p. 309)
standard enthalpy of reaction $\left(\Delta_r H^{\ominus}\right)$	The enthalpy change of a reaction when determined with reactants and products at 10^5 Pa and on the scale of the mole quantities given by the coefficients of the balanced equation. (p. 306)
standard entropy $\left(S^{\ominus}\right)$	The entropy of a substance measured under standard conditions. (p. 323)
standard entropy of formation $\left(\Delta_f S^{\ominus}\right)$	The entropy change when 1 mole of a substance is formed from its elements in their standard states. (p. 324)
standard entropy of reaction $\left(\Delta_r S^{\ominus}\right)$	The entropy change of a reaction when determined with reactants and products at 10^5 Pa and on the scale of the mole quantities given by the coefficients of the balanced equation. (p. 324)

standard Gibbs energy change $(G^{\ominus})$	$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$. (p. 327)
standard hydrogen electrode	The standard of comparison for reduction potentials and for which $E^{\ominus}_{H^+/H_2}$ has a value of 0 V (25 °C, 10^5 Pa) when $[H^+]$ = 1 m in the reversible half-cell reaction $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$. (p. 508)
standard reduction potential $(E^{\ominus}_{red})$	The reduction potential of a half-reaction at 25 °C when all ion concentrations are 1 m and the partial pressures of all gases are 10^5 Pa. (p. 507)
standard state	The condition in which a substance is in its most stable form at 10^5 Pa at the specified temperature. (p. 306)
state function	A quantity that depends only on the initial and final states of the system and not on the path taken by the system to get from the initial to the final state; *p*, *V*, *T*, *H*, *S* and *G* are all state functions. (p. 297)
statistical	Describes a polymer in which the sequence of monomers follows a statistical rule. (p. 1123)
steady-state approximation	A method to derive the rate law for a reaction, using the assumption that the concentration of any intermediate remains constant as the reaction proceeds. (p. 662)
step-growth polymerisation	A polymerisation in which chain growth occurs in a stepwise manner between difunctional monomers, generally with release of a small molecule. (p. 1123)
stereocentre	For carbon, a tetrahedral carbon atom with four different groups bonded to it; in general terms, any atom with sufficient atoms or groups arranged around it, so that stereoisomers may be formed on exchange of any two atoms or groups. (p. 751)
stereoisomers	Isomers with the same molecular formula and the same connectivity but different orientations of their atoms in space. (pp. 555, 746)
stereospecific reaction	A reaction in which one stereoisomer is formed or destroyed in preference to all others that might be formed or destroyed. (p. 719)
steric factor	A factor that reflects the fraction of collisions with effective orientations. (p. 655)
steric hindrance	The ability of groups, because of their size and shape, to hinder access to a reaction site within a molecule. (p. 789)
steric strain	The strain induced in a molecule arising from the repulsion between the electrons of the bonds in the molecule. (p. 692)
stoichiometric coefficients	Numbers in front of formulae in chemical equations. (p. 72)
stoichiometry	A description of the relative quantities by moles of the reactants and products in a reaction as given by the stoichiometric coefficients in the balanced equation. (p. 72)
stretching	A type of vibration that changes bond lengths. (p. 872)
strong acid	An acid that reacts completely with water to give quantitative formation of H_3O^+. (p. 438)
strong base	A base that reacts completely with water to give quantitative formation of OH^-. (p. 438)
strong nuclear	The attractive force between protons and neutrons that holds the nucleus

force together. (p. 1161)

strong-field Describes ligands that produce large crystal field splittings. (p. 572)

structural formula A depiction of a molecule or polyatomic ion that shows how the constituent atoms are arranged, to which other atoms they are bonded, and the kinds of bonds (single, double or triple) present. (p. 37)

structural isomers Isomers with the same molecular formula, but different orders of attachments of the constituent atoms. (p. 555)

styrene The common name for phenylethylene. (p. 728)

subatomic particles Electrons, protons and neutrons. (p. 8)

sublimation The phase change between solid and vapour. (p. 261)

substituent A group attached to the longest carbon chain of an organic molecule. (p. 54)

supercoiling The three-dimensional arrangement of all atoms of a nucleic acid. (p. 1095)

superconductor A material that offers no resistance to the flow of electricity. (p. 286)

supercritical fluid A phase in which the liquid–vapour transition is no longer possible. A supercritical fluid is able to expand to fill the available space (like a gas), but is resistant to further compression (like a liquid). (p. 263)

superhelical twist A change of conformation that results in compensation of strain introduced into circular DNA if the helical twist is changed. (p. 1095)

surface tension The resistance of a liquid to an increase in its surface area. (p. 254)

surroundings That part of the universe other than the system being studied and separated from the system by a real or an imaginary boundary. (p. 295)

symproportionation An electrochemical process in which two reactants that contain the same element in different oxidation states react to give a single product having an oxidation number intermediate between the two reactants. (p. 529)

syn addition The addition of atoms or groups of atoms from the same side or face of a carbon–carbon double bond. (p. 721)

syndiotactic polypropylene One diastereomeric form of polypropylene in which the methyl groups alternate from front to back along the carbon chain. (p. 1138)

system That part of the universe under study and separated from the surroundings by a real or an imaginary boundary. A system may be open, closed or isolated. (p. 295)

T

tautomerism A form of isomerism in which constitutional isomers are in equilibrium with each other. The isomers differ in the location of a hydrogen atom and a double bond relative to a heteroatom, most commonly O, S or N. (p. 962)

tautomers Constitutional isomers that differ in the location of hydrogen and a double bond relative to O, N or S. (p. 962)

template strand An alternative name for antisense strand; see also *coding strand*, *sense strand*. (p. 1102)

terminal carbon A carbon atom at the end of a chain of carbon atoms. (p. 38)

tertiary carbon atom A carbon atom attached to three other carbon atoms. (p. 51)

tertiary (3°) structure The three-dimensional arrangement in space of all atoms in a single polypeptide chain (p. 1072); the three-dimensional arrangement of all atoms of a DNA or RNA; see also *supercoiling*. (p. 1095)

tetrahedral	A geometry adopted by 4-coordinate complexes in which the central metal ion is coordinated to four ligand donor atoms located at the corners of an imaginary tetrahedron. (pp. 178, 554)
tetrahedral carbonyl addition intermediate	An intermediate formed from the addition of a nucleophile to the carbonyl group. (p. 942)
tetramethylsilane (TMS)	The reference standard used in NMR spectroscopy. Its signal is set at $\delta = 0$. (p. 885)
tetrapeptide	A molecule containing four amino acids units joined by peptide bonds. (p. 1066)
theoretical yield	The amount of a product determined by the stoichiometry of the reaction. (p. 88)
theory of resonance	The theory that some molecules have structures that cannot be represented by any single contributing structure so must be represented as a hybrid of two or more equivalent contributing structures. (p. 724)
thermochemical equation	A balanced chemical equation accompanied by the value of ΔH° that corresponds to the mole quantities specified by the coefficients. (p. 306)
thermodynamic equilibrium constant	An equilibrium constant defined in terms of activities. (p. 353)
thermodynamic temperature	A temperature scale in which temperature is measured in kelvin. (p. 295)
thermoplastic	A polymer that can be melted and moulded into a shape that is retained when it is cooled. (p. 1119)
thermosetting plastic	A polymer that can be moulded when it is first prepared, but, once cooled, hardens irreversibly and cannot be remelted. (p. 1119)
thiol	A compound containing an —SH (sulfhydryl) group. (p. 832)
third law of thermodynamics	At absolute zero, the entropy of a perfectly ordered pure crystalline substance is 0. (p. 323)
3′ end	The end of a polynucleotide at which the 3′ —OH group of the terminal 2′-deoxyribose/ribose unit is free. (p. 1090)
titrant	An acid or base of known concentration used in an acid–base titration. (p. 467)
titration curve	For an acid–base titration, a graph of pH versus the volume of titrant added. (p. 468)
Tollens' reagent	A solution of silver nitrate in aqueous ammonia. (p. 959)
toluene	The common name for methylbenzene. (p. 728)
torsional strain	A type of steric strain where repulsion from the electrons in bonds induces a twisting force away from an eclipsing interaction. (p. 691)
transcription	The process by which a complementary RNA copy of a sequence of DNA is created. (p. 1101)
transesterification	The reaction of an ester with an alcohol to produce a different ester. (p. 1022)
transfer RNA (tRNA)	Ribonucleic acid that carries a specific amino acid to the site of protein synthesis on ribosomes. (p. 1101)
***trans* isomer**	A stereoisomer that contains two groups that project on opposite sides of a reference plane. (p. 555)
transition metals	The elements in groups 3 to 12 of the periodic table. (pp. 14, 544)
transition state	The energy maximum on the potential energy surface of a reaction. It is the brief moment during an elementary process in a reaction mechanism when the species involved have acquired the minimum amount of potential energy needed for a

successful reaction. (p. 653)

transmutation The conversion of one isotope into another. (p. 1171)

transuranium elements Elements 93 and higher. (p. 1172)

triacylglycerol See *triglyceride*. (p. 1034)

triglyceride An ester of glycerol with three fatty acids. (p. 1034)

trigonal bipyramidal A geometry adopted by 5-coordinate complexes in which a central metal ion is coordinated to five ligand donor atoms located at the corners of a trigonal bipyramid. (pp. 179, 554)

trigonal planar The molecular shape in which a central atom is bonded to three other atoms lying in a plane at 120° angles to one another. (p. 177)

triol A compound with three alcohol groups. (p. 811)

tripeptide A molecule containing three amino acid units joined by peptide bonds. (p. 1056)

triple bond A bond between two atoms consisting of three pairs of bonding electrons. (p. 171)

triple point The temperature and pressure at which solid, liquid and vapour can coexist at equilibrium. (p. 264)

triplet A signal in ^{1}H-NMR spectroscopy that has been split into three peaks in a ratio of 1 : 2 : 1. (p. 892)

triprotic acid An acid that can donate three protons. (p. 429)

trisaccharides Carbohydrates containing three monosaccharide units joined by glycosidic bonds. (p. 991)

tropical oil A plant oil, such as coconut oil or palm oil, that contains a relatively high proportion of low-molar-mass saturated fatty acids. (p. 1039)

U

uncertainty principle The assertion that position and momentum cannot both be exactly known. (p. 127)

unimolecular reaction A reaction in which only one species is involved in the transition state of the rate-determining step. (p. 787)

unit A specific standard quantity of a particular property, against which all other quantities of that property can be measured. (p. 24)

unit cell The simplest repeating unit of a regular pattern, usually within a crystal. (p. 271)

universe A system and its surroundings taken together. (p. 295)

unsaturated hydrocarbon A hydrocarbon in which at least one carbon atom does not have the maximum possible number of atoms bonded to it. (p. 686)

upfield Describes a signal in NMR spectroscopy that is towards the right of the spectrum or of another signal. (p. 886)

UV/visible spectroscopy A technique used to study compounds that absorb light in the ultraviolet–visible region. (p. 905)

V

valence electrons The electrons of an atom that occupy orbitals of highest principal quantum

	number and incompletely filled orbitals. (p. 140)
valence-shell-electron-pair-repulsion (VSEPR)	The principle of minimising electron–electron repulsion by placing electron pairs as far apart as possible. (p. 176)
van der Waals equation	An equation that corrects the ideal gas equation for the effects of molecular size and intermolecular forces. (p. 238)
van't Hoff equation	$\frac{d\ln k}{dT} = \frac{\Delta H^{\ominus}}{RT^2}$. This shows how the value of an equilibrium constant varies with temperature. (p. 368)
van't Hoff factor (*i*)	The ratio of the observed freezing point depression to the value calculated assuming that the solute dissolves as un-ionised molecules. (p. 419)
vaporisation	Conversion of a liquid into its vapour. (p. 240)
vapour pressure	The partial pressure of a vapour in equilibrium with a condensed phase. (p. 255)
vibrational infrared	The portion of the infrared region with a frequency range of 400–4000 cm^{-1}. (p. 871)
viscosity	The resistance to flow of a fluid. (p. 255)
volt (V)	The SI unit of electric potential in joules per coulomb; 1V = 1 J C^{-1}. (p. 501)
voltmeter	An instrument for measuring potential difference. (p. 502)
vulcanisation	A chemical reaction in which the physical properties of an elastomer are changed by reaction with sulfur to form cross-links between the polymer chains. (p. 1147)
vulcanised rubber	Natural rubber that has been treated with, for example, sulfur that forms cross-links between the polymer chains and improves the properties of the rubber. (p. 1147)

W

wavelength (λ)	The distance between any two consecutive identical points on a wave. (pp. 110, 870)
wavenumber ($\bar{\nu}$)	The number of wavelengths per centimetre. The unit of wavenumber is the reciprocal centimetre (cm^{-1}) and is commonly used in infrared spectroscopy. (p. 871)
weak acid	An acid that reacts incompletely with water to form less than stoichiometric amounts of H_3O^+. (p. 438)
weak base	A base that reacts incompletely with water to form less than stoichiometric amounts of OH^-. (p. 438)
weak-field	Describes ligands that produce small crystal field splittings. (p. 572)
work (*w*)	The energy expended in moving an opposing force through a particular distance. Work has units of force × distance. (p. 298)

X

X-ray crystallography	The study of crystal structures by X-ray diffraction techniques. (p. 906)
xylene	The common name for the three isomeric dimethylbenzenes. (p. 728)

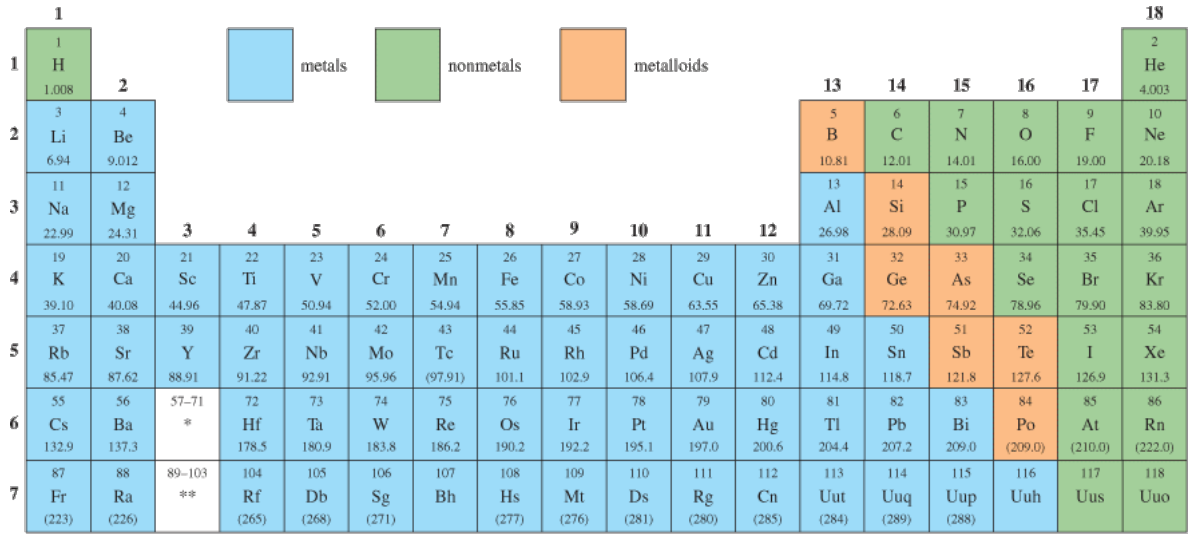
Z

Zaitsev's rule	A rule stating that the major product of a β-elimination reaction is the most stable alkene — that is, the alkene with the most substituents on the carbon–carbon double bond. (p. 794)
Z-DNA	One of the many possible DNA double helical structures; its helix is left-handed. (p. 1095)
Ziegler–Natta catalyst	A catalyst, typically based on titanium tetrachloride and the organometallic compound triethylaluminium, which is used in the production of unbranched, stereoregular polyalkene polymers. (p. 1137)
zinc–manganese dioxide cell	See *dry cell battery*; *Leclanché cell.* (p. 529)
zwitterion	An ionic salt in which both cation and anion are part of the same molecule. (pp. 445, 847, 1056)

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FRONT COVER

Periodic table of the elements



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc (97.91)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57–71 *	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209.0)	85 At (210.0)	86 Rn (222.0)
7	87 Fr (223)	88 Ra (226)	89–103 **	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (284)	114 Uuq (289)	115 Uup (288)	116 Uuh	117 Uus	118 Uuo

*lanthanoid series	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.1	71 Lu 175.0
**actinoid series	89 Ac (227)	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

atomic number

atomic mass

Atomic masses i to the longest-liv element.

Common physical constants

Mass of electron	$m_e = 9.109\,382\,15(45) \times 10^{-31}$ kg (5.485 799 10 × 10^{-4} u)
Mass of proton	$m_p = 1.672\,621\,637(83) \times 10^{-27}$ kg (1.007 276 467 u)
Mass of neutron	$m_n = 1.674\,927\,211(84) \times 10^{-27}$ kg (1.008 664 916 u)
Electronic charge	$e = 1.602\,176\,487(40) \times 10^{-19}$ C
Atomic mass unit	u = 1.660 538 782(83) × 10^{-27} kg
Gas constant	$R = 8.314\,472(15)$ J mol^{-1} K^{-1}
Molar volume of an ideal gas	$V_m = 22.710\,981(40)$ L mol^{-1} (at 0 °C and 1.00 × 10^5 Pa)
The Avogadro constant	$N_A = 6.022\,141\,79(30) \times 10^{23}$ mol^{-1}
Speed of light in a vacuum	$c = 2.997\,924\,58 \times 10^8$ m s^{-1}
Planck's constant	$h = 6.626\,068\,96(33) \times 10^{-34}$ J s
Faraday constant	$F = 9.648\,533\,99(24) \times 10^4$ C mol^{-1}

Name	Symbol	Atomic number	Molar mass (g mol^{-1})[a]
actinium	Ac	89	227.0278[b]
aluminium	Al	13	26.981 538 6(8)
americium	Am	95	243.0614[b]
antimony	Sb	51	121.760(1)
argon	Ar	18	39.948(1)
arsenic	As	33	74.921 60(2)
astatine	At	85	209.9871 [b]
barium	Ba	56	137.327(7)
berkelium	Bk	97	247.0703 [b]
beryllium	Be	4	9.012 182(3)
bismuth	Bi	83	208.980 40(1)
bohrium	Bh	107	[d]
boron	B	5	[10.806; 10.821] [e]
bromine	Br	35	79.904(1)

cadmium	Cd	48	112.411(8)
caesium	Cs	55	132.905 451 9(2)
calcium	Ca	20	40.078(4)
californium	Cf	98	251.0796[b]
carbon	C	6	[12.0096; 12.0116][e]
cerium	Ce	58	140.116(1)
chlorine	Cl	17	[35.446; 35.457] [e]
chromium	Cr	24	51.9961(6)
cobalt	Co	27	58.933 195(5)
copernicium	Cn	112	285.174[b]
copper	Cu	29	63.546(3)
curium	Cm	96	247.0704[b]
darmstadtium	Ds	110	281.162[b]
dubnium	Db	105	268.125[b]
dysprosium	Dy	66	162.500(1)
einsteinium	Es	99	252.0830[b]
erbium	Er	68	167.259(3)
europium	Eu	63	151.964(1)
fermium	Fm	100	257.0951 [b]
fluorine	F	9	18.998 403 2(5)
francium	Fr	87	223.0197[b]
gadolinium	Gd	64	157.25(3)
gallium	Ga	31	69.723(1)
germanium	Ge	32	72.63(1)
gold	Au	79	196.966 569(4)
hafnium	Hf	72	178.49(2)
hassium	Hs	108	277.150[b]
helium	He	2	4.002 602(2)
holmium	Ho	67	164.930 32(2)
hydrogen	H	1	[1.00784; 1.008 11] [e]
indium	In	49	114.818(3)
iodine	I	53	126.904 47(3)
iridium	Ir	77	192.217(3)
iron	Fe	26	55.845(2)
krypton	Kr	36	83.798(2)
lanthanum	La	57	138.905 47(7)
lawrencium	Lr	103	262.1096[b]
lead	Pb	82	207.2(1)
lithium	Li	3	[6.938; 6.997] [e]
lutetium	Lu	71	174.9668(1)
magnesium	Mg	12	24.3050(6)
manganese	Mn	25	54.938 045(5)
meitnerium	Mt	109	276.151 [b]
mendelevium	Md	101	258.0984[b]
mercury	Hg	80	200.59(2)
molybdenum	Mo	42	95.96(2)
neodymium	Nd	60	144.242(3)
neon	Ne	10	20.1797(6)
neptunium	Np	93	237.0482[b]
nickel	Ni	28	58.6934(4)
niobium	Nb	41	92.906 38(2)
nitrogen	N	7	[14.006 43; 14.007 28] [e]
nobelium	No	102	259.1010[b]
osmium	Os	76	190.23(3)
oxygen	O	8	[15.999 03; 15.999 77] [e]
palladium	Pd	46	106.42(1)

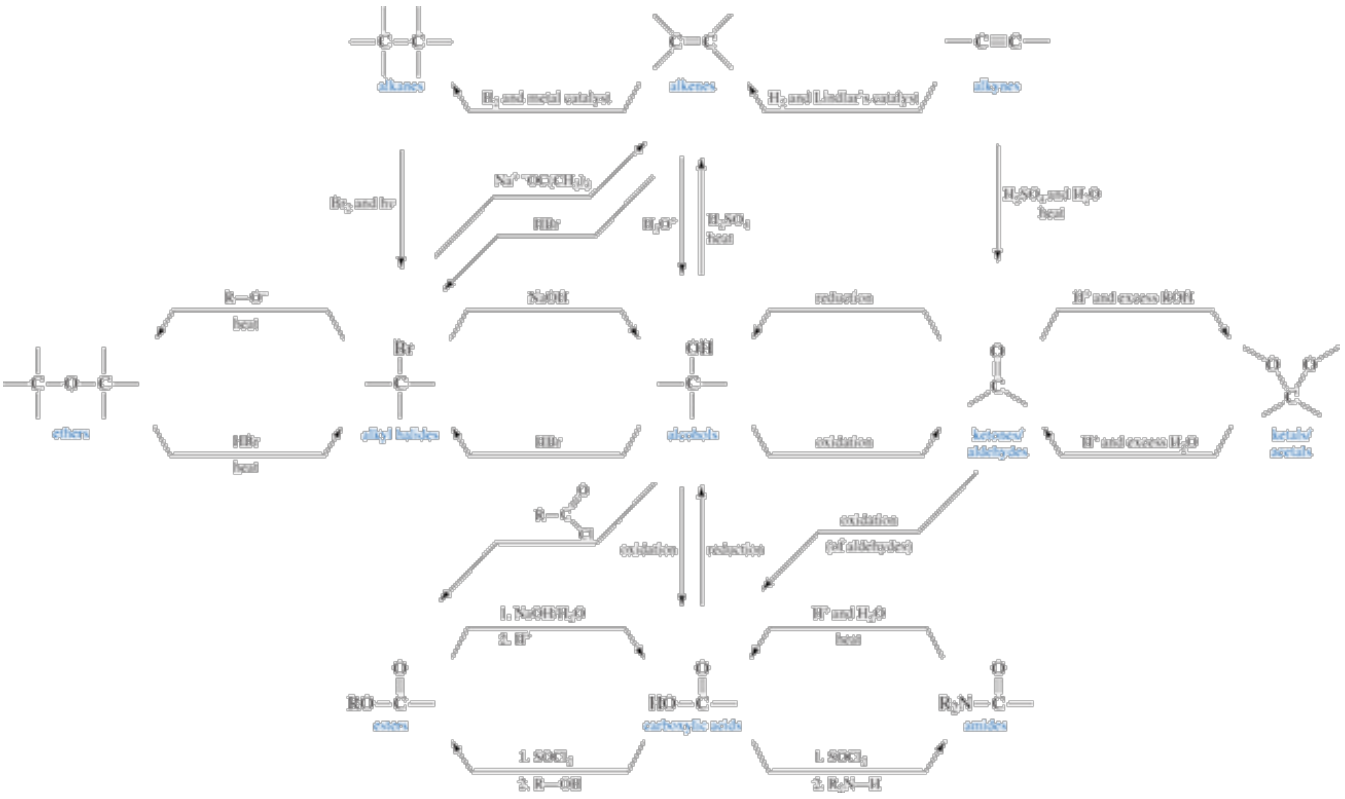
phosphorus	P	15	30.973 762(2)
platinum	Pt	78	195.084(9)
plutonium	Pu	94	244.0642[b]
polonium	Po	84	208.9824[b]
potassium	K	19	39.0983(1)
praseodymium	Pr	59	140.907 65(2)
promethium	Pm	61	144.9127[b]
protactinium	Pa	91	231.035 88(2)[b]
radium	Ra	88	226.0254[b]
radon	Rn	86	222.0176[b]
roentgenium	Rg	111	280.164[b]
rhenium	Re	75	186.207(1)
rhodium	Rh	45	102.905 50(2)
rubidium	Rb	37	85.4678(3)
ruthenium	Ru	44	101.07(2)
rutherfordium	Rf	104	265.1167[b]
samarium	Sm	62	150.36(2)
scandium	Sc	21	44.955 912(6)
seaborgium	Sg	106	271.133 [b]
selenium	Se	34	78.96(3)
silicon	Si	14	[28.084; 28.086] [e]
silver	Ag	47	107.8682(2)
sodium	Na	11	22.989 769 28(2)
strontium	Sr	38	87.62(1)
sulfur	S	16	[32.059; 32.076] [e]
tantalum	Ta	73	180.947 88(2)
technetium	Tc	43	97.9072[b]
tellurium	Te	52	127.60(3)
terbium	Tb	65	158.925 35(2)
thallium	Tl	81	[204.382; 204.385] [e]
thorium	Th	90	232.038 06(2)[b]
thulium	Tm	69	168.934 21(2)
tin	Sn	50	118.710(7)
titanium	Ti	22	47.867(1)
tungsten	W	74	183.84(1)
ununhexium[c]	Uuh	116	[d]
ununoctium[c]	Uuo	118	[d]
ununpentium[c]	Uup	115	288.192[b]
ununquadium[c]	Uuq	114	289.187[b]
ununseptium[c]	Uus	117	[d]
ununtrium[c]	Uut	113	284.178[b]
uranium	U	92	238.028 91(3)[b]
vanadium	V	23	50.9415(1)
xenon	Xe	54	131.293(6)
ytterbium	Yb	70	173.054(5)
yttrium	Y	39	88.905 85(2)
zinc	Zn	30	65.38(2)
zirconium	Zr	40	91.224(2)

(a) All known significant figures are given. Parentheses indicate that the figure is uncertain.
(b) Element has no stable nuclides. The molar mass of the longest lived isotope is given.
(c) Unnamed at September 2011.
(d) Accurate molar mass has not yet been determined.
(e) The molar mass interval reflects the set of molar mass values in normal materials.

Source: Wieser, ME and Coplen, TB, 'Atomic weights of the elements 2009' *Pure Appl. Chem.*, vol. 83, no. 2, pp. 359-96, © IUPAC 2010

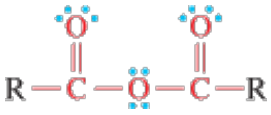
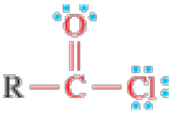
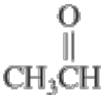
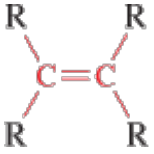
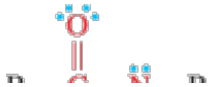
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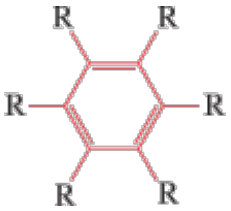
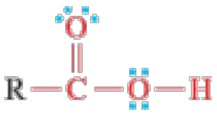
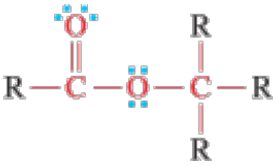
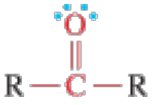
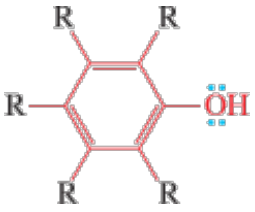
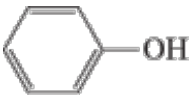
BACK COVER



A selection of interconversions possible for some of the simpler functional groups

Some important organic functional groups

	Functional group[a]	Example	Name
acid anhydride			ethanoic anhydride (acetic anhydride)
acid chloride			ethanoyl chloride (acetyl chloride)
alcohol		CH_3CH_2OH	ethanol (ethyl alcohol)
aldehyde			ethanal (acetaldehyde)
alkene		$CH_2 = CH_2$	ethene (ethylene)
alkyne		$HC{\equiv}CH$	ethyne (acetylene)
amide			ethanamide (acetamide)

			
amine, primary		$CH_3CH_2NH_2$	ethylamine
amine, secondary		$(CH_3CH_2)_2NH$	diethylamine
amine, tertiary		$(CH_3CH_2)_3N$	triethylamine
arene			benzene
carboxylic acid			ethanoic acid (acetic acid)
disulfide		CH_3SSCH_3	dimethyl disulfide
ester			methyl ethanoate (methyl acetate)
haloalkane X = F, Cl, Br, I		CH_3CH_2Cl	chloroethane (ethyl chloride)
ketone			propanone (acetone)
phenol			phenol
sulfide		CH_3SCH_3	dimethyl sulfide
thiol		CH_3CH_2SH	ethanethiol (ethyl mercaptan)

(a) Functional group shown in red. R = hydrogen, alkyl or aryl group, except for amines, alcohols, haloalkanes, ketones and thiols where R cannot be H.

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