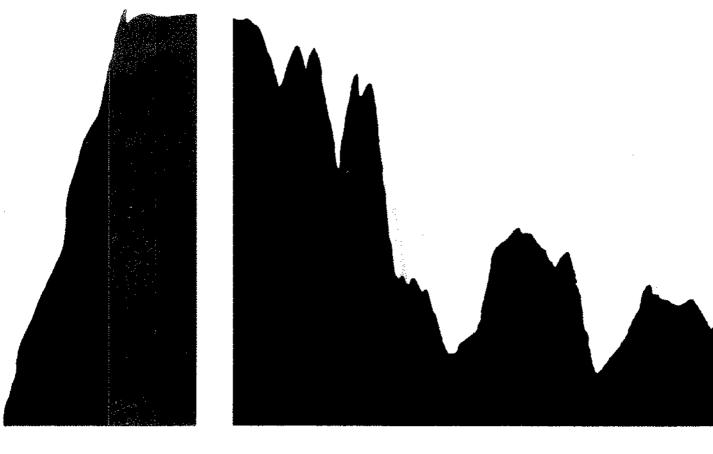
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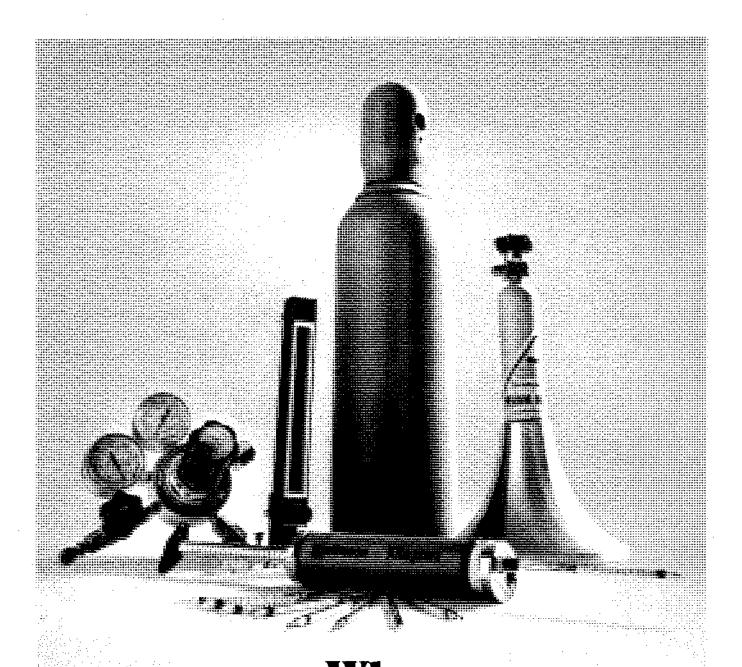
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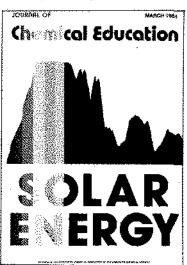
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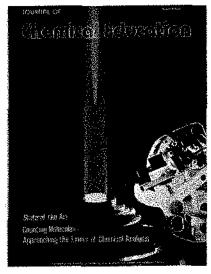
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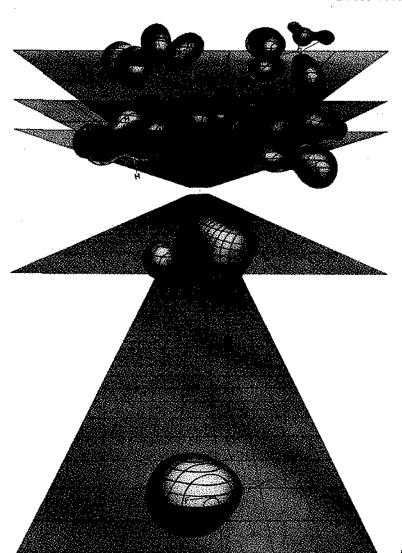
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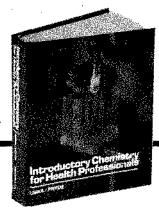
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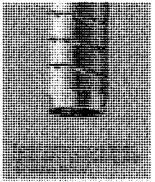
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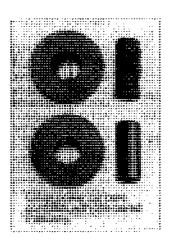
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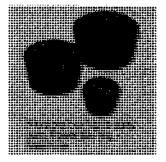
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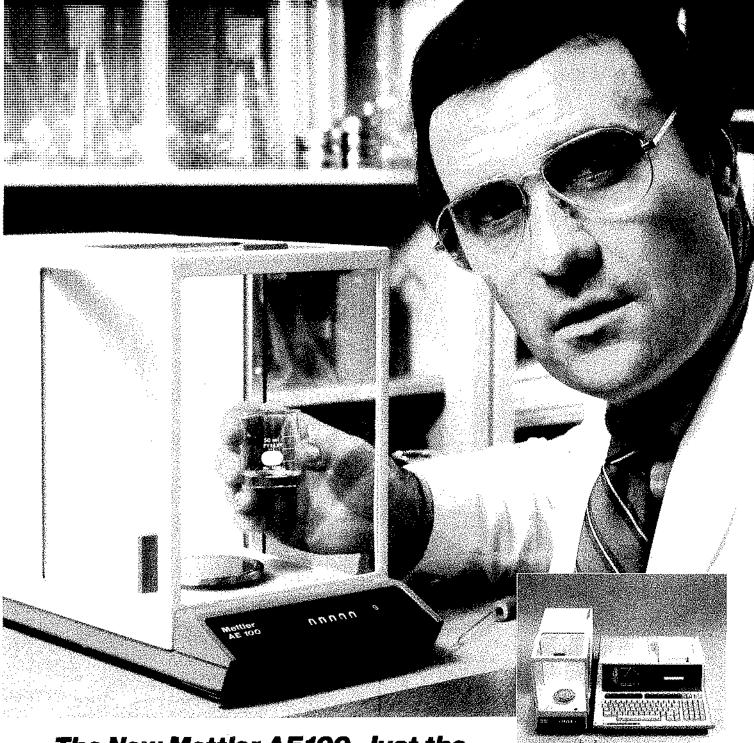


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Experiments Integrating Evaluation of Chemical Hazards into the Chemistry Curriculum

J. T. Plerce, S. M. McDonald, and M. S. Scogin University of North Alabama, Florence, AL 35632

One way of making students aware of the need for regular monitoring of laboratories is to offer an introduction to the science of industrial hygiene as part of the chemistry curriculum. Although laboratory safety and industrial hygiene may be discussed in a variety of laboratory settings, opportunities for students actually to sample and analyze contaminants are rare. We propose the use of two experiments that demonstrate important points concerning the desirability and the means of regular laboratory monitoring.

During the past year we have undertaken to monitor our own laboratories and have sponsored senior industrial hygiene projects directed to that end. We feel that these experiments have broader applicability and may be used as "whole class" experiments. Two promising areas for monitoring appeared to be the estimation of hydrogen sulfide levels in the general chemistry laboratory during qualitative analysis and the determination of the concentration of organic vapors associated with organic chemistry laboratories.

One of the problems that besets those charged with laboratory monitoring is the "selection" of suitable analytes given the large number of candidate materials. Given limited time and resources it may be desirable simply to select a few representative contaminants during preliminary stages. With the advent of microprocessor-controlled gas chromatography the ability to monitor large numbers of gases and vapors is enhanced. The methods we have selected allow the students to perform the sampling and analysis themselves relatively inexpensively.

As much as possible we use experiments that have been evaluated by the National Institute for Occupational Safety and Health (NIOSH). The methods described here are designated by NIOSH as P & CAM 127 (organic solvents) and S4 (hydrogen sulfide).

References from NiOSH outline the procedures for both sampling and analysis of hydrogen sulfide and organic solvent vapors in air, as well as many other substances (1-3). Vendors' information may also be useful, particularly technical bulletins (4). Should difficulties arise concerning the availability of equipment or the interpretation of references it is likely that an industrial hygienist in the area will be able to assist. Organizations that can provide the names of local industrial hygienists include the American Academy of Industrial Hygiene (certified industrial hygienes).

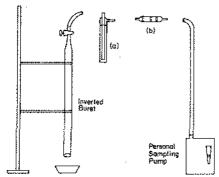


Figure 1. Calibration of impinger (a) and adeorbent tube (b).

J. T. Pierce is an associate professor of industrial hygiene at the University of North Alabama, and S. M. McDonald and M. S. Scogin are senior industrial hygiene students.

gienists) and the American Industriel Hygiene Association (both at 475 Wolf Ledges Parkway, Akron, OH) and the American Conference of Governmental Industrial Hygienists (6500 Glenway Ave., Cincinnati, OH).

Traditional industrial hygiene sampling has relied upon the use of small sampling pumps that could either be attached to a worker or placed in an area of interest. Such pumps individually cost several hundred dollars but are sometimes available on loan from a local industry. Those pumps selected should be capable of delivering air flowrates as indicated in references (I-3). In this work we used Du Pont Model P-30 Constant Flow Samplers. Pump calibration is easily accomplished using an inverted buret in the form of a "soap bubble" calibrator in line as shown in Figure 1. Further information on flow calibration is summarized in common references (5, 6). In our work the hydrogen sulfide was collected as cadmium sulfide when laboratory air was impinged in a cadmium sulfide solution. Arabinogalactin (Sigma Chemical Co., St. Louis, MO) was added to the impinger solution to prevent the decomposition of the cadmium sulfide collected. It may be possible to use inexpensive plastic impingers for this application (Cole-Parmer Co., Chicago, IL). The collected sulfide was spectrophotometrically determined using a methylene-blue-type reaction (N, N-dimethyl-p-phenylenediamine and ferric chloride solutions).

Activated-charcoal-filled tubes were used for the collection of organic solvents. Care should be taken to insure the air makes contact first with the larger of the two charcoal sections of these adsorbent tubes. After sampling these tubes were opened, and the first charcoal layer was desorbed and analyzed. A gas chromatograph equipped with flame ionization was employed. A variety of columns suitable for common organic materials may be used and an electronic integrator aids the analysis. Since this was a quantitative form of gas chromatography the solvent flush technique was employed as shown in Figure 2. The laboratory's ability to carry out such analyses proficiently may be checked by a proficiency analytical testing program such as the one currently carried out by NIOSH; samples are sent quarterly and results must

(Continued on page A85)



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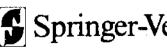
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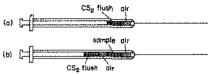


Figure 2. Solvent flush technique.

be returned within fifteen working days.

Selected results from our work are shown in the table. These results, excepting the

values for hydrogen sulfide¹, do not indicate overexposures, and, although other studies of academic laboratories have shown similar results (7), inter-laboratory variation prevents meaningful generalization.

Our laboratories were equipped with two 6-ft fume hoods which were not used during this work. We have since installed individual work station exhaustors so that each student has access to ventilation.

Although the specialized nature of laboratory environments makes the application of Occupational Safety and Health Administration standards awkward, it is still incumbent upen laboratory managers and educators to provide a healthful environment for learning. The experiments we have discussed not only provide useful data for assessment of risk but may also instill an appreciation of the possible presence of airborne contaminants.

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Results of Monitoring Contaminants in Academic Laboratories

Type	Conditions	Location	Time (m)	Volume (m³)	Welght (mg)	TWA#	Contaminant	TLV®6
Personal	Benzocaine preparation	Organic teaching lab	180	0.024	<0,126	<5.25	Diethyl ether	1200
Area	Paper chromatography	General chemistry teaching lab	155	0.015	3.99	259.7	Methyl ethyl ketone	590
Area	Distillation of benzene/ toluene mix	Organic teaching lab	160	0.016	0.576 0.562	36.41 36.04	Benzane Toluene	30 375
Area	Thioacetamide generation of H ₂ S	General chemistry teaching lab	15	0.001	5,13	2465	H ₂ S	21 (short-term exposure limit

^{*} Values measured expressed as time-weighted averages (mg/m³).

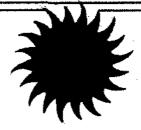
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¹ Editor's note: this high concentration of H₂S demonstrates the need for caution when using thioacetamide outside of a fume hood. (M.M.R.)



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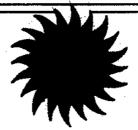
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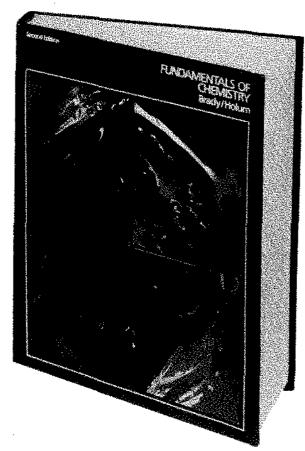
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Choosing the Right Instrument: The Modular Approach

Part II

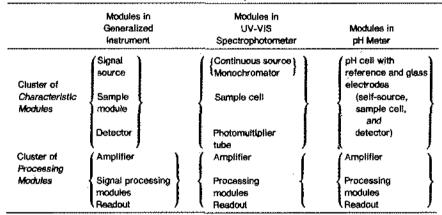
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instrument Specifications: Which Modules Determine What?

In Part I (which appeared on page A53 of the February issue) the modular approach to instrumentation was described as an effective way to ease the process of selecting an appropriate instrument for a particular measurement as well as to develop an understanding of an instrument's behavior that would lead to its more effective use. Further, attention was directed to the characteristic cluster of modules at the "front end" of an instrument as those to study in reaching a decision about which instrument to buy or use for a determination. How well can we relate instrument specifications, which represent a major part of the data furnished for review by a prospective user or purchaser, to the behavior of modules? Or to put the question more sharply, how often is a specification fixed by a single module? Since we shall now look critically at these matters, in

Table 2. Modular Clusters in Representative Instruments



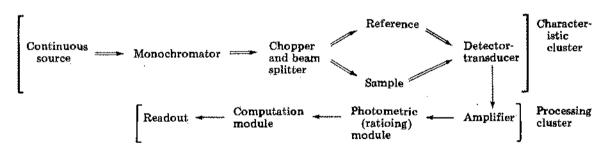


Figure 4. Line diagram of modules of a double-channel spectrophotometer.

Table 2 the terms characteristic cluster and processing cluster are defined and illustrated by application to a spectrophotometer and pH meter. A detailed analysis of the characteristic modules of each will be given below.

To tackle the queries about specifications effectively, we need to insure that complexities of design which are heyond the scope of this presentation can be ignored. Fortunately, most instruments, like the one in Figure 1, are of single-channel design. For these instruments we shall assume that manufacturers are employing modules of equal quality for

their instruments so that no module will limit performance as the "weakest link in the chain."

Even where the design departs from the single-channel pattern, as in double-channel instruments, the modification is usually a minimal change. For instance, to construct most double-channel layouts, a single-channel instrument is opened up at the sample module. Usually a chopper which alternately directs the "signal" from the preceding module to a reference-cell channel and sample-cell channel performs the function. Immediately beyond the reference and sample

modules, the separate channels are appropriately rejoined. One such arrangement is shown schematically in Figure 4. The two different signals falling on the detector are "sorted out" in the processing modules and compared. As is evident from Figure 4, the characteristic cluster of modules is essentially unchanged. The chopper becomes part of the processing set of modules.

Most other changes in design have to do with impositions of automatic control. For

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instrumentation

example, a feedback or control loop may be added to stabilize the output of an optical source. The general characteristics of the module are unaffected; the feedback loop insures that fluctuations in output are minimized. A similar result is secured with computer control as will be discussed later.

To examine the degree to which instrument specifications derive from specifications of individual modules we can consider in some detail the part played by modules in the two instruments deteiled in Table 2. For the UV-VIS spectrophotometer, a long list of specifications will be of interest. The most important of these are likely to be wavelength range, precision of wavelength setting, spectral slit width (resolution), precision in %T or absorbance, stray light, and scanning speed. What connections can we make between these instrument specifications and those for constituent modules? Other performance criteria seem to fall in the processing category, they are factors such as scale expansion, readout in absorbance, %T, or concentration of analyte, and availability of first and second derivatives.

Let us take the characteristic modules in turn. The first is the continuous source. Clearly, the more intense and the more constant its output, the greater the signal/noise (S/N) ratio of the spectrophotometer: precision in %T or absorbance will be enhanced.

The spectral range of the source will also establish the maximum wavelength range of the instrument. Where higher intensity in part of the range or a still greater range is desired, additional sources will be required. Whatever choice is made, the output of the source must be focused on the entrance slit of the monochromator for good coupling.

The monochromator is next. The wider its entrance and exit alits (widths are usually equal), the greater the S/N ratio and the precision in %T. As is well known, in a monochromator a better S/N ratio is gained at the expense of resolution. The wider its slits, the greater also is its spectral slit width and thus the poorer its resolution. The quality and size of the monochromator dispersing element (usually a grating) and optics will also directly enhance resolution and efficiency and reduce the level of stray light (at the exit slit). In essence, the monochromator will fix the resolution, S/N ratio, and level of stray light. It may also reduce the full spectral range provided by the source and thus fix the range practically available.

What of the other characteristic modules, the sampling module and detector? In the simplest case the sampling module will be a cuvette or cell. Cells that hold sample and reference should be matched io path length and transmission characteristics. As Part I reminded us, coupling between modules should facilitate the passage of signal. Since the output of the detector goes to the train of processing modules, the detector must not only respond to the intensity of the signal from the sample but also transduce it to an electrical output. Some other desired characteristics of detectors are high sensitivity, low noise, and a short response time.

Before considering how well the photomultiplier tube used in the spectrophotometer of Table 2 meets these requirements, let us look at it as an optical detector. Its response to light as a function of wavelength will be multiplied by (convoluted with) the intensity versus wavlength function available from the source-monochromator-sample cell combination. By choosing a photomultiplier tube with the broadest spectral response available, good sensitivity of detection is insured from 190 nm to beyond 800 nm. The higher its gain and the lower its noise, the better the possibility of working at trace concentration levels. The detector has the strongest influence on the limit of detection of measurement. Dynamic aspects of measurements will also depend strungly on the detector. If the spectrophotometer must scan rapidly, the detector must have a fast response.

What is gained from the brief analysis is a clear picture that the main optical specifications of the UV-VIS spectrophotometer in fact result from the performance "huilt into" it by its characteristic modules. Only if the subsequent mudules cause deterioration in performance will the instrument as a whole fail to live up to this "advance billing." Toward the end of the section, its process modules will also be examined.

The modular diagram of the pH meter is surprisingly simple as shown in Table 2. Inspection of the table and its performance also yields the result that its characteristic modules determine the specifications of the overall instrument. The cell is simultaneously

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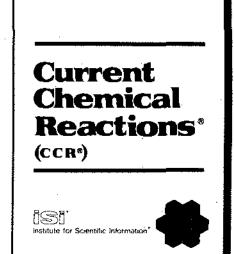
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a sampling module, a "self-source" (i.e., generates its own signal), and the detector! Such a "pile-up" of functions is commoo with electrochemical instruments.

The voltage of the glass-membrane pH electrode relative to the reference electrode of the cell is the desired measure of hydrogen-ion activity in the cell solution. The quality of the glass electrode must be high for a stable measurement and adequate shielding must protect its lead to the amplifier from pickup of stray currents. At low pH (below 1) and high pH (above 12) interferences cause errors. For this instrument a consideration of characteristic modules is brief indeed. Though not explicitly examined, specifications of the electrochemical cell determine those of the resulting pH meter. For electrochemical instruments a modular approach yields much less insight than for most other

It is important now to look at processing clusters of modules. Whatever signal amplitude may have been produced by a detector will nearly always need to be further boosted in the signal processing clusters by an amplifier. In designing such a cluster, after amplification there is a decision to be made about whether to carry out processing with the signal still in analog form (a signal of varying amplitude) or to convert it to digital form (a series of pulses whose number indicates the signal amplitude) by use of an ana-

conversion (often termed a change in domain) ordinarily insures higher precision and accommodates use of a microprocessor or computer for processing steps and instrument control as will be discussed below. The processing modules will also provide that the signal from the sample channel is ratioed to or corrected by the signal from a reference channel. For example, in the double-channel spectrophotometer shown in modular form in Figure 4, the ratio of power P transmitted by the sample to power P_0 transmitted by the reference must be taken to give P/P_0 and %T. If a computation module is incorporated, the negative logarithm of the ratio can be deduced to give the familiar Beer's law result: $A = -\log P/P_0 = -\log T$. The form of readout by the last module may be a needle deflection on a meter, a curve plotted by a recorder, or a digitally indicated value.

What conclusion can we draw about processing modules? Since they help amplify the signal, reject noise and background, and make calculations from data, they are indispensible. Yet the signal containing the desired information about the chemical sample originated in the characteristic modules and it is that they have set the instrument apecifications critical to the particular measurement technique.

Automatic Operation and **Computer Control**

How is the modular approach affected by the introduction of microprocessors? Further, how useful is this mode of analysis for complex new types of instruments? Let us consider the impact of microprocessors first. Then in the next section the modular approach will be applied to the new category of

"hyphenated" instruments like GC-IR, LC-MS, and MS-MS.

Three general degrees of control in instruments can be identified. They are:

1) Manual Operation. The operator is furnished sufficient information to permit him to operate the instrument. Either the user or the manufacturer (especially for simple instruments) sets the operating conditions for modules. For example, to operate a spectrophotometer values must be set for source intensity, monochromator slit width, scanning speed and range, amplifier gain, and system time constant, among others, and start and stop commands must be given. If performance varies, the operator must attempt to reset values appropriately.

2) Automatic Operation. In automatic operation the operator selects the mode of operation and starts the device. Stable operating conditions and an appropriate S/N ratio are provided even though conditions may change during a measurement or from sample to sample by incorporation of feedback loops with selected modules. These loops incorporate servomotors or electronic circuits to insure that modules are self-atandardizing and/ or operate automatically. For example, in an IR spectrophotometer, monochromator alit widths can be set by a cam that turns as a wavelength scan is made. If the cam is shaped to reflect the relative source emission intensity as a function of wavelength, the width of the slit can be varied during a wavelength scan in such a

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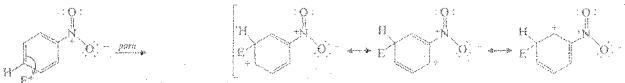
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way that the S/N of the beam falling on sample and reference cells is constant with wavelength. By such means automatic completion of a measurement is ordinarily assured during unattended operation.

3) Computer Operation and Control. For nearly complete control and automation one or more microprocessors (microcomputers) is wired into an instrument (or connections are made to a minicomputer). Nearly always programs for operation are entered by the manufacturer into the read-only memory associated with the computer. The programs include provision for the user to interact with the computer. According to the program called up, e microcomputer prompts the user to supply information about the kind of measurements to be made and the samples. The program indicated by these data provides for appropriate operation of modules and data acquisition. Subsequently the user, or more commonly, a second built-in microcomputer or a laboratory computer processes the data and extracts desired chemical information.

Some redesign of an instrument will, of course be required to effect computer control. Sensing devices such as position eocoders must be inserted to furnish data to the computer. Devices that the computer can actuate such as stepping motors must also he added

of individual modules even in sophisticated instruments.

The gains in having a microcomputer in an instrument are those already suggested and are well known to readers; greater ease, precision, and flexibility in use of an instrument and improved efficiency of data collection and processing. We will want also to consider these gains when reaching decisions about use and purchase of instruments.

The New Hyphenated Instruments

Is the modular approach applicable when an instrument has a plethora of modules? In the past few years increasing numbers of coupled, or as Hirschfeld has termed them, "hyphenated" instruments (7), with almost wice the usual numbers of modules have appeared. The first widely used hyphenated iostrument may have been a gas chromatograph-mass spectrometric (GC-MS) device, but MS-MS, LC-MS and many other coupled instruments have since been developed. Consideration of one of these apparently complex instruments seems worthwhile to demonstrate the general validity of the modular approach.

It proves helpful to begin hy asking where the instruments are joined. Take the GC-MS as a representative example. Its layout is sketched in line-modular form in Figure 5. Note that the output of the GC is the input of the MS. We can conclude that the GC resolves samples into their components and that the MS produces the spectrum of each of these in turn. Since the ability of the chromatograph to separate components is clearly being exploited, is it not reasonable to suggest that it is functioning here as a state-of-the-art sample module for the mass apectrometer? Perhaps "sampling module" would

interferences reduce the ability of an instrument to resolve aignals from substance of interest, or whanever the number of species in samples increases, upgrading the sampling module in some way will be necessary. Recall that what may be termed extra-instrument methods such as extraction of a substance of interest into a favorable solvent have long been employed and are still available for sample preparation. Where an instrumental solution is desired, chromatographic systems and devices such as mass spectrometers now offer their versatility, ease of use, and effi-ciency for "sampling." It is clear that this answer is attractive since hyphenated instruments are appearing in increasing numbers in research and other laboratory settings.

By application of insights from a modular analysis we see clearly how great is the contribution of this new class of hyphenated instruments in enhancing analytical power. For a more complete discussion of these devices the reader is referred to Hirschfeld's paper (7).

Conclusions

To understand the relative advantages of different instruments it is valuable to be able to view them as modular systems. Such a view cells for a qualitative knowledge of (1) the types of modules that comprise most instruments, (2) the performance characteristics of representative modules, and (3) the close correlation between the specifications for modules in the characteristic cluster of instruments and those of the resulting instruments. With this background, users of chemical instrumentation can ask appropriate questions that will help them reach de-

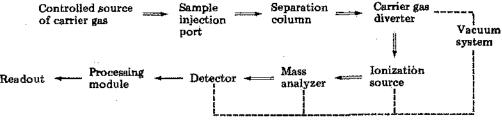


Figure 5. Line diagram of modules of a GC-MS hyphenated instrument.

to allow program control of scanning and other operations. A good account of the development of a sophisticated instrument with program control was given by Barnard (6).

We return to the query: How does the addition of microcomputers affect instrument performance? For an answer let us look both at the characteristic and processing clusters of modules. In the characteristic cluster currents, slit widths, etc. will now be set by a computer program instead of the user or manufacturer. In the processing cluster the microcomputer will take the place of several modules. Important gains in processing performance will result (in aignal massaging, data collection, and computation). Even in Fourier transform spectrometers a computer provides processing by shifting the domain of signals encoded with analytical information (from the interferometer in the IR spectrometer and from the detector in the NMR spectrometer). Recall that a shift of domain, from analog to digital, was already provided to accommodate the digital microcomputer. Yet every module will still interact with signals through its transfer function and input and output characteristics. Thus, we can conclude that instrument specifications always depend ultimately upon performance

be a name more descriptive of its role in this example. Can we describe the role of a sampling module? For a UV-VIS spectrophotometer, for example, we begin by stating that the sampling module holds the sample solution. But even the dissolving process can usefully be regarded as "part" of the module. Indeed it will need to be so considered whenever dissolving or diluting is mechanized, which is likely to be increasingly the case with sophisticated end sensitive instrumentation. The trend is certainly toward performing a greater number of operations on samples in instruments themselves.

Yet a still sharper focus on the role of the sempling module is warranted. Consider the characteristics of an ideal sample. For most measurements it would be ideal to have all "molecules" in the sample well separated to insure their separate reaction with "signal." Further, interfering substances should be masked or reduced to minimal concentrations to reduce spectral interferences and the kinds of chemical interferences often termed a matrix effect.

When will a regular sampling module meet these goals and when will we be well advised to select a hyphenated instrument with its state-of-the-art sampling module? Whenever cisions as to which instruments to use, buy, or lease for particular measurements.

The range of instruments examined should, of course, reflect kiods and number of measurements to be made, the types of systems to be examined, and the level of experience of persons who will use the instruments. Yet within that range the simplest instruments that have the desired sensitivity, accuracy, and operating features will be the best choice. There will be fewer parts to give trouble, spurious instrument responses will be more easily noted and traced to their source with greater ease, and maintenance will be simpler and less expensive. Usually the initial cost will be lower also.

To assist in the decision-making process, we also gain much by developing a working knowledge of widely used detector-transducer modules, signal-generator modules, and sampling modules. It is these types of modules that serve in the clusters of characteristic modules and that largely determine instrument specifications.

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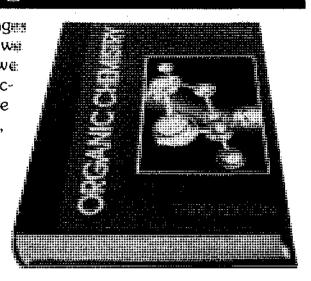
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ORGANIC CHEMISTRY, 3rd Edition T.W. Graham Solomons, University of South Florida (1-87032-3) 1984 1.097 pp.

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THETA MOLECULAR MODEL SET FOR ORGANIC CHEMISTRY Developed by Ronald Starkey, University of Wisconsin—Green Bay (0 471 86604-0) 1982

ORGANIC CHEMISTRY LABORATORY SURVIVAL MANUAL A Student's Guide to Techniques James W. Zubrick, Rensselaer Polytechnic Institute (0 471 87131-1) approx. 208 pp. 1984

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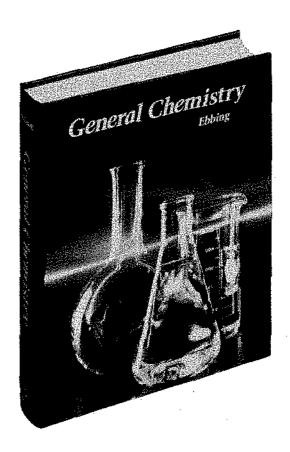
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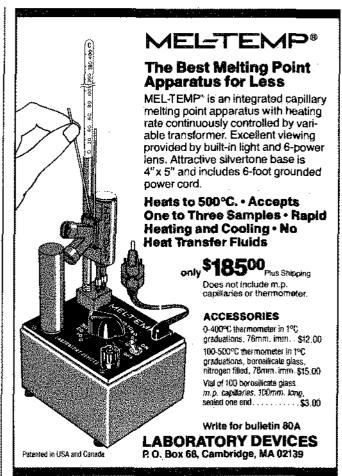
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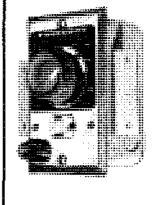
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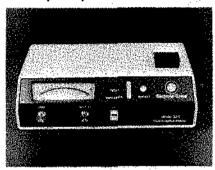
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JAMES A. GOLDMAN

New Apparatus and Equipment

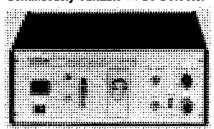
Meter Spectrophotometer



A low cost, compact spectrophotometer that features 8 nm bandwidth, solid state detector and electronics, and a diffraction grating monochromator has been introduced by Sequola-Turner Corp. Tha Model 320 Spectrophotometer has a continuous wavelength range of 330 nm to 1000 nm to cover all routine UV and colorimetric tests. This range can be extended to 210 nm with an easity installed Far UV accessory. This wide range is achieved by a monochromator having a plane diffraction grating in an f7 Ebert mounting. The monochromator utilizes a single casting to maintain alignment of the optics, sample, and solid state detector. Two controls simplify operation and a large analog meter provides easy readability in Absorbance and Percent Transmittance.

Circle #41 on Readers' Inquiry Card

Continuously Variable HPLC Detector

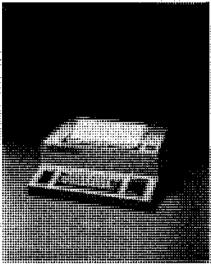


Knauer introduces an inexpensive, full-featured spectral detector for HPLC. Servo selection enables wavelength to be digitally set from 190-600 nm in 1-nm steps. Perfect for analytical and preparetive applications, this unit offers a complementally wide range of cells from micro to prep. Key front panel features include event mark, auto and manual zero offset, and eleven measuring ranges (from 2.56 to .0025 A.U. in binary steps). The 87.00's design incorporates a high pressure flow cell that is quickly and easily exchanged and cleaned, making occasional cell inspection quite simple. For automated systems all front panel features in the standard unit can be

externally controlled by computers and other devices. A microprocessor spectro controller which can change wavelength and range at preset times, as well as store scanned spectra, is available. It allows base-line correction, wavelength switching, spectrum substraction, and plotting after the chromatogram is completed.

Circle #42 on Readers' Inquiry Card

Chromatography Integrator



Perkin-Elmer's Model LCI-100 Laboratory Computing Integrator is a low cost chromatography data handling device. A simple, single-channel chromatography integrator, the LCI-100 offers flexibility in handling reporting functions and can replot and reintegrate chromatograms, it is preprogrammed for high high speed data acquisition, reduction and reporting. Key features of the LCI-100 include: all standard chromatography calculations (area percent, area normalization, external and internal standardization), multi-method/multipeak file storage with 128K bytes RAM, a choice of reporting peak height or peak area, run-timed events to customize data handling, e full alphanumeric keyboard, an interective Liquid Crystal Display, and a full size printer/ plotter.

Circle #43 on Readers' Inquiry Card

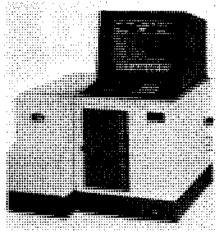
Microstructure Instrumentation

Erba Instruments, the U.S. sales and service organization of Carlo Erba, manufecturer of elemental analyzers, microstructure instruments and gas chromatographs, released a brochure highlighting the newest member in a family of specific surface area analyzers. The 6-page publication illustrates how the classical BET method can be automatically epplied for surface area determinations in a multitude of industries. Described are the

working principles, specific features and technical specifications of the SORPTY 1750. The instrument provides gas adsorption measurements and specific surface area analysis. The SORPTY 1750 is the only true single-point BET instrument designed for routine applications where results of surface area, density and chemi-sorption measurements are required within minutes.

Ctrcle #44 on Readers' Inquiry Card

Gas Chromatograph



Perkin-Elmer's new Model 8300 Gas Chromatograph is a compact, moderately priced instrument ideal for routine or process laboratories. The system incorporates built-in data handling with 12-in, video screen display and post run manipulation of data. Easy interchange between injector and detector types facilitates the analysis of a wide range of samples. The Model 8300 is available in two versions; the 8310 for packed column operation; and the 8320 for dedicated capillary systems. The Model 8300 provides enhanced performance through such features as automated bleed compensation; real time display of a chromatograph; and integral data handling facilities. The system is controlled by an advenced microprocessor, with user-interaction through the video display unit and simple keyboard with eight "soft keys." Screen graphics and integral data handling options allow the Model 8300 to be developed into a complete chromatography and data processing system. The screen graphics permit a chromatogram to be displayed in real time on the screen and replotted at the end of the run using variable screen widths and attenuations. Hard copy printouts can be obtained by connecting the Model 8300 to any coventional pen recorder or to a printer/plotter. At the end of an analysis, the built-in data handling system can fake over to display results in the form of

(Continued on page A102)

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a peak table and allows post-run manipulation of the data.

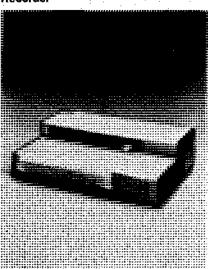
Circle #45 on Readers' Inquiry Card

Light Element Detector

A light-element detecting unit for energy dispersive X-ray analysis, called Econ III, is available from Edax International, Inc. Chief features of the new Econ III are: its ability to detect Boron (Atomic No. 5); remote window change for standard and light element ranges; and motorized controls with built-in protection against accidental vacuum loss, failure, or contamination. Design features of the new Econ III, based on Edax's seven years of experlence with Econ II (the first successful windowiess" detecting system for EDS) include smaller probe dimension for close distances to the specimen (for tighter X-ray geometry) and an improved electron trapping design for better noise ratios (for improved sensitivity). Motorized controls improve operator convenience and reduce likelihood of error during analysis.

Circle #46 on Readers' Inquiry Card

User Designed Chromatography Recorder



Linear instruments has announced the Model 1210 simplified, low cost recorder dedicated for use in liquid or gas chromatography. Nearly 3000 chromatographers were surveyed to learn those features which they wanted most, and least, in a recorder. The results were tabulated and the Model 1210 was built accordingly. Strikingly simple for high reliability and low price, the Model 1210 Chromatographic Recorder features a recessed zero adjustment and front mounted, push button control of power, chart drive and full scale spans. A convenient manual advance/rewind knob permits accurate chart positioning for parallel or overlay runs. Chart drive speed is 1 cm/min, but speeds of .25, .5, 2, or 4 cm/ min speeds are available through quick and simple gear changes. The 1210 is a flatbed model using 200 mm width paper, but can be wait mounted for space savings and accommodate fan-fold paper.

Circle #47 on Readers' Inquiry Card

Micro Gradient HPLC System

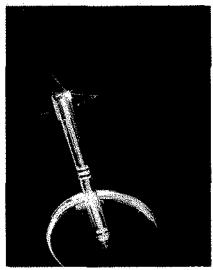


Becken instruments, inc. Alter Scientific Operations

In response to the growing interest in narrow bore chromatography, Beckman Instruments, Inc. has introduced the Model 344M Micro Gradient System. This system is designed to provide optimal performance when working with 2 mm HPLC columns. At the center of this system is the new Model 114M pump featuring user-selectable flow ranges of 0.001 to 1.00 mL/min or 0.01 to 9.99 mL/min, resulting in excellent reproducibility at low flow rates without sacrificing performance at high flows when they are required. A system organizer incorporates a low column dynamic mixer which is designed to blend and mix difficult solvent combinations effectively at low flow rates. The Beckman range of UV/Visible and fluorescence detactors is available with micro flow cells for optimal efficiency when used with this system. To complete the package, a range of 2 mm I.D. Ultrasphere columns is now available.

Circle #48 on Readers' Inquiry Card

pH Electrodes

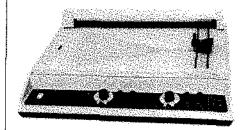


Curtin Matheson Scientific, Inc., hes introduced a line of pH electrodes, These products, named Silver Label pH Electrodes, provide these unique features: Porous Teflon liquid junction, which controls flow rate, resists clogs, inhibits "poison ion" penetration, and eliminates streaming potential; Stainless steel ceps; Low-noise cable; Special low-impedence full-span glass formula; and Patented technology. Manufactured in the United States, Silver Label pH Electrodes are available for

every application in the lab or in the field where reference, standard or combination electrodes are needed.

Circle #49 on Readers' Inquiry Card

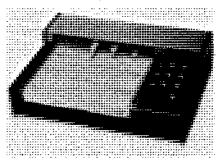
X-Y Recorder



introduced by Houston Instrument, the Series 200 X-Y Recorder provides users with both performance and reliability in a rugged and handsomely styled low-profile instrument. Designed for the working laboratory, the Series 200 meets the needs of both educational and industrial users. Reliability is enhanced by Houston Instrument's proven and patented capactive rebalance position transducer. This innovation eliminates the wear and electrical noise associated with slide-wire potentiometers. The Series 2000 X-Y Recorder has 11 switch-selected input ranges starting at 1/ mV/in., and 8 timebase ranges to drive the pen beam at speeds from 200 seconds/in. to 1 sacond/in. A slew rate exceeding 30 in./second assures accurate data representation.

Circle #50 on Readers' inquiry Card

Three Channel Flatbed Recorder

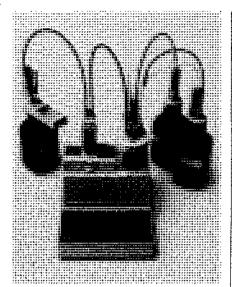


The Linear Model 595 Flatoed Recorder features three channel recording convenience and a large number of standard features. The Model 595 has 22 chart speeds, 10-in. (250 mm) chart width, 100% zero suppression, and 12 input ranges from 1 mV to 5 V. According to the manufacturer, this full size, sturdy recorder also features a remote programmable chart drive and an override event marker as standard. Other options are available.

Circle #51 on Readers' Inquiry Card

Karl Fischer Titrator

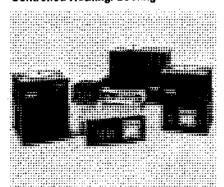
A microprocessor-controlled, precision instrument for water content determinations, capable of analyzing the moisture range from one part per million to 100 percent, is announced by Mettler instrument Corp. The Mettler DL18 Karl Fischer Titrator provides precise water content results with speed and extreme accuracy. The DL18 covers the full determination range which, until now, could only be done on two different instruments: coulomaters for trace analysis, and volumetric



titrators for high water content. Operation of the DL18 is quite easy; it is carried out via a "pushbutton dialogue" with the operator. Solvent dosing and evacuation of effluent ere ectivated simply with a push of a button. The result is determined automatically in percent, ppm, or mg of water. Many extras such as drift compensation, freely selectable stirring time and blank value correction are all standard. The same precision burette that is well-proven with Mettler's DL40RC MemoTitrator is also standard. By connecting the DL18 to a Mettler analytical balance and GA44 printer, convenience and reliability can also be increased. Sample weight may be accepted automatically and used for final calculation purposes. The printer will provide a complete record of resuits including date end sample number. The Karl Fischer method of determining water content is a procedure that has a permanent place in today's laboratories. Food, chemical and pharmaceutical manufacturers all need precise information about the water content of their products. And so do those in the petroleum and plastics industries. The Mettler DL18 Kerl Fischer Titrator is a cost-effective tool to provide this information.

Circle #52 on Readers' inquiry Card

Controlled Heating/Cooling

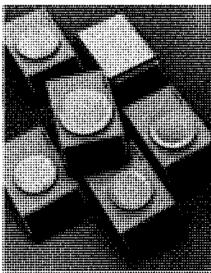


FTS Bio-Cool Controlled Rate Freezers provide a reliable and convenient means of obtaining precisely controlled cooling and heating rates for a variety of applications. Because the Bio-Cool is mechanically refrigerated, no liquid nitrogen is required for operation—only standard electrical current and a heat transfer medium such as methanol. Temperefure Ranges to -45°C, -70°C and -120°C are

available to satisfy virtually any production or laboratory requirements. All FTS Bio-Cools feature continuous digital temperature display. Three programmer models are available: a single-segment three-function, a four-segment three-function, and a sixteen-segment three function. The operator can select one digitally setable temperature, on ramp rate and one hold time per segment. The single-segment programmer offers as a standard an audible alarm which sounds when hold temperature has been attained. The four end sixteen segment programmers feature a non-voletile memory which will store a program for up to six months without electrical power. All programmers include an analog voltage output to facilitate future connection of the Bio-Cool to a temperature recorder, FTS supplied or other. The FTS line of Bio-Cool Controlled Rate Freezers can do it all: from the most basic on-site regimen to the most stringent laboratory protocol. All have the convenience, relieblity and low-cost that only FTS can offer.

Circle #53 on Readers' Inquiry Card

Laboratory Balances

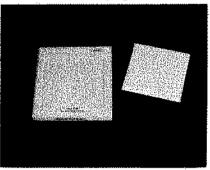


Four precision laboratory balances, two of which are equipped with exclusive Mettler DeltaRange are announced. These are designated Mettler models PE380, PE600, PE3600 and PE6000. These units, plus models PE160 and PE1600 introduced earlier, are designed to accept LabPac, Mettler plug-in software. LabPac dedicates the balance to laboratory routines such as not total weighing, percentage determinations, animal weighing, mean value (x), and standard deviation. Models PE360 and PE3600 feature DelfaRange, a fine weighing range that can be recalled at the touch of a button for weight determinations with a 10times better resolution. This makes it possible to accurately weigh very light components into heavy containers on one and the same balance. Model PE360 has a 0-360 g weighing range end reads to 0.01 g. Its DeltaRange weighing range is 60 g, reading to 0.001 g. For the PE3600, the ranges are 0-3600 g and 600 g; the readabilities are 0.1 g and 0.01 g. Models PE600 and PE6000 have capacities of 610 g and 6100 g, respectively with readabilities of 0.01 end 0.1 g respectively. Compared to previous models, the new PE balances show a number of interesting technological innovations. For example, a standby circuit makes sure that the balance is ready to operate as

soon as it is switched on. In this way, the warm-up time is eliminated. Automatic calibration is standard. And, in addition to obtaining weight indications in grams, the balance will convert them automatically to such nonmetric units as lb, oz, ozt, dwf, GN and ct on demand. The selected unit of weight lights up in the display and the results appear in large seven-segment numbers. Still another feature is the optimized integration of measurement values. This means that the balance always adapts itself to its environment and eutomatically calculates the optimum integration time.

Circle #54 on Readers' Inquiry Card

HPTLC/TLC Developing Chamber



An advanced-design Developing Chamber for high performance thin layer chromatography (HPTLC) and conventional TLC plates has been announced by Advanced Separation Technologies Inc. (Astec), Designated Vega-T 10X Developing Chamber, the unit is precision manufactured of white PTFE with a laboratory glass cover. Adjustable leveling legs and an Astec ACCUFLAT level ensure linear solvent fronts. HPTLC and TLC plates developed in the Vega-T10X Chamber have exhibited excellent R_i reproducibility in tests at a leading university and in the field. Uniquely, the Vega-T10X Chamber has two solvent compartments, one et either end, each of 5.0 ml capacity. This permits simultaneous development from either end of the TLC plate or sequential development. Further, mobile phases can be different in each solvent compertment or the same in both, greatly extending the number of samples under development, when mobile phases are the same or allowing differing mobile phases to be used in, e.g., optimization procedures. A feature of the Vega-T10X Chamber is the unit's versatility. It can accommodate one 10 X 10 cm TLC plate, up to two 5 X 10 cm plates simultaneoully or up to four 2.5 X 10 cm plate simulteneously, in operation the mobile phase(s) is "wicked up" from either (or both) of the solvent compartments to contact the TLC plate sorbent. Capillary action ensures an even, constant mobile phase supply and, as one result, separations exhibit excellent linearity. Vega-T10X TLC Developing Chambers are supplied with wicks (package of 25) and an ACCUFLAT. Replacement wicks, cover glasses and saturation sheets (used when saturated-chamber development is required) are all readily available from Astec and from selected laboratory supply dealers.

Circle #55 on Readers' Inquiry Card

HPLC Contamination Protection

Two types of guard columns to prevent liquid chromatography samples with non-aluting

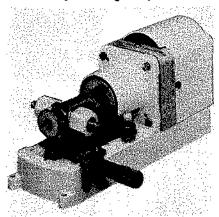
(Continued on page A104)

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materials from contaminating HPLC colums have been introduced by IBM instruments, inc. The guard columns are compatible with HPLC instrumentation and cost less than standard HPLC versions. The new columns are deeigned to prolong the life of analytical columns without degrading chromatography, reducing the cost per sample analyzed. Two types of guard columns are available, with normal (silica) or reversed-phase (octadecyl) pellicular packings. Each guard column kit contains 4.5 mm X 50 mm repackable hardware and 6 g of packing material. Replacement packing is available in 10 g units.

Circle #58 on Readers' Inquiry Card

3A Sanitary Metering Pump



FMI RP-SAN pumps conform to the 3A Sanitary Code of the U.S. Public Health Sarvice. Designed for high accuracy and dependability, the pumps provide long trouble-free service in food, deiry, drug, and pharmaceutical applications. Because of its high reliebility and accuracy, Model RP-SAN is an excellent tool for pumping expensive substances such as concentrated vitamins, flavors, odorants, colorants and other additives commonly used in the dairy, food, and drug industries. The pumps have only one moving part (the piston) and do not rely on valves that can clog or stick-the piston does the veiving. The cost effectiveness realized from 1% or better repeat accuracy makes the RP-SAN an excellent pump for critical metering needs. Standard units are available for flows to 1 liter per minute and pressures to 100 psig.

Circle #57 on Readers' inquiry Card

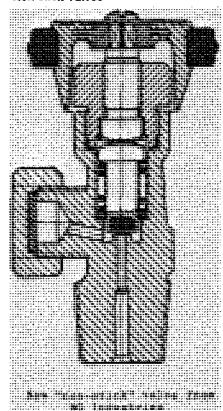
Autosampler Vials

Phase Sep announces e complete selection of borositicate glass vials for LC, GC, AA and other autosemplers. Original equipment equivalent replacements are available for all commercially available autosamplers, according to company. A variety of vial size and types are offered, compatible with original manufacturer specifications. Screw or crimp type closures are available with a broad renge of seal and septa materials to ensure compatibility with application and auto sampler type. Vials are made of borosilicate glass to prevent sample contamination from glass

impurities, and to permit autoclaving and reuse. Vial closures and seals are sold separately to accommodate vial re-use. Vials are sold in quantities of 100 with discounts allowed on volume orders. Crimpers, decappers and other accessories are also available. All items are sold from stock for prompt availability. Prices, say the company, are lower than those from other suppliers.

Circle #58 on Readers' Inquiry Card

Non-slick Valves

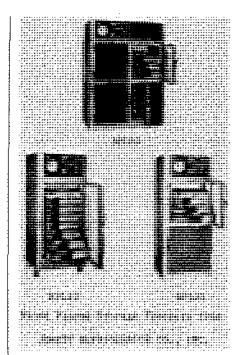


MG Scientific Gases, a division of MG Industries, announces e unique diaphragm velve for cylinders used for high purity, rare gases and ges mixtures. According to Rudi Endres, General Manager, "The newly designed velves incorporate an easy-to-use, energy efficient handwheel that eliminates the traditional problems of freezing and sticking. We have incorporated CGA & DIN type threads for domestic as well as international applications. Tests show that the valves have proven to be extremely effective with reactive as well as nonreactive gases. In our opinion, this will eliminate a big headache for many users." Features of the V6 diaphragm-type valve include smooth operation, superior airtightness, significantly lower gas losses, high gas tightness and a long service life. The soft-to-thetouch hendwheel provides a positive grip and is resistent to thermal and mechanical stress. MG valves are atocked and distributed from over 50 locations throughout the U.S.

Circle #59 on Readers' Inquiry Card

Blood Plasma Storage Freezers

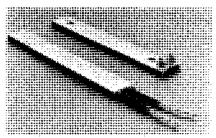
The Jewett Refrigerator Co., Inc. has introduced three models of blood plasma storage freezers equipped with constant security and surveillance system modules. Each meets or exceeds the strict temperature standard requirements set by The American Association



of Blood Banks, The American Red Cross and The Federal Food and Drug Administration, A mobile single door unit (model BPL 13) has capacity for 294 of the standard 400 ml capacity packs, double-door units (BPL 21) with 462 pack capacity and four-door models (BPL 41) holding 768 plasma packs all have temperature monitoring safety alarm systems featuring the built-in surveillance modula guaranteeing safe storage. Module design includes: a constant LED digital display of interior temperature in tenths of degrees Celsius, a monitor light and audible signal indicating safe operation, or warning alarm when temperature gets too high, door-ajar warning signal and a battery operated power failure alarm. A seven-day temperature recording thermometer is standard. Durable stainless steel interior construction with removable drawers and four Inch thick polyurethane vapor sealed insulation insures many years of energy-saving, trouble free operation. Uniform cabinet temperatures of -35°C are maintained by a rapid recovery fan circulation system. Jewett blood plasma storage freezers are equipped with safe eutomatic defrost, condensate evaporators and door fasteners with cylinder locks for security.

Circle #60 on Readers' Inquiry Card

Strip and Platen Heater

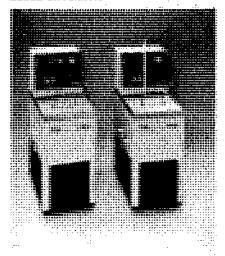


Watlow Electric Manufecturing Co. has introduced the Thincast Strip and Platen Heater, a cast-in aluminum heater, designed to produce efficient, uniform heat up to 800 degrees F. Tha heater is just ½-in, thick, yet provides the exceptionally long life for which cast-in heaters

are known, ideal for extruder die heads, heat sealing machines and heating and cooking surfaces, Watlow's new Thincast Heater is available in widths of 1.5 to 6 in. and lengths from 6 fo 22 in. It is available with welded stud terminals or flexible lead wires. Ceramic terminal covers are available and standard lead length is 10 in.

Circle #61 on Readers' Inquiry Card

Lauda Circulators



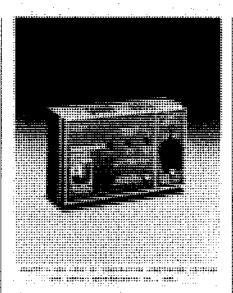
LAUGA REFRIGERATING CIRCUX ATORS, MODELS RMS-6 AND RMT-8

Brinkmann Instruments Co., Division of Sybron Corp., announces the line of Lauda constant temperature circulators, including immersion. heating and refrigerating models, most with digital temperature readout. Additional features includes a variable over-temparature safety shut-off which can be set to any temperture within the operating range of the circulator, independent of the set point temperature. If overheating occurs, an alarm sounds and power to the circulator is cut off. Several models also feature protection against low liquid level operation and duplex pumps for circulation to open external systems. Heater wattage automatically adjusts to maintain the set temperature with an accuracy of up to ±0.01°C, regardless of load. Zero cross-over switching/RFI suppression eliminates the possibility of electrical interference with other sensitive laboratory instrumentation. Energyefficient refrigerating models offer up to 75% savings in power consumption compared to conventional cooling systems. A microprocessor-based programmer accessory is available for heating and refrigerating models.

Circle #82 on Readers' Inquiry Card

Temperature Monitoring Systems

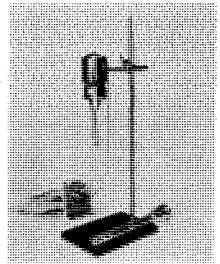
The Jewett Refrigarator Co., Inc. has introduced a line of 15 Temperature Monitoring and Temperature Power Monitor systems. Not only does the TPM system monitor temperature and power failure condition, but in the event of power loss, it continues to watch temperatures while signaling the source of the problem. A steady or flashing red light along with preset audible alarm signals, indicate varied alarm conditions with particular frequency pitches; the factory set units insure accuracy within £.2° centigrade. Designed for Blood Bank Refrigerators and Plesma Freezers, the TPM unit is easily adaptable for continuous moni-



toring of any liquid or other environment requiring controlled temperatures. The units are equipped with rechargeable nicad batteries that are maintained at full capacity through a trickle charge system. These batteries take over in the event of power failure to signal the problem and continuously survey temperatures. An included hermetically sealed relay allows simple connection to a master remote station as an alternate mode of installation, or the TPM may be paired with the TPMR remote monitor up to ½ mile away.

Circle #63 on Readers' Inquiry Card

Rotary Mechanical Homogenizer

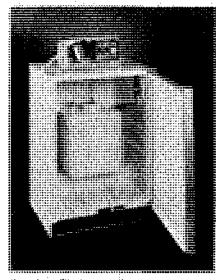


Heat Systems-Ultrasonics announces a complete line of rotary mechanical homogenizers and accessories. The Astramixer units mix, emulsify, disperse and homogenize by high intensity or mechanical and hydraulic shearing action, included in the line are two laboratory size units. The micro mixer is available with three different rotor/stator sets; 7 mm, 12 mm and 21 mm, allowing processing of samples from 250 microliters to 1 liter. The standard laboratory unit is available with 35 mm and 45 mm rotor/stator sets for processing 100 ml through 20 litter batches. An in-line attachment allows processing up to 5 gallons per minute on a flow thru basis. Also available are industrial scale units capable of 6000 gallons on a batch basis and 1785 gpm on a flow thru basis.

The manufacturer offers technical assistance on its toll free applications line.

Circle #84 on Readers' inquiry Card

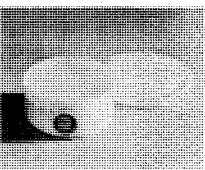
Refrigerated Composite Sampler



dimenin han alam amenda be meteika afika lilili fuhipentari kengabb Bergin. The americanation: Hill silicon a ling at and a statement of the community and a indian blu in it illing in a live in it հաննամ անն աննա առաքը առմոլից, , . . . իայ քարի. sample purge is adjustable in duration from 10-90 seconds. Liquid is discharged under pressure to the 5 gallon polyethylene composite container. The sampler may be operated on a timed-cycle basis or in proportion to the flow rate. The sample liquid is held during the collection period in a refrigerated compartment maintaining a 4-10°C range. For outdoor use, the 6300 is available with a weatherproof fiberglass enclosure which may be optionally equipped with insulation and 500

Circle #65 on Readers' Inquiry Card

Mercury Collector



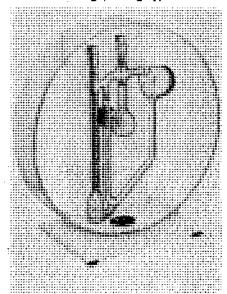
Chemtrix, Inc., announces a unique item that no laboratory which is concerned about safety should be without, the Mercury Collector. When a mercury spill occurs, the foam-lined fid is placed on top of the mercury and pressed firmly. The special foam holds the droplets until the lid is screwed onto the plastic collector; whereby, the mercury is released to the bottom of the collector for safe disposal.

Circle #66 on Readers' Inquiry Card

(Continued on page A106)

out of the editor's basket

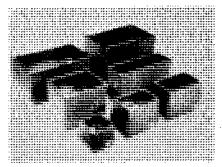
Oil McLeod Gage, Tilting Type



A mercury-free, oil McLeod gage, tilting type has been added to the Gilmont line of laboratory instruments. The degassing design is similar to the earlier patented design breakthrough of the oil swivel type. A high diffusion pump oil takes the place of the conventional mercury and its attendant toxicity. At the same time, the sensitivity of measurement is improved. Principal design features of the gage are: Teffon valve on closed end simplifies filling and cleaning, Additional tetton valve isolates gage from system, Sensitivity range from 1 millitorr to 2 torr, Accuracy: ±2% of reading or ±1 mm of scale, whichever is larger, Accuracy achieved with lerger preclsion bore capillaries and adjustment of bulb volume to $\pm 1\%$, Built-in rotary check valve for personnel/gage safety, Corrosion resistant plastic for long life, High vacuum Viton O-rings for all seals, Requires only 10 ml of diffusion oil, and Cicumferential acrylic housing for gage

Circle #67 on Readers' Inquiry Card

Ultrasonic Cleaners

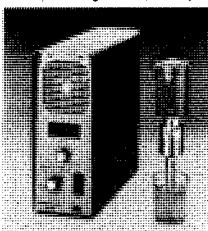


Chemtrix, inc., introduces a complete line of industrial ultrasonic cleaners which can remove oil, tar, agar, food, rust, ink, blood, etc. from glassware, laboratory equipment, surgical and dental instruments, electronic components, precision parts and many other items

that are hard to clean by conventional methods. Made of stainless steel, the tanks of the cleaners have capacities ranging from one pint to two gallons with 40 watts to 200 watts of cleaning power. Larger models have bottom-mounted drains and are available with heaters/timers.

Circle #68 on Readers' Inquiry Card

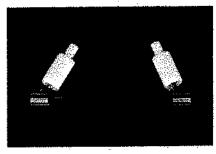
Ultrasonic Homogenizer/Cell Disrupter



B. Braun instruments announces the Braun-Sonic 2000, a high energy, ultrasonic homogenizar and cell disrupter. Consisting of a generator, transducer and a wide selection of probe tips, the main unit occupies 70 space-saving square in. of bench space. Modulation of the voltage waveform is a unique feature of the instrument. The acoustic wave from the probe tip is a function of the voltage waveform energizing the four piezoelectric elements of the transducer. The result is less generated heat and longer running periods. . . . up to a continuous half hour.

Circle #69 on Readers' Inquiry Card

Ultra Low Volume Cell



Ultra low volume flow-thru capitlary cells are now available from Harrick Scientific Corp. for liquid and gas chromatography studies. These cells have a gold-plated 3 mm bore and lengths of 5 or 10 cm, with volumes of 0.35 and 0.7 cc, respectively (other tengths cen be specially made). Windows are removeable and sealed to the tubulation via miniature O-rings. Construction is such that there is no dead volume. These light pipe cells can be used in most spectrophotometers with appropriete 4× beam condensers.

Circle #70 on Readers' Inquiry Card

Piastic Column

Valves, needles, etc. with luer fittings will snap snugly in place on the specially designed tip of the Isolab Quik-Sep luer-tipped polystyrene column. Column volume is 6.5 mL (total), with 6.0 cm berrel height. Interior diameter is 8.0 mm. The bottom of the column barrel is flat, not tapered, providing less opportunity for mixing in the tip. Available empty, with plastic filter disc (average pore size 50 μ m), or glass microfiber filter disc (S&S no. 24). For use with aqueous systams only.

Circle #71 on Readers' inquiry Card

Tissue Holder

Ever reach for tissues just to find that they're either out of reach or buried underneath something? Not any more! The hendy isolab Kimwipe Holder, wall or cabinet mounted, provides ready access to the standard size $(5\frac{1}{2}-in. \times 3-in. \times 4\frac{3}{4}-in.)$ Kimwipe box.

Circle #72 on Readers' Inquiry Card

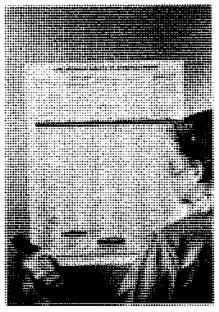
Liquid Dispensing

The Micro-Pipex is a light, hend-held instrument for conveniently dispensing liquids from glass capillary micropipets without using e mouth tube. Liquid is drawn into or dispensed from tha pipet by rotating a thumbwheel. A fast-release button allows suction by capillary action alone or quick delivery of pipet contents. The Isolab Micro-Pipex gives smooth and precise control over what has been e tedious procedure.

Circle #73 on Readers' Inquiry Card

New Literature

Hazardous Waste Chart

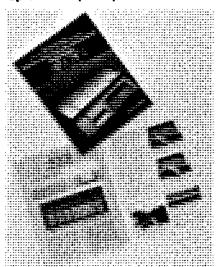


Anyone who collects, stores or trensports chemicel weste must determine if the waste is considered hazardous under the provision of the Resource Conservation and Recovery Act, and if the waste is considered hazardous, it must be identified with a RCRA number. This information can be found in the Federal Register but only with difficulty. To make it easier to obtain this informetion, Lab Sefety Supply Co. has published a chert that makes this information more readily available. This 17-in. X 22-in. chart aids in identifying the classes

of chemicals that are considered hazardous, and provides the actual hazardous waste number for over 650 chemicels. This chart helps in the identification of hazardous wastes and speeds up paperwork procedures required under RCRA.

Circle #74 on Readers' Inquiry Card

Split-Beam Spectrophotometer



A full-color 8-page brochure detailing the Spectronic 1001 split-beam spectrophotometer is available from Bausch & Lomb, in the split-beam optical system of the 1001, a small fraction of the abundant energy is split off and used as a reference beam to give the instrument a level of stability previously associated only with double-beam spectrophotometers. High energy that begins with high-intensity source lamps is conveyed to each sample with minimum loss by way of silica-coated toroidal mirrors and a Bausch & Lomb holographic grating. As a result, the 1001 provides stable readings throughout the wide 190-950 nm wavelength range, and accurate measurement of samples from near 0A to beyond 3A with no dilution. A high-resolution 2 nm spectral bendwidth and low stray radiant energy contribute eccuracy and fine-structure definition. The brochure discusses typical communications with the 1001 with graphic illustrations. The user-friendly, dual function membrane keyboard allows alphanumeric entries to be made easily. The "keys" have been carefully organized so that any user will be commanding the instrument comfortably and confidently within a short period of time. The 1001 can be preprogrammed for various test types and operations. The internal RS-232-C computer interface eccessory further expands the capabilities of the 1001 by permitting two-way communication between the instrument and virtually any computer. This brochure on the Spectronic 1001 spectrophotometer provides technical data; discusses product features and routine test procedures; describes the individual keyboard functions; lists custom sampling accessories, test types, and operations: and provides samples of the display prompts for a specific test program format.

Circle #75 on Readers' Inquiry Card

Common Organic Solvents IR

The Infrared Spectra Handbook of Common Organic Solvents is a compilation of the infrared spectra, physical constants and other

supporting data of the 400 most commonly used solvents. It is the most comprehensive book available on organic solvents and serves as a convenient and practical desk reference which is invaluable to chemists in solvent Identification and analysis. Information for each solvent is arranged on two pages in a large, easy-to-read format with the infrared spectrum appearing on the page directly opposite the supporting chemical deta. The spectra are presented in a transmittance vs. wavenumber format over the spectral region 4000 to 400 cm⁻¹, end all are clearly labeled with the source of sample and the sample preparation technique used. All spectra are prepared in Sadtler's own laboratories, under the direction of Sadtler's spectroscopists, using standard preparation and evaluation techniques which insure that these reference spectra are of the best possible quality. Each compound is listed by its Chemical Abstracts name or its most readily recognizable name, together with frequently used synonyms. In addition, the CAS Registry Number and the NIOSH Number are given when available. Also, the data page provides the molecular formula and literature values of physical properties such as melting point, boiling point, flash point, density and refractive index. Additional information regarding use, solubility, flammability and toxicity appears for most compounds, and nearly all of the solvents are depicted by a conventional drawn structure and by the Wiswesser Line Notation. The compounds in The Infrared Spectra Handbook of Common Organic Solvents are indexed both alphabetically and by molecular formula, allowing for the rapid tocation of any spectrum. In addition, the solvents in the Handbook are classified into four main groups; hydrocarbons, compounds having only one type of characteristic atom or functional group, compounds having more than one type of characteristic etom or functional group and deuterated compounds.

Ctrcle #76 on Readers' Inquiry Card

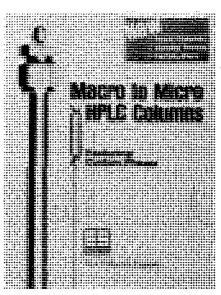
Scientific Spectroscopy

The Harrick Scientific Catalog of IR-VIS-UV Accessories presents a complete line of spectroscopic products. Crystals, polarizers, solid/liquid-gas sampling and other transmission accessories, specular external and internal reflection as well as diffuse reflection attachments, vacuum chambers, beam condensers, and skin analyzers, for both dispersiva and Fourier Transform UV-visible and infrared spectrophotometers. Other products include plasma cleaners, pyrolysis chambers, spectrometer systems and much more. Many products ere new and listed for the first time. Harrick Scientific also specializes in custom instrumentation-designs to fit any spectrometer and meet all custom needs.

Circle #77 on Readers' Inquiry Card

HPLC

A HPLC Brochure featuring microbore technology and custom synthesized HPLC phases and packings is available from ES Industries. Included in this latest company literature is a complete time of Chromega HPLC Columns, Packings and Accessories for a wide range of preparative, analytical, and micro analytical applications. In addition, the brochure introduced a line of Microbore HPLC Columns and a service for custom packings. This new service makes it possible to specify particle size,



shape, and pore diemeter and to define and select by structure the desired stationary phase. The μ Chromega Microbore HPL Columns ere available in most Chromegabond packings and come in standard lengths of 30 cm, 50 cm, and 1 meter.

Circle #78 on Readers' Inquiry Card

HPLC Biomedical Applications

An exciting set of applications is available from KBL Instruments, Inc., describing their line of ton Exchange and Gel Filtration Columns. Chromatograms are optimized for high resolution, rapid analysis, linearity, and selectivity. Compounds separated are proteins, peptides, and amino acids on a preparative and analytical scale. The instrumentation required to optimize results is discussed and ranges from state-of-the-art pulse-fee solvent delivery systems to LKB's "intelligent fraction collector. Complete systems can be operated automatically using the HPLC controller and new euloinjector.

Circle #79 on Readers' Inquiry Card

Gas Chromatographs

A 16-page four-color brochuse describes Varian's Vista 6000/6500 Gas Chromatographs. Key features of both the 6000, with its powerful built-in microcomputers, and the dual-column 6500 Satellite Chromatograph are covered in photographs and illustrations that complement the informative text. Expansion capabilities, modular construction, unique CRT and keyboard features, and conveniencedesigned, large column oven, separate pneumatics compartment and universal injector and detector bases are described in detail. Six detector choices, a versatile injector system, and advanced capillary systems also are delineated, as is the optional 18080 AutoSampler that provides total automation.

Circle #80 on Readers' Inquiry Card

Refractometers

Sixteen-page, fully litustrated catalog of complete line of refractometers, including hand-held, Abbe, and digital instruments, ia announced by NSG Pracision Cells, Inc. The

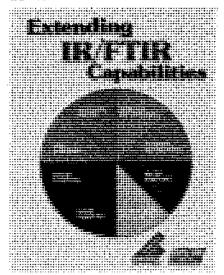
(Continued on page A108)

out of the editor's basket

refractometers are used for measuring the sugar content of all types of food products. Also included are a series of clinical refractometers for determining serum protein and urine specific gravity. Separate tables list the Brix and refractive index and provide a guide for selecting the correct instrument.

Circle #81 on Readers' Inquiry Card

IR/FTIR Accessories



Barnes Analytical/Spectra-Tech has published a 16-page 1984 Catalog titled Extending IR/ FTIR Capabilities. The Catelog, which describes more than 1,000 IR and FTIR accessories, is reported to be one of the most comprehensive laboratory purchasing guides of its kind ever produced. For the sake of trouble-fee reference, the Catalog is divided into eight mein sections, according to Spectra-Tech. The sections are internal Reflectance; External Reflectance; Micro Sampling; Temperature/Pyrolysis; Solid Sampling; Liquid Sampling; Gas Sampling; & Crystals & Prisms. Information in the Spectra-Tech Catalog includes guidalines on accessory use, prices and other facts "designed to make selection as easy as possible," the company stated. Special pages feature detailed reports on two of Spectra-Tech's newest developments: the CIRCLE for FTIR work with aqueous solutions; and the Collector for research with DRIFTS (Diffuse Reflection Infrared Fourier Transform Spectroscopy).

Circle #82 on Readers' Inquiry Card

AA Spectrophotometers Accessories

Verian Associates' complete line of accessories and supplies for its atomic absorption spectrophotometers is datineated in an 18-page color catalog. Photographs and descriptions of the AA support meterials are accompanied by ordering information, and listings on replacement parts, and spare board kits and cables, information also is included on available audio-visual training programs, technical manuals, and other reference and training materials.

Circle #83 on Readers' inquiry Card

Recorder

A four-color brochure from Houston instrument describes the extensive built-in intelligence, touch-panel controls and dependable mechanical features of the 4500 Microscribe. Photos and accurate descriptions define the features which give the 4500 Microscribe enhanced capability at a lower cost than a basic strip-chart recorder. Microprocessor control joins Hi's patented capacitance servo rebalance system to assure flexibility and reliability unprecedented in strip-chart recorders. In addition, an automatic self test function and daylight-readable liquid crystal display (LCD) continuously inform the operator of recorder parameters and status. The brochure contains thorough performance specifications, as well as details of general features and accessories.

Circle #84 on Readers' Inquiry Card

Calibration Devices for Instrumentation

Tracor Atlas, Inc., specialists in H₂S measurement and instrumentation, has recently compiled and published a catalog revealing their line of calibration equipment. This catalog offers an overview of the devices including principles of operation and typical applications for each instrument. Technical field services offered by the company are also mentioned. This easy to read, informative catalog pictures each device clearly. The products in the catalog include: kits for liquid and gas sample preparation; a pocket size generator for H₂S samples; a standard reference gas generator; a gas calibration cylinder; and a linear motion syringe-drive for injecting gas, liquid or solid samples. A Spanish edition is also available.

Circle #85 on Readers' Inquiry Card

Ultramicrobalance

A six-page brochure from Perkin-Elmer describes the ultramicrobelance, the AD-6 Autobalance, highlighting instrument features and benefits that simplify micro-weighing tasks now more than ever before. The AD-6 offers 0.1 microgram sensitivity with 5 grem capacity, and nonvolatile memory for up to 899 samples. All operations are microproceasor controlled through simple keyboard commands, which means weights can be stored, recalled, factored and statistically analyzed faster and easier.

Circle #86 on Readers' Inquiry Card

Laboratory Water Systems

A catalog on laboratory water purification systems is available from Millipore/Continental Water Systems. The catalog (CG150) includes a review of current standards for laboratory reagent grade water, as well as descriptions of the company's complete line of products and services for the laboratory. Included are water systems specifically designed for applications requiring organic-free (less than 50 ppb) water for such applications as critical HPLC, and ultrapure, pyrogen-free water for use in sensitive biological areas.

Circle #87 on Readers' Inquiry Card

Water Analysis

Thomas Scientific announces their 1984/85 Water Analysis Catalog. The catalog contains 248 pages and is the most comprehensive water testing catalog available. It is arranged alphanumerically for easy reference, and contains over 2,500 items and over 800 photographs and illustrations. Featured in the catalog are LaMotte water testing kits, instruments, and associated apparatus, individual test kits, multiparameter kits, portable meters, and reagent systems are offered for more than 60 chemical parameters. The catalog also contains a listing of virtually eny piece of laboratory apparatus or reagent, representing over 135 different manufacturers, needed in the water/wastewater testing field. As a new feature, all prices in this catalog will be held firm by Thomas Scientific until January 1, 1985.

Circle #88 on Readers' inquiry Card

Viscometers and Rheometers



A 24-page, full-color catalog details the Fenn Instruments product line of viscometers, consistemeters and related rheological instrumentation for industrial, commercial, scientific and academic applications, in addition to direct-indicating viscometers, recording and high-temperature rheometers, consistemeters and accessories, the new Fenn catalog includes frequently needed viscosity computations and conversion factors.

Circle #89 on Readers' Inquiry Card

Minimize Gas Stream Contaminants

Scott's comparative study determines that regulators with stalnless steel diaphragms minimize gas stream contaminants. Laboratory Report E-R63-1 gives details of the study where three two-stage regulators were tested, including Scott's Model 16 high purity regulator.

Circle #90 on Readers' inquiry Card

Miscellany

Six Millionth Substance in CA

Chemical Abstracts Service has recorded the six millionth chemical substance in the files of its Chemical Registry System. The total includes all unique chemical substances indexed

in Chemical Abstracts since January 1965, when the Registry began operating as an adjunct to Indexing operations at CAS. The six millionth substance to be registered, 2-cyciohexyl-3-methyl-4-(pentylamino)-2-cyclopenten-1-one, was disclosed in a West German patent application filed by Masayoshi Minai and Tadashi Katsura of Sumitomo Chemical Company, Ltd., of Japan. It was one of 360,000 new substances added to the Registry file in the past year. The patent application also describes 66 other cyclopentenone derivatives synthesized by the inventors. Including reactants involved in the syntheses, CAS indexed 137 substances from the patent document.

CAS developed the Chemical Registry System in the early 1960's to provide a means for determining whether a chemical substance reported in the scientific literature hed been indexed previously in *Chemical Abstracts* and retrieving the previously assigned index name if it had. The system now performs about 6000 substance identifications each working day in support of indexing operations at CAS. The Registry also is the basis for the CAS ONLINE search service, which makes it possible to search the file of 6 million substances by name or structural characteristica to retrieve structure diagrams, names and bibliographic citations for substances of interest.

Circle #91 on Readers' Inquiry Card

Software Programs

UV Software Notes, written by Perkin-Elmer personnel and users of Perkin-Elmer instruments, computers, and software are available. The typical UV Software Note describes a specific application, usually quite small and not covered by Perkin-Eimer price listed software, and includes simple instructions on how to run the program. Programs are formatted for the Perkin-Elmer model 3600 Data Station and are written in either the BASIC or OBEY language of the Perkin-Eimer Computerized UV (PECUV) application software. Current programs include: 1) A program for Hard Copy Printout on the PR-100 Printer, 2) A program to Label a Spactrum, 3) Wavelength Programming for Lambda 3, 4) User Programming with Lambda 5, and 5) First Order Kinetics.

Circle #92 on Readers' Inquiry Card

ion Chromatography Software

A dedicated software package developed for Ion chromatography applications has been introduced by Nelson Analytical, Inc. This software is offered as part of the standard chromatography software package for Nelson Analytical's 4400 series multi-instrument data systems, which are based on the HP 200 series desktop computers. Data from up to 10 ion chromatographs (20 detectors), or conventional gas and liquid chromatographs can be processed on the same system simulteneously. Each ion chromatograph is connected to the Model 4416 data system through a Nelson Analytical intelligent interface-a 20-bit precision analog-to-digital converter. This interface collects the analog signal from the chromatograph and stores it in digitized form. Data sampling rates for this system renge from one point per 10 seconds to 100 points per second. With the chromatography software installed, the Model 4416 system lets the operator construct ion chromatography methods for the specific application required.

These include: peak detection algorithms in the software for negative peaks; changing the baseline treatments; and altering bunching factors within a specific run.

A routine customized for ion chromatography allows the operator to designate the baseline so that negative excursions in the chromatogram-typical in ion chromatography-do not affect the baseline and peakdetection treatments. Quantitations by internal or external standards are possible, and final results displaying area percent reports, replotted chromatograms with baselines and peak names are included in the software. All raw data is stored on disk for easy recall of stored runs, or alteration of baselines for new calculations, in eddition, the chromatograms can be recalculated with different integration parameters and calibration curves. Special routines in the software allow the user to recall and graphically compere stored ion chromatograms, subtract chromatograms and perform ratio calculations. The Nelson Analytical Model 4416 data system includes hardware, A/D Interface, and software for ion chromatography.

Circle #93 on Readers' Inquiry Card

General Chemistry Software

A software program for high school, college and university students named "Introduction to General Chemistry" has been given a 1983 Learning Computer Software award. The COMPress program is designed as a supplement to an introductory course in General Chemistry for students with no previous Chemistry background. By simulating Chemistry experiments on the computer, students are exposed to realistic laboratory situations which saves time and the cost of actual experiments. Additionally, the program allows students to gain experience in collecting and interpreting data. Extensive use of color animations in an interactive format keeps student interest high. "introduction to General Chemistry" is presently a seven-disk series. "We plan to add six disks to the series in 1984. said Thomas L. Sears, General Manager of COMPress. "We are proud of the industry recognition for this program and the program authors, Professor Stanley Smith, University of Illinois, Dr. Ruth Chabay, and Dr. Elizabeth Kean." All entries for Learning Computer Software Awards are judged by a committee of teachers, subject specialists, computer educators and instructional media developers.

Circle #94 on Readers' Inquiry Card

Educational Computer Labs

Fisher Scientific Company, Educational Materials Division, located in Chicago, Illinois, has installed fifty-two Commodore 64 Computer Laboratories in selected elamentary, junior high, and senior high schools in the District of Columbia Public Schools, These laboratories will be used for teacher training and computer literacy instruction for students. Thirteen labs were in use this summar for a Summer Computer Camp Program. Each laboratory consists of ten Commodore 64 computers and monitors which are networked to a common disk drive via the MUPET networking system that allows studenta to share a common disk drive and printer. All computers are individually housed and secured to computer furniture.

Circle #95 on Readers' inquiry Card



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Publications of the DIVISION OF CHEMICAL EDUCATION, A.C.S.

SAFETY IN THE CHEMICAL LABORATORY Vol. 1—Edited by N. V. Steere

This paperback report contains all of the contributions to the monthly feature, "Safety in the Chemical Laboratory" which have appeared in *J. Chem. Ed.* from January 1964 through January 1967. Paperback, 132 pp., US \$10.35, Foreign \$11.25. (Postpaid)

Vol. 2-Edited by N. V. Steere

Contains all of the articles from the "Safety in the Chemical Laboratory" column which have appeared from February 1967 through January 1970. 1971 Paperback, 132 pp., US \$10.35, Foreign \$11.25. (Postpaid)

Vol. 3-Edited by N. V. Steere

Contains all of the articles from the "Safety in the Chemical Laboratory" column which have appeared from February 1970 through January 1974, 1974 Paperback, 157 pp., US \$10.35, Foreign \$11.25, (Postpaid)

Vol. 4---Edited by M. M. Renfrew

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editorially speaking

The Subjective Nature of Science

The importance of science as a component in the existence of most contemporary societies cannot be seriously debated. There is, however, considerable disagreement among highly respected individuals who have thought deeply about the questions that arise when the demands of scientific objectivity clash with the obligation to pursue societal goals. For welltrained scientists, objectivity becomes as natural as breathing, yet the character of many societal issues, which ranges from rather explicit questions of ethics to less well-defined questions that appear to have their solutions in economic considerations and/or politics, generally does not seem amenable to solution by those trained as scientists. A clear code of behavior has evolved over the last few centuries to guide the process of science. The ethos of science involves the acceptance or rejection of the reported findings of others on pre-established impersonal criteria, as well as the public presentation of scientific findings so that they are available to the entire scientific community. The latter is usually, and preferably, done after critical review by those knowledgeable in the fieldreferees, symposium chairmen, and editors. A part of the ethos involves organized skepticism that subjects reported findings to continuing critical review with no assurance of finality. Scientists are expected to point out the limitations and/or levels of uncertainty in their findings and in the inferences they draw. They are also expected to acknowledge their indebtedness to others whose work-whether published or unpublished-has contributed to their accomplishments. Science is, thus, a communal enterprise in which every contribution builds upon the work of others.

These characteristics of science are the basis for the widely held opinion that "science is objective" yet a point also can be made for a fundamental subjectivity in science. Some have argued that science is subjective because its progress is driven by choice. Scientists choose the areas of knowledge they wish to develop as well as the methods by which that knowledge will be sought. Thus, in the final analysis, science can be seen as a subset—a possibly minor one—of the human condition. Although many scientists have acquired some very powerful tools of logic within the context of their profession, they are not necessarily well-equipped by their training to deal with the subjective aspects of perceived problems that face society.

The consummate scientist will refuse to move beyond his/her technical competence when faced with questions requiring information that is either unavailable or exceeds the level of maturity of the science. Yet, these are the very situations when the public turns to science—rightly or wrongly—for informed judgment. Thus, even when a scientist's training dictates that a scientifically acceptable comment cannot be made with precision, that same training should produce an appraisal of the limits of uncertainty of any responses and/or the inferences drawn.

The training of scientists is not totally devoid of skills that might well be useful in addressing societal issues. For example, a sense of responsibility is among the highly desirable traits that are honed to a fine edge in the training of scientists. The essence of scientific responsibility derives from an inner need to get to the hottom of things. Scientists tend to persist until they understand the true nature of the problem hefore them. Furthermore, scientists are supposed to be able to express their reservations fully and honestly, and to be prepared to admit error. That's not a bad list of traits to be able to bring to bear on societal problems.

JJL

in this issue

G. N. Lewis Symposium

The last four papers of the proceedings of the G. N. Lewis Symposium appear in this issue. The papers by Stranges (page 185), Jensen (page 191), and Pauling (page 201) each treat a different aspect of the development and acceptance of the Lewis theory of bonding. The fourth paper, by Kasha (page 204), relates the details of Lewis' last major investigative work—research with Kasha to confirm their ideas on the triplet states of molecules.

All of the papers in the G. N. Lewis Symposium in the last three issues have been designated by a drawing of Lewis that is adapted from an original that appeared in CHEMTECH. We wish to thank the artist, Alan Kahan, and CHEMTECH for allowing us to use this drawing as our Symposium logo.

Solar Energy

Solar energy has captured the imagination of a large segment of the population which is interested in alternatives to fossil fuel resources. The existence of a "free" source of energy is very seductive, particularly to those who perceive our current energy sources as either an environmental or economic threat. The heat generated by these latter perceptions constitutes a secondary energy source in itself; however, the teacher of chemistry can exploit this intense interest to shed some light on difficult concepts involving semiconductors and thermodynamics as well as on the limits of science to solve social problems. Three articles in this issue focus on one of the technical aspects of solar energy utilization and include discussion of practical applications and limitations.

There are two modes of solar energy use which are of current interest: the direct storage and use of heat energy from infrared solar radiation and the conversion of light to electrical or chemical energy. McDevitt (page 217) in his article "Photoelectrochemical Solar Cells" explores the latter mode, explaining the role of semiconductors in effecting the energy conversion and the problems involved in finding processes which efficiently utilize the solar spectrum. He also gives directions for preparing a workable photoelectrochemical cell which demonstrates many of the principles involved in this complex problem.

Adamson, Namnath, Shastry, and Slawson (page 221) take a more basic approach to solar energy by deriving the theoretical limitations to the efficiency with which light energy can be converted to work. They show how application of Einstein's law of photochemical equivalence places a limitation on how much of the available spectrum can be used for a particular conversion process and bow the application of the laws of thermodynamics produces yet another limit on the conversion's theoretical efficiency. They conclude that solar energy is more efficiently utilized when it is absorbed directly for heating purposes. Their approach, which includes chemical examples, would make a useful classroom presentation since it points out clearly that not all of that "free" energy is just laying around waiting to be turned into electricity as some in the popular press would have us believe.

Even the direct use of solar energy in the form of heat energy has its technical problems, particularly in those areas where fairly large amounts of heat energy have to be stored to compensate for the unpredictability of the energy source. Spears and Spears (page 252) recycle an old favorite, the demonstration which uses CoCl₂ to illustrate the facile change in coordination number by some transition metals, and use its endothermic reaction as a heat storage device in an experiment that can be performed at the advanced high school or first-year college level.

Organic Chemistry

Organic chemistry covers such a wide range of compounds and, by extension, theoretical and experimental approaches that it is one of the key building blocks of the undergraduate curriculum. It appears in many guises, from theoretical treatments involving thermodynamics to practical applications of natural products that are intimate parts of our daily lives. Several articles in this issue are about one of these many aspects of organic chemistry.

Before it is decided whether a particular reaction or theory is appropriate for the organic course, it is necessary to examine what the objectives of the organic course as a whole should be. In this month's Goals feature (page 239), two authors, Clapp and Johnson, from a university and a high school, respectively, give their views on the values as well as the contents of the organic course at each of their institutions.

The recognition of the bond resonance in benzene is the very heart of much of the bonding theory of organic chemistry. George, Bock, and Trachtman (page 225) evaluate the empirically derived resonance energies as thermodynamic reaction energies. Another application of resonance theory has been in explaining the anti-Markovnikov addition. In this month's Textbook Forum, Tedder (page 237) points out that the explanations of free radical addition to alkenes given in most texts are often misleading and sometimes wrong, partly due to the reluctance of authors to develop the more complicated, but accurate, picture.

Teachers looking for some interesting history as well as some practical applications of organic chemistry will find Cummings' Profiles in Chemistry on Wallace Hume Carothers both informative and useful. Another article with a "real world" biochemistry application is this month's Thumbnail Sketches feature in which Fernelius answers the question: "Is Sugar from Sugar Beets the Same as Sugar from Sugar Cane?"

An experiment which teaches the theory and application of HPLC by expanding the traditional organic exercise on the separation of a carotenoid from the chlorophylls of a vegetable is provided by **Silveira**, **Koehler**, **Beadel**, and **Monroe** (page 264). Another aspect of the organic laboratory, the dangers involved in unsuspected peroxide formation is aging solvents, is discussed by **Nagel** (page 250) in this month's *Safety Tips* feature.

Reflections on the Electron Theory of the Chemical Bond: 1900-1925

Anthony N. Stranges

Department of History, Texas A&M University, College Station, TX 77843



Science has so deeply influenced our lives that we sometimes tend to see scientific ideas as something final, something eternal and static. In reality, scientific ideas are human creations with their own history, and their historical study often contributes to a more complete understanding of modern science. The electron theory of the chemical bond is one of the many important ideas that became a part of modern science.

This essay will examine its history (1).

The first electrical theories of the chemical bond accounted successfully for the large number of inorganic compounds that chemists and physicists knew were clearly electrical in behavior. When applied to the much larger number of organic compounds, they proved inadequate. The bond in organic compounds did not receive a successful interpretation until 1916 when G. N. Lewis (1875-1946) at the University of California. Berkeley, announced his theory of the shared electron pair. Lewis showed further that the formation of electrical compounds was only a special case of his more general theory. His theory remains to this day the foundation of modern chemical bond theory.

Nineteenth Century Ideas on Electrical Combination

Quite early in the 19th century, natural philosophers, the chemists and physicists of that time, had agreed that all bodies—solid, liquid, and gaseous—consisted of atoms. They called a body that contained atoms of one kind, an element; a body composed of two or more different kinds of atoms was a compound. Natural philosophers also recognized at this time that an electrical force held the atoms together. Construction of the first electrical battery and the discovery of the electric current by the Italian Alessandro Volta (1745-1827) in 1800 established that a chemical reaction between different kinds of atoms produced an electric current (2). A demonstration of the opposite effect followed almost immediately. William Nicholson (1753-1815) and Anthony Carlisle (1768-1840) in London showed that an electric current could separate a compound into its atoms. They found that the compound, water, consisted of two gases: hydrogen and oxygen (3). After other investigators, chiefly Humphry Davy (1778-1829) at the Royal Institution in London and J. J. Berzelius (1779-1848) in Sweden, succeeded in decomposing numerous chemical compounds with an electric current, the identity of the attractive force as electrical seemed complete. An electric current separated a chemical compound into its elementary constituents; an electric cell produced its electricity only with an accompanying chemical change.

The model which illustrated most clearly an atom's electrical behavior assumed that certain atoms were naturally electropositive, others electronegative, and that the attraction between them explained the well-known attraction of unlike charges in large bodies. Berzelius in 1811 developed a much more elaborate electrical theory of attraction. He imagined each atom to consist of one or more electric poles; the positive and negative electrical charges resided in opposite parts of his atom like the poles of a magnet. Attraction between atoms resulted from neutralization of the opposite electrical charges at the poles (4).

Electricity was the rage of the early 19th century, and the-

ories that supported an electrical attraction between atoms dominated the physical sciences. But near the middle of the century these theories began to diminish in popularity among chemists. The reasons for their fall are several, but the one of most importance was the rise of organic chemistry. Chemists increasingly studied substances of vegetable and animal origin and were content only to analyze the number, kind, and arrangement of the atoms, usually carbon, hydrogen, and oxygen, in those substances. They paid no attention to the force holding these atoms together.

The rapid rise of the chemical industry, particularly in Germany in the second half of the 19th century, made evident organic chemistry's newly acquired prominence. German chemists carried out analyses and syntheses of dyes, drugs, and petrochemicals, all organic substances, without assuming any electrical theory of attraction. A simple line represented the bond uniting atoms in these compounds. The British chemist, William Tilden (1842–1926), pointed out this 19th century development much later in a lecture before the London Chemical Society (5)

We have a universally acknowledged system of combination exhibited by atoms without necessarily forming any hypothesis on the nature of their attractive force.

Organic chemistry had diverted the attention of chemists from any theoretical explanation of the bond between atoms. The excitement of discovering new compounds was, apparently, sufficient justification for not considering such a speculative problem. At the same time, organic chemists revealed the fundamental weakness of the electrical theory of attraction. They showed that in organic compounds, the most prevalent bond was the bond between two carbon atoms. But carbon atoms were all alike, and, therefore, they should not have the opposite charges required to attract and bind one to

The physicists, unlike most chemists, never abandoned their helief in the electrical properties of atoms. But their investigations centered mainly on the atom's kinetics, the fields of force around an atom, and the question of whether the atom had an internal structure, as spectroscopy seemed

Of course, the increasingly empirical direction which chemistry had taken in the last half of the 19th century troubled both physicists and chemists. In 1881, Hermann von Helmholtz (1821-94), in a well-received annual Faraday Address before the London Chemical Society called for a return to the earlier electrochemical ideas of Berzelius which suggested the identity of the attractive force and electricity. "I think the facts leave no doubt," Helmholtz said, "that the very mightiest among the chemical forces are of electric origin. The atoms cling to their electric charges, and opposite electric charges cling to each other" (6).

The Swedish chemist and later Nobel Laureate, Svante Arrhenius (1859-1927) in 1887 argued that his electrolytic experiments with aqueous solutions also indicated that the atom's attractive force was electrical (7). Arrhenius showed that, in solution, electrically active molecules were identical with chemically active molecules. He had reduced chemical

and electrical activity to the same cause—the presence of charged atoms. But in spite of the reasonable arguments of Arrhenius and Helmholtz, conclusive evidence on the role played by electric charges in the union of atoms was still lacking. Indeed, the evidence did not appear until 10 years later.

In that year, 1897, J. J. Thomson (1856–1940), the physicist who directed the Cavendish Laboratory at Cambridge University, England, demonstrated in his research on the electrical conductivity of rarefied gases that atoms were not, as previously believed, indivisible. Instead, they contained exceedingly light particles of electricity (8). These sub-atomic particles, later called electrons, were removable and carried a negative charge (9). As the 20th century dawned, it became increasingly clear that all atoms contained one or more identical, negatively-charged electrons and that the electron, because of its small mass, rather easily moved from one kind of atom to another.

Early Twentieth Century Theories of Electrical Attraction

J. J. Thomson lost little time in pointing out that the electron was responsible for an atom's electrical attraction. He proposed his theory in papers published in the *Philosophical Magazine* (10) and in the Silliman lectures which he gave while visiting Yale University in May of 1903 (11). An attraction between two atoms, Thomson said, resulted whenever one of the atoms donated an electron to the second atom. As one of the atoms now contained an extra electron, it was negatively charged; the other atom, having lost the electron, carried a positive charge; and the two oppositely charged atoms then attracted one another. Thomson's theory of attraction was, of course, similar, though on a sub-atomic level, to the long-established law of attraction that governed the macroscopic behavior of bodies.

Other physicists, among them Oliver Lodge (1851-1940) in Britain and Johannes Stark (1874-1957) in Göttingen, discussed the electrical structure and attraction of atoms in their publications. Lodge wrote in his monograph, "Modern Views on Matter" (12):

... it becomes a reasonable hypothesis to surmise that the whole of the atom may be built up of positiva and negative electrons interleaved together, and of nothing else; an active or charged ion having one negative electron in excess or defect, but the neutral atom having an exact number of pairs. The oppositely charged electrons are to be thought of on this hypothesis as flying about inside the atom, as a few thousand specks.

In his 1903 publication, "Dissoziierung und Umwandlung chemischer Atome," Stark suggested that chemical union resulted from the sharing of an electron by a pair of atoms in a molecule. He represented the sharing with electrical lines of force that ran from the electron to each of the bonded atoms. The electron attached itself with a larger number of lines to the more negative atom and with a smaller number to the more positive atom (13).

Chemists who belonged to the new school of physical chemistry also examined the atom's electrical behavior. These chemists believed that their science required more than preparing new compounds and cataloguing their behavior. Like the physicists, they placed before themselves the much higher ideal of gaining a clear insight into the electrical atom and the forces acting within it.

William A. Noyes (1857–1941) then at the Bureau of Standards, expressed the physical chemists' conviction in an address he delivered to the International Congress of Arts and Sciences in St. Louis in 1904 (14)

Chemists should not be content with rounding out organic chemistry as a descriptive science nor even with adding to the number of empirical rules which enable us to predict certain classes of phenomena. We must instead, place before ourselves the much higher ideal of geining a clear insight into the nature of atoms and molecules and of the forces or motions which are the real reason for the phenomena which we study.

In Germany, the chemist Richard Abegg (1869–1910) by 1904 had already developed an electrostatic theory of atomic bonding that was identical to Thomson's (15). His "rule of eight" gave some indication of the maximum number of electrons involved in atomic union (15). Abegg observed that the same atom in its different compounds had either a positive or a negative charge and that the sum of the two was often eight. Chlorine had a ~1 charge in sodium chloride (NaCl) and a +7 charge in perchloric acid (HClO₄); nitrogen's charge was ~3 in ammonia (NH₃) but +5 in nitric acid (HNO₃). According to Abegg, most atoms thus had available for bonding anywhere from one to eight electrons. Abegg's rule was the first publication dealing with the number of bonding electrons (valence electrons) an atom contained and enjoyed great popularity among physical chemists.

Indeed, the efforts of Noyes, Abegg, and other physical chemists to move chemistry away from its empirical and descriptive state generally received a warm reception although G. N. Lewis in describing the origin of his electrical theory of the atom wrote (16)

I went from the Middle-west to study at Harvard, believing that at that time it represented the highest scientific ideals. But now I very much doubt whether either the physics or the chemistry department of that university furnished real incentive to research.... A few years later [1902], I had very much the same ideas of atomic and molecular structure as I now hold, and I had a much greater desire to expound them, but I could not find a soul sufficiently interested to hear the theory. There was a great deal of research work being done at the university, but, as I see it now, the spirit of research was dead.

The opponents of the new theoretical or physical chemistry were clearly a minority, however. Their opposition was also short-lived. Lord Kelvin (1824–1907) refused to accept that interactions between atoms were electrical. He was an avowed opponent of the electrical theory of matter applied to chemistry and believed in a Boscovichian law of force as the ultimate explanation of the behavior of chemical atoms. Kelvin agreed with Roger Boscovich (1711–87) that atoms were really points or identical centers that reacted according to an oscillatory law in which the force between atoms varied (with distance) from an attractive to a repulsive force (17)

We might be tempted to assume that all chemical action is electric, and that all varieties of chemical substance are to be explained by the numbers of electrions required to neutralize an atom or a set of atoms; but we can feel no satisfaction in this idea when we consider that great and wild variety of quality and affinities manifested by the different substances or the different 'chemical elements,' and as we are assuming the electrions to be all alike, we must fall back on Father Boscovich, and require him to explain the difference of quality of different chemical substances by different laws of force between the different atoms.

In the United States, the well-known chemist Edgar Fahs Smith (1856–1928) at the University of Pennsylvania looked upon physical chemistry as something that chemists should acknowledge rather than believe in (18). Louis Kahlenberg (1870–1941) at the University of Wisconsin remained skeptical of electronic theories (19)

The electron theory considers electricity itself to be material in character and to consist of corpuscles or electrons that weigh about 0.0005 as much as a hydrogen atom. This theory has developed from a study of radium rays and the discharge of electricity through rarefled gases. The electrons are considered to be negative electricity itself. Positive electrons appear to be much more difficult to isolate. J. J. Thomson has recently attempted to construct a theory that the atoms of the various elements are composed entirely of electrons, and has shown that, on the besis of such an assumption, the properties of the elements would exhibit periodicity as indicated by the periodic system. The electron theory has not yet been tested as to ita value in the study of chemical changes.

Thus, by the close of the first decade of this century,

mainly through the efforts of J. J. Thomson in England, Richard Abegg in Germany, and an outstanding group of physical chemists at the Massachusetts Institute of Technology which included G. N. Lewis, chemists and physicists had arrived at the following picture of the structure of matter:

1) matter consisted of divisible atoms.

every atom contained one or more nearly weightless, negatively charged particles called electrons,

3) every atom contained a second kind of particle, considerably heavier than the electron, that accounted for most of the atom's mass and had sufficient positive charge to balance the electron's negative charge.

 the transfer of electrons produced the attractive force holding atoms together.

The use of the electron to account for the bond between atoms gave rise at this time to considerable debate between physicists and chemists. The issue was whether an atom's electrons were stationary or in motion; in other words, was the atom's electronic structure static or dynamic? Certain physical problems, those relating to atomic spectra, as well as the physicists' fundamental problem of accounting for the atom's stability clearly dictated a dynamic atom. The planetary atom that Niels Bohr (1885–1962) proposed in 1913 dealt essentially with these problems (20). As it happened, the chemists' major goal, to explain the union of atoms, received from G. N. Lewis in 1916 a clever and resourceful, but expedient, solution which did not question the atom's structure and thus the ultimate structure of the chemical bond.

When J. J. Thomson put forward his theory that a bond between two atoms occurred when one of the atoms donated an electron to the second atom, chemists in the United States and abroad gave it a favorable reception. Among his earliest American supporters were K. George Falk (1880–1953) and his school at Columbia University, William A. Noyes at the University of Illinois, Harry S. Fry (1878–1949) at the University of Cincinnati, and Julius Stieglitz (1867–1937) at the University of Chicago. In numerous papers published mainly in the Journal of the American Chemical Society from 1909 to 1917, they carried out a systematic application of Thomson's theory to numerous chemical compounds (21).

The theory was often called the positive-negative theory because, as a result of combination, each of the atoms in a compound always contained either a positive or a negative charge. It worked exceptionally well for polar or inorganic compounds, those resulting from the union of a metal with a nonmetal. In forming the compound, sodium chloride, for example, the metal, sodium, transferred one of its electrons to nonmetallic chlorine. The sodium was now positive, Na⁺, the chlorine negative, Cl⁻, and the resulting attraction of two oppositely charged atoms held the compound together, Na⁺—Cl. Since chemists could demonstrate experimentally with electrolysis the actual presence of positive sodium and negative chlorine atoma in sodium chloride, the theory's fundamental postulate seemed verified.

hydrogen chloride

methane

carbon tetrachloride

Examples of Electron Structures According to the Positive-Negative Theory

It was the application of the positive-negative theory to the compounds of organic chemistry or to nonpolar compounds that led to serious difficulties. Atoms with positive and negative charges should have existed in those compounds also, but every attempt to establish their presence proved a failure. William A. Noyes tried for 20 years to isolate these atoms

before abandoning his search in 1921 (22), Harry Fry invented new types of electrical compounds called electromers which he claimed proved the existence of charged atoms in organic compounds. According to Fry, electromers were compounds whose atoms had the same arrangement, but opposite electrical charges (23):

electromers of hydrogen chloride and nitrogen trichloride

Julius Stieglitz argued that the elusive charged atoms of organic compounds were different from those of inorganic compounds and incapable of isolation (24).

The evidence was, however, overwhelmingly against the positive-negative theory when applied to organic compounds (and to certain inorganic compounds which chemists and physicists had shown not to consist of charged atoms). Stuart Bates (1887-1961) at Illinois (25), Roger Brunel (1881-1924) at Bryn Mawr College (26), and G. N. Lewis, by then at Berkeley (27) summarized the evidence in their papers on the chemical bond. They pointed out that polar compounds generally liberated their charged atoms in solution and were electrolytes, while nonpolar compounds were not. Polar compounds, when compared to nonpolar compounds, usually had higher dielectric constants, larger dipole moments, and greater specific inductive capacities. They argued that the two classes differed so significantly in their physical and chemical behavior that one could not possibly claim any similarity in their electrical structures. But Lewis alone in 1916 proposed the first successful alternative theory of the electron's role in nonpolar bond formation (28).

The Contribution of G. N. Lewis: The Shared Electron Pair

In his theory of bond formation, Lewis assumed that instead of the electron's complete transfer from one atom to another, as in the positive-negative theory, only a partial or incomplete transfer of two electrons, one from each of the combining atoms, occurred. The two atoms shared a pair of electrons between them. The electron pair attracted and held to it the resulting positive cores of the combining atoms but belonged to neither. This eliminated the formation of oppositely charged atoms in compounds whose physical and chemical properties gave no indication that they contained charged atoms. With his theory of electron sharing, Lewis had overcome the major shortcoming of the positive-negative theory when applied to nonpolar compounds.

electron structures of hydrogen chloride

- (A) according to the positive-negative theory
- (B) according to Lewis, where each dot represents a shared electron

Lewis also pointed out that his theory could account just as well for the formation of polar compounds, those known to contain oppositely charged atoms. For each bond formed between two atoms in a polar compound, one of the atoms always had a much stronger attraction for electrons than the other, and according to Lewis, a much greater share of the electron pair. Indeed, in the extreme case the electron pair belonged to it completely. This atom, therefore, appeared negative, the other, positive. The positive-negative theory of combination was then only a special case of Lewis' more general theory.

The reason why the Lewis theory required two electrons in forming a chemical bond and not some other number was a direct consequence of the static atomic model Lewis had adopted. By 1916 chemists recognized that most chemical compounds contained an even number of outer or valence electrons

Number of Valence Electrons in Atom	Total Number of Valence Electrons in Molecule
N = 5 H = 1	$NH_3 = 8$
C = 4 $H = 1$	CH ₄ = 8
C = 4 $O = 6$	$CO_2 = 16$
S = 6 O = 6	$SO_3 = 24$
C = 4 Cl = 7	$CCl_4 = 32$

Lewis showed that he could easily account for their structures if each of the combining atoms shared two electrons each time it formed a chemical bond with another atom. His theory thus provided a satisfying picture of the electronic arrangements in numerous compounds. The Lewis theory also solved several other long-standing structural problems that had proved embarrassing to chemists, those of ammonium chloride and the oxyacids, and predicted correctly the structures of a recently discovered class of compounds, the metallic hydrides.

To express conveniently and clearly his theory of the shared electron pair bond, Lewis proposed a new electronic symbolism now known as electron dot or Lewis formulas. Each pair of dots or colon placed beside a chemical element's symbol represented the pair of electrons that constituted the hond (28). In short, the theory's great serviceability accounted for its success, for within 10 years of its introduction in 1916, chemists had universally accepted the Lewis theory.

In 1918 F. Russell von Bichowsky (1889–1951) who had studied under Lewis at Berkeley devised a theory of color for inorganic compounds based on the Lewis valence theory. He was also the first after Lewis to use the dot notation to represent the chemical bonds in a molecule (29). The following year Joel Hildebrand (1881–1983), Lewis' longtime colleague at Berkeley, adopted the Lewis theory and electron dot notation in his textbook, "Principlea of Chemistry" (30). In 1920 two other Berkeley colleagues, Wendell Latimer (1893–1955) and Worth Rodebush (1887–1959), used Lewis' theory when they introduced the idea of a hydrogen bond in their discussion on the association of liquids (31); while Robert N. Pease (1895–1964) at Princeton analyzed in a 1921 publication the molecular volume of water, ammonia and methane according to the Lewis valence theory (32).

Other chemists in the United States, among them another Berkeley graduate Ermon D. Eastman (1891-1945), Ernest C. Crocker (1888–1964), Wallace H. Carothers (1896–1937), James B. Conant (1893–1978), and Howard J. Lucas (1885– 1963), began applying the Lewis theory to the reactions of organic compounds in the 1920's. Some of the investigations they carried out were the study of the electronic structures of double- and triple-bonded molecules, the addition reactions of the double bond, the addition compounds of ketones and the structures of aromatic molecules (33). Indeed, Lucas and Archibald Y. Jameson (1902-1935) at the California Institute of Technology demonstrated convincingly in 1924 that the electron pair theory was far superior to the positive-negative polar theory in accounting for the addition and rearrangement reactions of organic molecules (34). In the period 1924-26 Lucas and his collaborators provided the evidence that led to the extensive development and firm establishment of the electron pair displacement theory (33).

British chemists and physicists, among them Nevil Sidg-

wick (1873–1952), Ralph H. Fowler (1889–1944), and Thomas Lowry (1874–1936), gave a favorable reception to the shared electron pair (35). Sidgwick applied the theory successfully to a previously troublesome class of chemical compounds called coordination compounds and wrote a well-known monograph that contained a masterly presentation of Lewis' ideas (36).

But the greatest exponent of the Lewis theory was Irving Langmuir (1881–1967), a research chemist at the General Electric Company in Schenectady, New York. In the two-year period, 1919–1921, Langmuir wrote extensively and lectured widely on the Lewis theory in the United States and abroad (37). His interesting and convincing personality and his admirable methods of presentation clearly aided the theory's acceptance. Indeed, following Langmuir's popularization of the Lewis theory, chemists sometimes called it Langmuir's theory, or the Lewis-Langmuir theory of valence (38). This obvious neglect of Lewis, the author of the shared electron pair theory, resulted in a long-lasting grudge between the two men. Lewis believed that Langmuir had never observed the eatablished rules of priority regarding the origin of the theory (40). In a letter to Langmuir in 1919, Lewis wrote (43)

... to be perfectly candid I think there is a chance that the casual reader may make a mistake which I am sure you would be the last to encourage. He might think that you were proposing a theory which in some essential respects differed from my own, or one which was based upon some vague suggestions of mine which had not been carefully thought out.... It seems to me that the views which I presented were about as definite and concrete as was possible considering the condensed form of publication. I think if any confusion should arise it would be due to points of nomenclature. For example, while I speak of a group of eight, you speak of an octet.

The dispute with Langmuir had one favorable consequence; Lewis recognized that chemists had forgotten who had originated the theory. Langmuir had almost completely overshadowed Lewis. This turn of events more than anything else led Lewis in 1923 to publish his classic monograph on the theory of the shared electron pair bond.8 Entitled "Valence and the Structure of Atoms and Molecules" (45), Lewis' lucid and concisely written book was required reading for chemists in its day. A monograph which Lewis claimed in the preface would soon belong "to the ephemeral literature of acience," became instead a classic in the history of chemistry. "Valence" contained not only all of the ideas Lewis presented in his 1916 paper but also those which very likely would have appeared before 1923 had World War I not occurred. Its contents included the Lewis theory of acids and bases (the electron pair acceptor, electron pair donor theory), an examination of double and triple honds in molecules, and a discussion on the source of chemical affinity which Lewis still believed to be magnetic in origin. Even today the fundamental ideas Lewis presented in his monograph remain correct.

In this regard see Joel Hildebrand's comparison of Lewis and Langmuir (39). "Lewis was an indoor man, an omnivorous reader, much given to reflection, a scientific philosopher. Langmuir frequented the out-of-doors; he observed natural phenomena with a keen eye. In his Hitchcock lectures he told about lying on the ice of Lake George studying with a magnifying glass a curious pattern of bubbles he had noticed in the ice. I could not imagine Lewis doing anything of the kind. . . . Langmuir's mind was the more inductive; that of Lewis was more deductive."

² Langmuir seemed to give Lewis some priority when he wrote in 1919 (47): "This theory, which assumes an atom of the Rutherford type, and is essentially an extension of Lewis' theory of the 'cubical atom' . . . " Again, in 1920 Langmuir wrote (42): "This work of Lewis has been the basis and the inspiration of my work on valence and atomic structure."

³ Lewis was at first somewhat reluctant to write his monograph on "Valence" as he was already committed to writing his textbook on "Thermodynamics" (44).

There is little doubt that by 1932 Lewis' publications on the electronic structures of atoms and molecules and their chemical reactions did much to convince the chemical community to acknowledge the superiority of his valence theory. William A. Noyes, a leading advocate of the polar or electrostatic valence theory, accepted the Lewis theory in 1921 (46). In 1920 and 1921, K. George Falk published two monographs, "Chemical Reactions: Their Theory and Mechanisms" and "The Chemistry of Enzyme Actions," in which he still adhered to a polar theory of valence (47). But by 1924, in the introduction to the second edition of "The Chemistry of Enzyme Actions," Falk had also accepted the Lewis theory. The Lewis electron pair theory, he wrote, was proving extremely useful as a classifying principle for chemical reactions and in developing new lines of research (48).

Conclusion

By the mid-'twenties, Lewis had placed the electron pair theory of the chemical bond on a firm qualitative basis. But his idea had no theoretical basis until quantum mechanics established its correctness mathematically.

In 1925 Wolfgang Pauli (1900–58) in Hamburg enunciated his famous exclusion principle (49). According to this principle, no two electrons in an atom could have the same numerical value for each of the four quantum numbers used to describe an electron's energy state. A pair of electrons having identical values for the n, l, and m quantum numbers, had to have their spin axis, designated by the s quantum number, oriented in opposite directions to one another. In other words, the two electrons were paired. Pauli's principle therefore limited the total number of electrons possible in an atom and permitted their correct distribution within each atom. Applied to the hypothesis of electron pairing in the chemical bond, it appeared equivalent to what Lewis had suggested in 1924. If the electrons in a nonbonded atom were paired, Lewis wrote, then a pairing also occurred between two electrons in different atoms upon forming a nonpolar bond (50), Indeed, Lewis' shared electron pair consisted of two electrons in identical energy states except for their opposing or paired spins (51). Thus its saturation followed directly from Pauli's principle.

Lewis believed that the electron interactions and the source of the bond energy were magnetic. But Werner Heisenberg (1901–76) in Copenhagen and Paul Dirac (b. 1902) at Cambridge using the new quantum mechanics showed independently in 1926 that the electron interactions within a molecule actually resulted from a resonance or exchange effect (52). The following year, Walther Heitler (b. 1904) and Fritz London (1900-54) in Zurich applied the conception of resonance or exchange energy to account for the energy of the electron pair bond in the hydrogen molecule (53).

By 1928 the quantum mechanical treatment of the electron pair bond in the hydrogen molecule seemed beyond doubt. In that same year, London suggested that the resonance or exchange energy of two electrons, one from each of the atoms undergoing combination, was in every case the energy of the nonpolar bond. The two electrons forming the bond had paired their spins and were, therefore, incapable of further combination (54). Linus Pauling (b. 1901) at the California Institute of Technology agreed that London's theory was in simple cases entirely equivalent to the Lewis theory. Quantum mechanics, he added, provided a theoretical justification for the rule of eight, or octet theory, at least for the first row elements (55):

The shared electron structures assigned by Lewis to molecules such as H2, F2, Cl2, CH4, etc., are also found for them by London. The quantum mechanics explanation of valence is, moreover, more detailed and correspondingly more powerful than the old picture. For example, it leads to the result that the number of shared bonds possible for an atom of the first row is not greater than four, and for hydrogen not greater than one, for, neglecting spin, there are only four quantum states in the L-shell and one in the K-shell.

Within a few years, in 1931, Pauling gave a formal quanturn mechanical proof to the Lewis idea that a pair of electrons constituted the nonpolar bond (56). Quantum mechanics has subsumed the Lewis electron pair bond; but because of quantum mechanics' mathematical complexity, chemists still use the Lewis theory on a working level. It remains today the foundation of modern valence theory.

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The Amazino Periodic Table

The study of the periodic table is a vital part of any chemistry curriculum. It is surely the single most important tool available to organize the vast amount of chemical information known today. The typical introductory textbook describes the periodic table in great detail, but little or no attempt is made to point out how amazing it is that such a simple pattern exists in the first place. Students, and instructors, should realize that the relationships portrayed in the periodic table represent an incredible degree of order almost without equal in nature. I have developed a useful exercise to dramatize this point for my beginning students.

I ask a dozen boys to line up in front of the class in order of increasing height. The rest of the class is then told to look for patterns. For example, usually several boys are wearing glasses, and attention is focused on the students just to the right of each boy with glasses. Careful scrutiny does not reveal any consistent pattern of similarities among this group. After a few more attampts at pattern finding the boys are sent back to their seats with thanks.

then turn to the blackboard and list the first 20 elements in order of increasing atomic number. The similarities of He, Ne, and Ar are noted. Then the elements just to the right of each of these elements are found to resemble one another, but with very different properties than the noble gases. Next the elements to the left of each of the inert gases are examined, and again they are found to have similar chemical properties. At this point I usually rewrite the list of elements in the usual periodic table format and continue to check for the presence of additional chemical families

At the end of this session students have a good idea of the experimental basis for the periodic table, and an appreciation of how astounding it is that such unexpected order exists in the world.

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Abegg, Lewis, Langmuir, and the Octet Rule

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Contrary to the virtually universal opinion of introductory chemistry textbook authors, the octet rule was not invented by G. N. Lewis. Without a doubt Lewis' concept of the shared electron pair bond played a key role in giving the octet rule its present form. However, Lewis himself remained curiously ambivalent about the importance of the rule, and the recognition of the significance of the number eight in valence relationships actually has a long history that extends back to the last quarter of the 19th century and the work of Mendeleev on the periodic table. Though at first glance such ancient origins might seem surprising, a moment's reflection on the necessary relation between valence and chemical periodicity makes this connection quite reasonable.

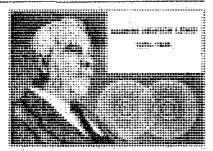
Early History of the Octet Rule

In 1871 Mendeleev (Fig. 1) published an extended review on the chemical and physical periodicity of the elements, which, in revised form, served as the core for the chapter on the periodic table in his classic textbook "The Principles of Chemistry" (1,2). Among the properties discussed was, quite naturally, the topic of valence, and Mendeleev enunciated two rules relating periodicity and valence in which the number eight played a key role. The first of these limited the maximum valence displayed by a given element to one of eight possible valence types, RX_n (where R is the element in question and X a univalent ligand or test element) and, by implication, asserted that the maximum possible valence of any element in the periodic table could never exceed eight. Although Mendeleev was unable to illustrate the entire series of maximum valence types using a single univalent test element

¹ A review of 20 recently published introductory cotlege-fevel chemistry texts showed that all of them explicitly or implicitly ettributed the octet rule to Lewis.



Figure, 1, D. Mendeleev.



(Table 1, row 1), he was able to illustrate the entire series using bivalent oxygen as the test element (Table 1, rows 2 and 3), where the examples for the RO_4 ($\cong RX_8$) class were taken from the triad of elements headed by iron, cobalt, and nickel and belonging to what is today called group VIII.

Mendeleev's second rule established a relationship between an element's maximum valence as measured relative to hydrogen and its maximum valence as measured relative to oxygen, asserting that their sum was never greater than eight and that, indeed, for elements in groups IV through VII (so-called higher types) it was in fact equal to eight. In other words, if a given element of higher type had a hydride of the form RH_n , its highest oxide necessarily had a formula of the form R_2O_{8-n} (Table 2).

Though receiving wide circulation through the medium of his extremely popular textbook, Mendeleev's initial obser-

Table	4	Mar	deleev's	Etrat	Dida
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Univalent:	RX	RX_2	RX_3	RX_4	PiX₅	RX€	AX ₇	RX8
Divalent:	R_2O	PO	H_2O_3	PO_2	R_2Q_5	RO_3	P12O7	RO₄
Example:	K ₂ O	CaO	B_2O_3	SiO ₂	$P_{2}O_{5}$	SO ₃	Cl ₂ O ₇	O ₆ O ₄

Table 2. Mendeleev's Second Rule

Hydride RH _n	Oxide R ₂ O _{8-n}
CH₄	$C_2O_4 \cong CO_2$
NH ₃	N ₂ O ₅
SH ₂	$S_2O_6 \cong SO_3$
CłH	Cł ₂ O ₇
none	DsO ₄



Figure 2, R. Abegg.

vations on the role of the number eight in valence relations did not receive further elaboration until 1902, when they came to the attention of a 33-year-old professor of chemistry at the University of Breslau named Richard Abegg (Fig. 2). Abegg was originally trained as an organic chemist, taking a PhD under A. W. Hofmann in 1891 for a dissertation on amidochrysene. However, shortly after graduation Abegg shifted to the field of physical inorganic chemistry, doing post-doctoral work under Ostwald, Arrhenius, and Nernst, and eventually becoming Nernst's assistant at Göttingen. There he specialized in the electrochemistry of both simple and complex ions and was naturally led to a study of those factors determining the ability of an ion to form complexes and to speculation on the possible electrical origin of chemical valence (3).

In 1899 Abegg published a joint paper with Guido Bodländer attempting to correlate the stability of complexes with the "electroaffinities" of the constituent ions and these, in turn, with the ions' redox potentials (4). In 1902, in the course of a lecture at the University of Christiania, Abegg extended this work to the more general problem of the origin and periodicity of chemical valence and postulated his at-one-timefamous rule of normal and contravalence (5).

Reviving the earlier electrochemical dualism of Berzelius and Davy, Abegg postulated that all elements were capable of exhibiting both a maximum electropositive valence and a maximum electronegative valence and that the sum of the two was always equal to eight (Table 3). The maximum positive valence of an element was identical to its group number N and its negative valence to 8 - N. Whichever of the two valences was less than 4 corresponded to the element's normal valence (as exhibited in the vast majority of its stable compounds), whereas the complementary valence corresponded to its contravalence (as exhibited in less stable, rarer combinations). For elements in group IV (e.g., silicon and carbon) there was no natural preference for either of the two valence types and such elements tended to be amphoteric (a term introduced by Abegg). Abegg was, of course, aware that in practice many elements failed to exhibit the full range of their potential valences. Indeed, he noted that elements in groups I–III never exhibited their contravalences (thus in effect restricting his law to Mendeleev's higher types) and that in the other groups the tendency to do so generally increased as one moved down the group (compare, for example, fluorine, with just HF, to iodine, with both HI and IF7).2

Mendeleev's original formulation of his hydrogen-oxygen rule was without electrochemical implications. His maximum valence was strictly a stoichiometric valence derived from the classic relation

$$valence = \frac{utomic\ weight}{equivalent\ weight} \tag{1}$$

Within the context of Abegg's theory, however, hydrogen became a test element for establishing an element's negative valence, oxygen a test element for establishing an element's positive valence, and their sum a reflection of Abegg's rule of normal and contravalences.

Abegg's views were elaborated in greater detail in a long (50 pages) paper published in 1904 (6). Most of this paper dealt

with various experimental criteria for establishing the relative polarity of an element's valence in a given compound. However, near the end of the paper Abegg ventured some speculations on the possible origins of polar valence. Though not adverse to the concept of both positive and negative electrons, he tended to favor a unitary theory in which positive charge was due to electron deficiency, and within this context gave a simple and prophetic interpretation of his rule (6):

The sum 8 of our normal and contravalences possesses therefore simple significance as the number which for all atoms represents the points of attack of electrons, and the group-number or positive valence indicates how many of these 8 points of attack must hold electrons in order to make the element electrically neutral.

Unlike most other chemists and physicists encountered in the history of the octet rule, Abegg is now virtually forgotten, though there can be no doubt that his rule formed a key step in the development of both the octet rule and the electronic theory of valence (7). The rule was explicitly referred to by all of the pioneers in the field who followed Abegg and, indeed, served as the "chemical law of valence" against which they tested their own theories of valence and atomic structure. The most likely reason for Abegg's eclipse was his premature death at age 42 in a ballooning accident, and it is tempting to speculate on how the history of the electronic theory of valence might differ had he lived, especially if he had been able to modify his initial commitment to an extreme dualism (which, given his training as an organic chemist, is not improbable). Interestingly, at the time of his death, Abegg was, in true Germanic fashion, in the process of editing an enormous multivolume "Handhuch der Anorganische Chemie" in which he was attempting to use his rule as a unifying theme to organize the descriptive chemistry of the elements (8).

Abegg's rule established an explicit connection between the numerical limits of valence and the electronic theory of matter, then in its infancy. However, it did not attempt to provide an explicit model of atomic structure, contenting itself instead

Table 3. Abegg's Rule of Normal and Contravalence (θ)

	Сгирре:						
	1	2	3	4	5	6	7
Normalvalenzen Kontravalenzen	+1 (7)	+2 (6)	+3 (~5)	±4	3 +5	-2 +6	-1 +7



Figure 3. J. J. Thomson.

 $^{^2}$ in a short note published in 1902 (*Chem. News*, 64 (August 8, 1902)) the British chemist Geoffrey Martin suggested that the recent discovery of various intermetablic compounds by Kurnakov had finally revealed species in which the elements of groups I-III displayed their maximum valence (or contravalence in Abegg's terminology). Quite independently of Abegg, Martin generalized Mendeleev's earlier observations with the equation and statement: "Hence, $V_1 + V_2 = 8$, i.e., the sum of the highest and lowest degrees of valence with which an element acts towards other elements is a constant whose value is 8." Martin also noted that "An element tends to act toward radicals of like electrical sign with its highest valence," thus placing an electrochemical interpretation on Mendeleev's rule equivalent to that of Abegg.

with the vague concept of "points of attack." This deficiency was made up in large part by the work of the English physicist J. J. Thomson (Fig. 3). Ever since his discovery of the electron in 1897 (which for some peculiarly British reason he persisted in calling a negative corpuscie—a term more appropriate to Boyle and the 17th century than to 20th century physics), Thomson had doggedly pursued a workable electronic model of the atom. By 1907 his search had given birth to the famous plum-pudding model and to at least four valuable concepts which, though no longer used in the explicit forms given them by Thomson, are nevertheless an implicit part of all currently accepted electronic theories of valence: 1) the concept of an electronic shell structure for the atom; 2) the concept that chemical valence is largely a function of only the outermost electronic shell: 3) the concept that chemical periodicity implies a periodic repetition of the outer electronic shell structure; and 4) the concept that the stability of the rare gases is connected with shell completion and that the valence of other atoms can be correlated with an attempt to attain similar closed-shell structures via electron transfer (9).

In a manner unusual for a physicist, Thomson was quick to point out the chemical implications of his model, explicitly connecting it with Abegg's rule and in the process enshrining the number eight as the central numerical deity of chemical valence (10). Summarizing his views in 1914, he also added what would, with the gift of historical hindsight, prove to be an interesting caveat (11).

We regard the negatively electrified corpuscles in a atom as arranged in a series of layers, those in the inner layers we suppose are so firmly fixed that they do not adjust themselves so as to cause the atom to attract other atoms in its neighbourhood. There may, however, be a ring of corpuscles near the surface of the atom which are mobile and which have to be fixed if the atom is to be saturated. We suppose, moreover, that the number of corpuscles of this kind may be anything from 0 to 8, but that when the number reaches 8 the ring is so stable that the corpuscles are no longer mobile and the atom is, so to speak, self-saturated. The

number of these mobile corpuscles in an atom of an element is equal to the number of the group in which the element is placed on Mendeleev's arrangement.

... Thus we see that an atom may exert an electropositive valence equal to the number of mobile corpuscles in the atom, or an electronegative valence equal to the difference between eight and this number. Each atom can, in fact, exert either an electropositive or electronegative valency, and the sum of these two valencies is equal to eight. In this respect the theory agrees with Abegg's theory of positive and negative valency. ... It is possible that the number of corpuscies which form a rigid ring may depend to some extent on the number in the inner rings, i.e. on the atomic weights of the elements, and that for elements with atomic weights greater than forty (i.e., Ar) this number may not be eight. If this should prove to be the case, the sum of the positive and negative valencies for such elements would not be equal to eight.

Kossel and Lewis

The year 1916 saw the publication of two extremely important papers on the electronic theory of valence. The first, published in the March issue of the Annalen der Physik, was by a 28-year-old physicist at the University of Munich named Walter Kossel (Fig. 4). Kossel's paper, or rather his monograph (133 pages!), was an explicit attempt to develop and extend Abegg's valence views for relatively polar inorganic compounds using the electron transfer model briefly hinted at by Abegg near the close of his 1904 paper (indeed Ahegg is explicitly cited by Kossel no less than 20 times (12). In keeping with this goal, Kossel was less interested in an explicit atomic



Figure 4. W. Kossel.

model (though he was fully aware of the Bohr-Rutherford model) than in accurate experimental counts of the total number of electrons per atom, data not available to Thomson in 1907. These he obtained from the work of the physicist A. van den Broek and used to construct his now famous plot of maximum positive and negative oxidation states for the first 57 elements (Fig. 5). This was a plot of the total electron count per atom or ion versus its atomic number, with the values for the neutral elements themselves appearing along the diagonal, those for the elements in their maximum positive oxidation states appearing as extensions below the diagonal, and those for their maximum negative oxidation states as extensions above the diagonal.

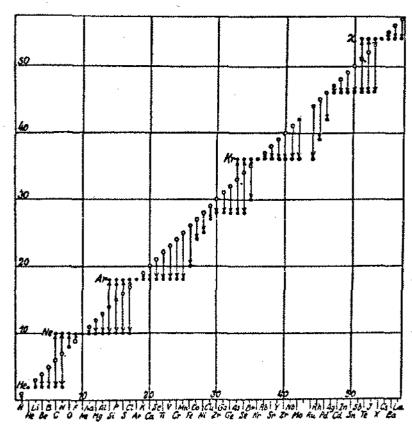


Figure 5. Kossel's plot of maximum positive and negative oxidation states (12).

This plot allowed Kossel to assess in one stroke the validity of both Abegg's rule and Thomson's suggestion that electron transfer was associated with attempts to attain a closed-shell, rare gas structure. As can be seen from the figure, both Thomson's postulate and Abegg's rule held fairly well for the s- and p-block elements (using modern terminology) as indicated by the clumping of the oxidation states about the rare gas counts, and the symmetrical disposition of oxidation states on either side of the diagonal for elements in groups IV through VII. However, problems were readily apparent for the d-block elements. Although the elements up to group VIII appeared to attain a maximum positive oxidation state corresponding to a rare gas electron count, in the case of groups IVA-VIIA (e.g., Ti-Mn) they failed, in violation of Abegg's rule, to attain the corresponding negative states of their group B analogs³ (e.g., Si-Cl), a fact which Kossel felt to be of a great significance in differentiating the two classes of elements.

Beginning with group VIII there was an erratic variation in the maximum oxidation state, culminating in a second asymmetrical clumping of positive oxidation states about the counts for the last members of the group VIII triads (e.g., Ni and Pd). Today we associate these clumpings with the attainment of a pseudo-rare gas $(n-1)d^{10}$ configuration. However, since Kossel was using total electron counts, rather than configurations, the 10-valence electron count became associated with Ni and Pd instead. This led Kossel to postulate that these elements represented a kind of imperfect or weakened analog of the rare gases as, like the rare gases themselves, they bridged the gap between one cycle of repeating maximum oxidation states (e.g., K[I]-Mn[VIII]) and another (Cu[I]-Br[VII]). The striving for a maximum positive oxidation state corresponding to either a rare gas or pseudorare gas electron count was virtually universal. The striving for a maximum negative oxidation state corresponding to a rare gas electron count, however, fell off rapidly as one moved to the left of the rare gases and was nonexistent in the case of pseudo-rare gas counts, thus accounting for the asymmetry in the behavior of the group A d-block elements. In no case did the maximum oxidation state of an element exceed eight.

The rest of Kossel's paper was essentially an application of the resulting ionic bonding model to the problems of coordination chemistry, the autoionization of protonic solvents, and the relative acidity and basicity of oxides. Also included were some simple calculations using Coulomb's law and an attempt to visualize the resulting bonds in terms of Bohr's atomic model. When combined with Fajans' later work on ionic po-



Figure 6, G. N. Lewis.

larization, Kossel's treatment of coordination compounds proved quite useful and was popular among European chemists up until the Second World War, though it never attained a similar popularity among American and British chemists (13).

The second 1916 paper, published one month after Kossel's in the Journal of the American Chemical Society, was by a 40-year-old chemist at the University of Berkeley named G. N. Lewis (Fig. 6) and, in contrast to Kossel's epic, was quite terse (22 pages) (14). Lewis had actually begun speculating on the electronic theory of valence as early as 1902 (about the year of Abegg's lecture at Christiania) and had independently arrived at a dualistic electron-transfer model similar to Abegg's. However, like Thomson, Lewis had also proceeded to develop a specific static model of the atom, which he called the cubical atom, and had thus apparently also independently arrived at the concept of periodically repeating electronic shells and the concept of the relative stability of rare gas structures (Fig. 7).

Fortunately Lewis became increasingly skeptical about the ability of the electron-transfer model to account for the relatively nonpolar compounds of organic chemistry and by 1913 was willing to publish a paper stating his belief that two radically distinct kinds of bonds were required in chemistry, the polar electron-transfer bond of typical ionic salts and some kind of nonpolar bond to represent the valence stroke of structural organic chemistry (15). Largely for this reason, apparently, Lewis was unwilling to publish his cubical atom model.

However, some time between 1913 and 1916 Lewis was able to resolve his dilemma by using the cubical atom to arrive at the concept of the shared electron pair bond (Fig. 8). The resulting "simple assumption that the chemical bond is at all times and in all molecules merely a pair of electrons jointly held by two atoms" not only provided the missing bond mechanism for the nonpolar valence stroke, but also allowed Lewis to resolve the dichotomy of two distinct bond types "so repugnant to that chemical instinct which leads so irresistibly to the belief that all types of chemical union are essentially one and the same," through his realization that the progressively uneven sharing of the electron pair between atoms of in-

³ According to IUPAC notation.

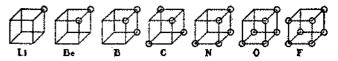


Figure 7. Lewis' cubical atom (14).

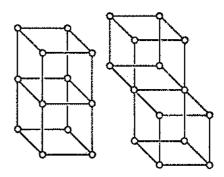


Figure 8. Single and double electron pair bonds viewed using the cubical atom (14).

creasingly different electronegativities could yield the ionic electron-transfer bond as a limiting case.

The idea that a chemical bond could result from the sharing as well as from the transfer of electrons was not unique with Lewis. The chemists A. L. Parson (16), W. C. Arsem (17) and H. Kauffmann (18), as well as the physicists J. Stark (19) and J. J. Thomson himself (11), had suggested similar ideas. The difficulty with all of these proposals, however, was that no reasonable restraints had been placed on either the total number of electrons per bond or on the number of atoms that could share a common electron. As a consequence the resulting models were too open-ended to be operationally useful. Lewis, by restricting both the number of electrons per bond and the number of atoms so bonded to two, provided the necessary restraints to give a workable theory. Robert Kohler, who has studied the origins of the shared electron pair bond, has suggested that the concept resulted from Lewis' attempts to accommodate the electron-sharing concepts of Parson and Thomson within the context of his own dualistic cubical atom model, and that the restraints so necessary to its success were a natural consequence of the geometrical restraints imposed by the cubical atom itself (20)

It is worth pointing out that Kossel had also recognized the necessity of a nonpolar bond for organic compounds as well as the concept of a progressive change in bond type. Early in his paper Kossel had noted that the electron-transfer model was unsuitable for nonpolar organic compounds and that an electron-sharing model similar to Stark's would probably be required. Near the end of the paper Kossel proposed some specific models using two-dimensional Bohr-Rutherford ring atoms in which all of the valence electrons (e.g., 10 in the case of N_2) were held on a common ring placed symmetrically between the two bonded atoms (Fig. 9). As the polarity of the bond increased, this ring was progressively displaced toward the more electronegative atom, and in the ionic limit became its sole property.

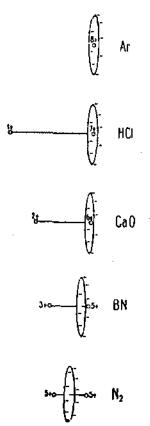


Figure 9. The progressive change from ionic to covalent bonding in terms of Kossel's ring atom model (12).

Like his predecessors, Lewis had recognized both the importance of the number eight in valence relationships (which he called the rule of eight) and its correlation with the attainment of rare gas structures. However, within the context of the ionic model, as formulated by Kossel, this correlation was only possible in the case of maximum oxidation states (e.g., P5+ and Cl- in PCl₅). Attempts to construct ionic formulas for lower oxidation state compounds failed to give ions having either rare gas or pseudo-rare gas electron counts (e.g., P³⁺ in PCl₃). The importance of the shared electron pair bond for the octet rule was that it allowed the extension of the rule. to these lower oxidation state species as well as to purely homonuclear species such as Cl2 and N2. In contrast, Kossel's formulation of homonuclear species precluded their obeying the octet rule (e.g., N_2) and, indeed, Kossel went so far as to suggest that the rule was limited only to polar compounds. Though Lewis was well aware of the implications of the electron pair bond for the octet rule, their full exploitation was to be largely the work of Irving Langmuir.

irving Langmuir

Irving Langmuir (Fig. 10) was a 38-year-old research chemist at General Electric when he first began to write on the subject of Lewis' electron pair bond in 1919 (21). In the course of three short years he managed, in addition to numerous popular lectures, to publish more than 12 articles, extending, refining, and popularizing Lewis' work. Lewis had originally restricted his discussion of the cubical atom and chemical bonding to the s- and p-block elements, feeling that the ambiguities then present in the chemistry and electronic structures of the d-block elements made attempts to extend the model too speculative. Langmuir, in his first and most ambitious paper (66 pages), published in the June 1919 issue of the Journal of the American Chemical Society, attempted to remedy this defect (22). Through the use of 11 basic postulates covering the arrangement of the electrons in isolated atoms and their preferential sharing in compounds, Langmuir undertook to deduce the entire structure of theoretical and descriptive chemistry. The full extent of his ambition is revealed in a popular lecture published in 1921 (23). Langmuir wrote



Figure 10. I. Langmuir.

These things mark the beginning, I believe, of a new chemistry, a deductive chemistry, one in which we can reason out chemical relationships without falling back on chemical intuition.... I think that within a few years we will be able to deduce 90 percent of everything that is in every textbook on chemistry, deduce it as you need it, from simple ordinary principles, knowing definite facts in regard to the structure of the atom.

Despite his enthusiasm, Langmuir's extension of the static atom (Fig. 11) proved to be short-lived. By 1921 Bohr, on the basis of spectral evidence (24) and Bury, on the basis of chemical evidence (25), had shown that Langmuir's postulated shell sequence of 2, 8, 8, 18, 18, and 32 electrons was wrong as was his postulate that a new electron shell could be started only if the preceding shells were completely filled. In addition, most theoretical physicists, who by this time were firmly committed to a dynamic atom model, were less than impressed by Langmuir's extended static model. The German physicist Sommerfeld characterized Langmuir's 11-postulate deductive chemistry as "somewhat cabalistic" (26), and the English physicist E. N. Andrade was even more blunt (26),

It is scarcely necessary to insist on the artificality of this picture The electrons in Langmuir's atom have, in fact, so few of the known properties of electrons that it is not immediately clear why they are called electrons at all.

Thus, in actual practice, Langmuir's development of Lewis' model was restricted to the same atoms as Lewis had originally discussed. Nevertheless, a number of valuable concepts did evolve out of Langmuir's refinements, including the electroneutrality principle and the isoelectronic (isosteric) principle (27), the last of which has been characterized by Kober, in a recent article, as the "last important nonquantum mechanical bonding principle" (28).

Even more important to the present discussion was Langmuir's use of his postulates to deduce a general mathematical expression for the "octet" rule (a term introduced by Lang-

Table 4. Examples of Langmuir's Octet Equation

Species	Σσ	n	Н	$\nu = \frac{1}{2}(8n - \Sigma \theta) + H$	Structure
NH ₃	8	í	3	3	H H
co	10	2	0	3	∤C≔Oί π
H₂CO	12	2	2	4	H (=0)
NaCi	8	1	0	0	Na ⁺ [IČII]-
CS ₂	16	3	0	4	⟨ 5 — C —8⟩

muir to replace Lewis' more cumbersome "rule of eight")

$$\Sigma e = \Sigma s - 2B \tag{2}$$

where Σe is the total sum of available valence electrons in a species, Σs is the sum of the valence electrons required for complete shell formation for each of the heavier atoms (i.e., excluding hydrogen), and B is the number of covalent bonds between the heavier atoms. Restriction of the heavy atoms to those lying below Ar converts eqn. (2) into the major equation of Langmuir's "octet theory"

$$\Sigma e = 8n - 2B \tag{3}$$

when n is the number of heavy atoms requiring octet completion. Addition of the covalent bonds, H, to any protons present gives the final total number of covalent bonds in a species

$$v_{\text{cov}} = H + B = H + \frac{1}{2}(8n - \Sigma e)$$
 (4)

Some example applications of eqn. (4) are shown in Table 4

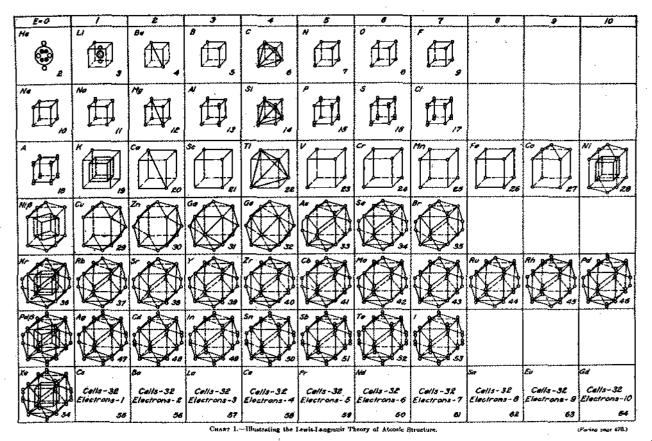


Figure 11. Langmuir's extended cubical atom models (from Washburn, E. W., "introduction to the Principles of Physical Chemistry," 2nd ed., McGraw-Hill, New York, 1921, p. 470.)

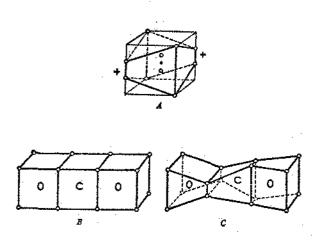
and some examples of Langmuir's original structures in Figure

In 1921, in what was essentially his last major paper on the octet theory, Langmuir gave a comprehensive survey of the limitations of eqn. (4) (29). By this time he had succeeded in reducing his original 11 postulates to three, the third of which represented the first explicit statement of the electroneutrality principle

- The electrons in atoms tend to surround the nucleus in successive layers containing 2, 8, 8, 18, 18, and 32 electrons respectively.
- Two atoms may be coupled together by one or more duplets held in common by the completed sheaths of the atoms.
- The residual charge on each atom or group of atoms tends to a minimum.

Shell completion was desirable because it resulted in a spherically symmetrical electron distribution which tended to minimize external electrical fields about the atom. Minimization of the residual charges was also desirable because it minimized the coulombic energy required to maintain charge separation on adjacent atoms.

Langmuir pointed out that the requirements of postulates 1 and 3 were frequently in conflict and used this conflict to rationalize the limitations of his octet equation. His resulting classification of chemical compounds is shown in Table 5. Species obeying postulate 1 were termed "complete compounds" and tended to obey the octet rule either through the formation of ionic compounds (Class IA) or through the formation of "covalent" compounds (Class IB)—another term



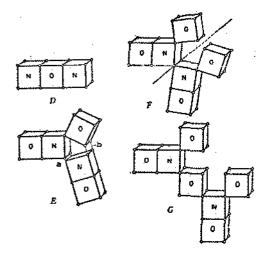


Figure 12, Some of the "cubical atom" molecular structures which Langmuir deduced using his octet equation (27).

introduced by Langmuir. In the latter case, Langmuir further distinguished between those species obeying the octet rule proper (i.e., $\Sigma s = 8n$) and those obeying an extended rare gas rule (i.e., s = 18), the former being restricted to combinations among elements corresponding to Mendeleev's higher types and the latter being the first explicit statement of the 18-electron rule much beloved of the organometallic chemist.

On the other hand, the "incomplete compounds" of Class II failed to obey postulate 1 and thus the octet rule. In Langmuir's opinion this was because shell completion in these species required, in violation of postulate 3, the buildup of prohibitively large net ionic charges (and here Langmuir was generous in allowing charges as high as 6+ and 4- in contrast to Pauling's later restriction of 2± or lower). Finally, Langmuir included a class of "exceptional cases" whose bonding apparently required a special kind of electron-sharing beyond that proposed in postulate 2.

The Debate

Lewis' opportunity to comment on Langmuir's work came in 1923 with the publication of his classic monograph, "Valence and Structure of Atoms and Molecules" (30). With the exception of a short retrospective essay written in 1933 (31), this was essentially Lewis' last major contribution to the electronic theory of valence and represented his matured views on the nature of the electron-pair bond.

Already in his 1916 paper, Lewis, faced with the inability of the cubical atom to represent a triple bond and the overwhelming evidence of organic chemistry that the valences of carbon were tetrahedrally directed, had speculated that the electrons of the cubical atom were drawn together to form a tetrahedron of electron pairs (Fig. 13). By 1923 Lewis had also abandoned his earlier defense of the static atom (32) and was willing to compromise with the dynamical atom models favored by the physicists, suggesting a model in which the electrons of the static atom corresponded to the average positions of electrons moving in small directional orbits. In keeping with these views, the cubical atom was presented only in an historical context in the 1923 monograph. Cubical



Figure 13. Lewis' tetrahedral atom with close-paired electrons (14).

Table 5. Langmuir's Classification of Compounds via the Octet Rule

. Complete Compounds

- A) Compounds Without Covalence (B=0)
 - Electropositive main group elements (N ≤ 3) plus electronégative elements (N ≥ 4), e.g., NaCl, NB, Al₂O₃
 - Early transition elements in their maximum oxidation state plus electronegative elements, e.g., ScCl₃, TaBr₅, CrF₆
 - Certain halides of the electronegative elements in their higher oxidation states, e.g., PCI₅, SF₆
- B) Covalent Compounds
 - Among the electronegative elements, where s = 8, (N ≥ 4), e.g., C, N, O, F, Si, P, Cl
 - Among the transition elements, where s = 18, e.g., Mo(CO)₈, Fe(CO)₅ and ni(CO)₄
- II. incomplete Compounds
 - A) Intermetallics
 - B) Salts of the later transition elements, e.g., CrCi₃, CuCi₂, ZnO
- Exceptional Cases
 - A) Triply bonded species, e.g., N2, CO, CN"
 - B) Hydrogen-bonded species, e.g., HF₂"
 - C) Boranes



Figure 14. Langmuir's cubical structure for N2, CO, and CN" (27).

models of molecules, such as those used by Langmuir (recall Fig. 12), were used nowhere in the book, extensive use being made instead of the less structurally explicit electron dot formulas, though in several places tetrahedral atom models were also used.

Langmuir's failure to abandon the cubical atom accounted for his classification of N_2 , CO, and CN⁻ as "exceptional cases." Lacking a triple bond, he was forced to postulate a special electronic structure for these species in which both kernels were simultaneously enclosed within a single cube of electrons, the remaining two electrons being shared as a normal duplet between the kernels (Fig. 14), a proposition which Lewis was to later characterize as "ad hoc" (30).

Though, as Kohler has suggested, the cubical atom probably played a central role in the initial inception of the electron pair bond, Lewis was quick to obtain an empirical base of support for the hond, the most impressive evidence being the observation that virtually all stable chemical species contained an even number of electrons. Indeed, the few "odd molecule" exceptions to this rule tended to be highly reactive and frequently underwent dimerization reactions to give products with even electron counts. Lewis also became increasingly convinced, in large part through the influence of A. L. Parson's magneton model of the atom, that magnetic interactions between electrons were responsible for the formation of electron pairs, a thesis discussed at length in a separate chapter of the 1923 monograph and in a review published the next year (59). These considerations led Lewis to postulate that the formation of electron pairs or the "rule of two," as he called it, was a much more important bonding principle than the rule of eight and account, in part, for his evaluation of Langmuir's octet equation. Lewis wrote (30)

The striking prevalence of molecules in which each atom has its full quota of four electron pairs in the outermost shell has led Langmuir to attempt to make the octet rule absolute, and he even proposes an arithmetrical equation to determine, in accordance with this rule, whether a given formula represents a possible chemical substance. I believe that in his enthusiasm for this idea be has been led into error, and that in calling the new theory the "octet theory" he overemphasizes what is after all but one feature of the new theory of valence. The rule of eight, in spite of its great importance, is less fundamental than the rule of two, which calls attention to the tendency of electrons to form pairs.

Langmuir, on the other hand, felt that Lewis' neglect of transition metal chemistry had misled him concerning the necessary instability of "odd molecules," and that their relative scarcity was due less to an inherent instability resulting from their unpaired electrons than to the relative abundance of closed-shell species, or in Langmuir's own words (29)

... the remarkable tendency, pointed out by Lawis, for most compounds to contain an even number of electrons is due merely to the relative abundance of complete compounds compared to incomplete ones. In other words, the even number of electrons in most compounds results from the tendency of Postulate 1 [i.e. closed-shell formation] rather than from any more general tendency for electrons to form pairs.

Thus Langmuir viewed the prevalence of even-electroncount species as a consequence of complete shell formation and as a reflection of the octet rule for elements lying below Ar, whereas Lewis viewed it (and the octet rule itself) as a consequence of the "rule of two."

Table 6. Lewis' Examples of Species Violating the Octet Rule

1) Odd Molecules: NO, Cl₂O

2) Electron Deficient: NaCH3, BR3, BF3, SQ3, HPO3, CO3 $^{2-}$, NO3 $^-$,

possibly even NaCl_(q)

3) Electron Rich: PCI₅, SF₆, UF₆, SiF₆²⁻, PtCI₆²⁻ and Mo(CN)₆⁴⁻

Lewis even included a chapter in his monograph dealing with "Exceptious to the Rule of Eight" in which he discussed the examples summarized in Table 6. In viewing this list one is struck by the fact that Langmuir's own discussion of this subject was in some ways more thorough. Although the odd molecules in Class 1 certainly violate the octet rule, their supposed scarcity and high reactivity could be used to support the stability of the octet just as well as the stability of the electron pair. On the other hand, all of Lewis' electron-deficient examples and most of his electron-rich examples could be (and were) accommodated by Langmuir's octet equation by using an ionic formulation. Finally, several of the electron-rich examples were not fair game (e.g., $PtCl_6^{2-}$, UF_6 , and $Mo(CN)_8^{4-}$) as Langmuir had never claimed that the octet rule was valid for elements above Ar.

Lewis' purpose was, of course, less to find examples which could not be fitted by Langmuir's equation than to find examples which could be fitted only by postulating structures (usually ionic) which were at variance with their known physico-chemical properties. Indeed, in looking at the positions taken by Langmuir and Lewis regarding the octet rule, one receives the impression that Langmuir, in his desire to emulate the rigor of physics, wished to be guided by the deductions of his postulates, whereas Lewis, more open to the experimental data hase of chemistry, was more willing to be guided by the empirical evidence.

There is little doubt that the personal interaction between Lewis and Langmuir also tended to color the positions they took regarding the octet rule. Langmuir was a popular and dynamic lecturer and Wilder D. Bancroft has left us with an amusing picture of what it was like to be a member of one of Langmuir's audiences (33).

Langmuir is the most convincing lecturer I have ever heard. I have heard him talk to an audience of chemists when I knew they did not understand one-third of what he was saying; but thought they did. It's very easy to be swept off one's feet by Langmuir. You remember in Kipling's novel Kim that the water-jug was broken and Lurgan Sahib was trying to hypnotize Kim into seeing it whole again. Kim saved himself by saying the multiplication table ... [so] ... I have heard Langmuir lecture when I knew he was wrong, but I had to repeat to myself "He is wrong, I know he is wrong, he is wrong" or I should have believed like the others.

Naturally Lewis was initially quite pleased with the publicity given his theory as a result of Langmuir's lectures and papers. However, as time passed and more and more of the publicity accrued to Langmuir instead of Lewis, Lewis became increasingly upset, expressing his true feelings in a letter written to W. A. Noyes in 1926 (34).

Perhaps I am inclined to be too caustic in this matter, but I really do feel that while people were justified in being carried away a bit by Langmuir's personal charm and enthusiasm some years ago, to persist, especially as they do in England, in speaking of the Langmuir theory of valence is inexcusable.

Another of Langmuir's talents was the ability to coin catchy terminology, such as duplet, isostere, octet rule, and covalent bond, and it is not without note that the first two terms do not appear in the index of Lewis' monograph and that the terms octet theory and covalence appear only once. In fact Lewis recommended that the term covalent be dropped because Langmuir had "associated this term with an arithmetrical equation by which he attempts to predict the existence or nonexistence of chemical compounds" (30). In private Lewis rather humorously expressed his resentment over the

manner in which Langmuir had ignored Lewis' own terminology (34),

... sometimes parents show a singular infelicity in naming their children, but on the whole they seem to enjoy having the privilege.

In public Lewis was, of course, less outspoken and in his 1923 monograph gave an evaluation of Langmuir's contributions which can only be viewed as a masterpiece of diplomatic understatement (30).

It is a cause of much satisfaction to me to find that in the course of this series of applications of the new theory, conducted with the greatest acumen, Dr. Langmuir has not been obliged to change the theory which I advanced. Here and there he has been tempted to regard certain rules or tendencies as more universal in their scope than I considered them in my paper, or than I now consider them, but these are questions we shall have a later opporunity to discuss. The theory has been designated in some quarters as the Lewis-Langmuir theory, which would imply some sort of collaboration. As a matter of fact Dr. Langmuir's work has been entirely independent, and such additions as he has made to what was stated or implied in my paper should be credited to him alone.

In the final analysis there can be little doubt that Langmuir played a key role in accelerating the acceptance of Lewis' electron-pair bond. Robert Kohler, who has studied the interaction between Lewis and Langmuir in some detail, has concluded that by 1920 the chemical community was still, by and large, content to use the ionic electron-transfer bond and that no crisis in chemical bonding was evident which might draw chemists to a model similar to Lewis' electron-pair bond. The widespread and rapid acceptance of the electron-pair bond was rather a consequence of Langmuir's dynamic personality and the unique manner in which he spanned both the industrial and university chemical communities. As Kohler has written (21)

What made the difference was, of course, Langmuir himself and his personal reputation. The new theory was well received because it was "Langmuir's theory" and not because of its intrinsic intellectual worth. Once received, of course, its worth become evident. What I wish to stress is that the advantages of the new theory were not immediately obvious and that had it not been "Langmuir's theory," the rediscovery and adoption of Lewis' theory might well have awaited a real crisis in the theory of bonding.

Summary, Conclusions, and Prospects

The major events in the development of the octet rule are summarized in Table 7, though obviously many additional contributions were made by lesser-known chemists which could not be touched upon for lack of space. These events allow one to draw at least three major conclusions about the origins and development of the octet rule:

- 1) Within the context of the dualistic or electrovalent model the octet rule essentially corresponded to a maximum valence rule only. While the striving for a rare gas structure determined both which elements could exhibit negative valences and the value of these valences, in the case of the positive valence it merely determined the maximum value, placing no necessary restrictions on the lower values.
- 2) The covalent model, by providing a means, via electron sharing, of rationalizing both the lower positive oxidation states and homonuclear species in terms of rare gas structures, substantially strengthened the identification of the octet rule with the formation of rare gas structures.
- 3) At no time, within the context of either the electrovalent or covalent model, was it claimed that the octet/rare gas structure relation was generally valid for elements beyond Ar.

Table 7. Summary of Major Events in Development of the Octet

Mendeleev: 1871

Eight as a maximum valence rule and the sum of the hydrogen and oxygen valences for higher types.

Abegg: 1904

Electrochemical interpretation of Mendeteev's rule of eight in terms of electron gain and loss.

Thomson: 1904, 1907

Concept of chemical periodicity in terms of recurring outer electron configurations. Rule of eight as striving for completion of stable rare gas shells.

Kossel: 1916

Extension of lonic model, Eight as a maximum valence rule for polar compounds only.

Lewis: 1916

Continuity of bond type and electron pair bonding mechanism for octet completion.

Langmuir: 1919-1921

Elaboration and popularization of the Lewis model, Mathematical formulation of the octet rule.

The debate over the validity of the octet rule did not, of course, end with Lewis and Langmuir. Between the 1920's and the 1940's a number of vigorous discussions took place in which not only the validity of the octet rule was questioned but the validity of the electron-pair bond itself (35-37), and aspects of this debate are still with us (38, 39). More recent quantum mechanical calculations, however, have tended to discount the importance of octet expansion and have reinstated the general validity of the octet rule for the p-block elements (40). In keeping with this conclusion, modern bonding theory has also provided a satisfactory resolution of the problems associated with both electron-deficient and electron-rich species and has done so in a manner which shows that neither Lewis nor Langmuir was totally correct in the positions they took. Langmuir, in his desire to maintain the octet rule, was willing, in spite of the physico-chemical evidence, to postulate ionic structures for many of these species, whereas Lewis, in his desire to maintain the supremacy of the 2c-2e covalent bond, was willing to propose both hextet and expanded octet structures. The current consensus maintains both the octet rule, on the one hand, and the presence of covalent bonding, on the other, by abandoning the explicit assumption of both Langmuir and Lewis that the covalent bond must at all times be a localized two-centered bond. Thus electron deficient species have been accommodated via the closed 3c-2e bond popularized by Lipscomb for the boron hydrides (41) or via the use of delocalized π -electron systems (e.g., BF₃, CO₃²⁻, etc.), whereas electron-rich species (e.g., PCl₅, XeF₄) have been accommodated via the open 3c-4e bond popularized by Rundle (42), Pimentel (43), and others (44,

The case of the d-block elements is more ambiguous. The generalized rare gas rule first hinted at by Langmuir was independently formulated by the English chemist N. V. Sidgwick in 1923 (46). Sidgwick, however, preferred to use total electron counts rather than valence electron counts and consequently called his technique the effective atomic number rule (EAN). Not until 1934 did Sidgwick explicitly connect his EAN rule with Langmuir's earlier 18-electron rule and derive an equation, related to Langmuir's (though based on total electron counts), for predicting the structures of polynuclear metal carbonyls and nitrosyls (47). Extensive applications of the EAN rule to the structures of metal carbonyls were made by Blanchard in the 1940's (48) and the importance of the rule exploded along with the field of organometallic chemistry in the late 1950's and 1960's, despite its many violations. More recent theoretical work has provided both quantitative (49) and qualitative (50) rationales for why the 18-electron rule is weaker than the octet rule.

Even Langmuir's arithmetical equation is still with us and

⁴ Some minor contributions, though hardly by lesser-known chemists, include the work of Ramsay and Nernst. Ramsay was one of the first to apply Abegg's rule of eight, and Nernst expressed some suggestive views on the saturation of ions. For a discussion, see Stranges (7).

in modified form is used extensively in the field of solid-state chemistry. If one applies eqn. (3) to only the more electronegative or anionic components of a solid-state compound, one obtains

$$\sum e_a = 8n_a - 2B_a \tag{5}$$

where Σe_a includes not only the valence electrons from the anionic components but any electrons transferred from the cationic components, n_a is the number of anionic components per unit formula, and $2B_a$ the number of anion-anion bonding electrons. In general the anionic components are restricted to elements lying to the right of the Zinti line in the periodic table (i.e., groups IV-VII, again shades of Mendeleev's higher types). Rearrangement of the equation and redefinition of $2B_a$ $= b_a$, gives

$$8 = \frac{\sum e_{\rm a} + b_{\rm a}}{n_{\rm a}} \tag{6}$$

This is called the generalized 8 - N rule and is the subject of an extensive literature (51-56). The equation can also be applied to the structures of pure elements lying to the right of the Zintl line. Some example applications are shown in Table 8.

Extended versions of Langmuir's original equation have also appeared in the literature which incorporate the possibility of the multicentered bonds required for the description of both electron-deficient (57) and electron-rich (58) species.

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Table 8. Examples of the Generalized 8 - N Rule

Species*	$\Sigma e_{\mathbf{a}}$	b _a /n _a	$(\Sigma e_a + b_a)/n_a$	Structural Array of the Zinti Atoms
C	4	4	8	3[C _{4/4}]
P	5	3	8	² [P _{3/3}] or P ₄ tetrahedron
Se	6	2	8	[8e _{2/2}]
Cl	7	1	8	Cl ₂ discrete pairs
CsSn	5	3	6	(Sn ₄) ⁴ " tetrahedra
CaC₂	10	3	8	((C≡Ci)² tripie bonded discrete pair
CaSi ₂	10	3	8	2 [Si _{3/3}]1~
LaP	8	2	8	1 [P _{2/2}] 1-
CaP.	7	1	8	P ₂ ² discrete pairs
Na/	8	0	8.	isolated I

- * Anionic Zinti aloms in italics
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Chemistry Olympiad Mentor Applications Invited

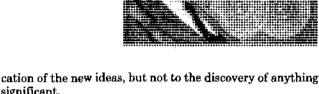
Applications are invited from chemistry teachers interested in serving as mentors for a group of American high school students entering the International Chemistry Olympiad (ICO) in Frankfurt, Germany, this summer. Duties involve helping plan and conduct a special study camp for student finalists to be held at a U.S. site in June, accompanying four student participants to the 30 June–9 July ICO competition in Germany, and serving there as a member of the ICO jury.

Applications are invited from both experienced high school and university teachers of chemistry possessing strong background in the teaching of general chemistry and a broad, working knowledge of both theoretical and descriptive chemistry; experience in organic and analytical chemistry is also sought. Applicants must be prepared to commit full time to ICO activities from mid-June to mid-July this year, as well as a comparable time period in 1985. All mentor expenses and travel costs will be covered and an honorarium paid for the provision of the services described above. Interested individuals should apply by mailing a letter of application, resume, summary of relevant experiences, and the names and addresses of three references to Prof. Marjorie Cardner, Department of Chemistry, University of Maryland, College Park, MD 20742, (301) 454-3307. To guarantee consideration, applications should be received by April 30.

G. N. Lewis and the Chemical Bond

Linus Pauling

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My first knowledge of Gilbert Newton Lewis came from reading his paper on "The Atom and the Molecule," published in 1916 in the Journal of the American Chemical Society (1). During the year 1919-20 I had a full-time job as instructor in quantitative analysis in the Oregon Agricultural College. At the beginning of 1919 I had not returned to the college, because of lack of money, and I was pleased when I had the opportunity to teach the courses in quantitative analysis. My office was in the chemistry library, where copies of the Journal of the American Chemical Society and of other journals were available. My teaching load was very heavy, but I had some spare time to read the journals, and when I ran across the 1919 papers by Irving Langmuir (2) I read them with great interest. and also read G. N. Lewis' paper. I spoke on the subject of the electronic theory of valence in the chemistry seminar that year-chemistry seminars were rare, only about one each year. In 1922, when I received my degree of Bachelor of Science in Chemical Engineering, I was offered and accepted an appointment as teaching fellow in the California Institute of Technology. In September of that year, in the middle of the train ride from Oregon to Pasadena, there was a stopover of a few hours in the Bay area. I went to the chemistry building. Gilman Hall, and found a young chemist, Roy Newton, at work in a laboratory on the first floor. He was good enough to talk to me for about half an hour about the work that he was doing and about the nature of graduate work in chemistry. I did not see Lewis at that time, nor did I see any other person in the building—perhaps it was Saturday.

I first met Lewis in 1924, when my wife and I went to Berkeley to see my old friend Lloyd Alexander Jeffress, who had got me interested in chemistry when we were both 13 years old. It is my recollection that I talked with Lewis about the work that I was doing on the determination of the structure of crystals by the X-ray diffraction method, and that I got his permission to say in my application to the National Research Council for a fellowship to begin in July of 1925 that I would do the work in Berkeley. It turned out, however, that I did not go to Berkeley; instead I resigned the fellowship in the middle of the 1925-26 year, after having spent the first few months in Pasadena, in order that I might go immediately to Europe on a Guggenheim fellowsbip.

In 1928 Lewis spent a day or two in Pasadena. I learned about 50 years later that he had come to offer me a job, hut that Arthur A. Noves, the Chairman of the Division of Chemistry and Chemical Engineering in the California Institute of Technology, had persuaded him not to do so.

For five years, beginning in the spring of 1929, I spent one or two months each year in Berkeley as visiting lecturer in physics and chemistry. During these extended visits to Berkeley I had the pleasure of talking with Lewis for many hours, in his office, his home, and his Marin County country place. My lectures were largely on new ideas about the chemical bond and molecular structure based in part on the theory of quantum mechanics and in part on the empirical analysis of the properties of substances. Lewis was, of course, intensely interested in the work. I am now, in retrospect, rather surprised that he and I did not write a paper together. So far as I can remember, our discussions led to some clarifisignificant.

G. N. Lewis' 1916 paper introduced the theory of the shared electron pair chemical bond and revolutionized chemistry. Comparison is often made of G. N. Lewis' paper and the paper by W. Kossel (3) that was published in the same year. Kossel's paper (133 pages) was much longer than Lewis' (22 pages). Even so, I think that Kossel's paper represented no significant contribution. Much of it is nonsense. He gave a long discussion of electrostatic valence, but nothing about covalence, although he suggested electronic structures for some molecules in which the electrons were related to two nuclei. He mentioned the suggestion by Niels Bohr that in the hydrogen molecule two electrons occupy the same circular orbit in a plane perpendicular to the midline between the two nuclei, and he suggested that in the nitrogen molecule the two nuclei, each with a pair of K electrons, are held together by 10 electrons moving in the same circular orbit in the plane midway between the nuclei and in the plane perpendicular to the internuclear line. On the other hand, the two papers that Irving Langmuir published in the Journal of the American Chemical Society in 1919, comprising 84 pages, contained many significant

VALENCE

The Structure of Atoms and Molecules

GILBERT NEWTON LEWIS PROPERSOR OF CHEMISTRY IN THE UNIVERSITY



American Chemical Society Monograph Series

BOOK DEPARTMENT

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contributions and additions to the theory of the shared electron pair chemical bond. For some reason Lewis was antagonistic to Langmuir, and in my opinion did not give him proper credit. In his 1923 book "Valence and the Structure of Atoms and Molecules" (4), Lewis mentions that after publishing his 1916 paper he had intended at a later time to present in a more detailed manner the various facts of chemistry that made necessary his radical departures from the older valence theory. He then continued (5)

This plan, however, was interrupted by the exigencies of war, and in the meantime the task was performed, with far greater success than I could have achieved, by Dr. Irving Langmuir in a brilliant series of some twelve articles, and in a large number of lectures given in this country and abroad. It is largely through these papers and addresses that the theory has received the wide attention of scientists.

It has been a cause of much satisfaction to me that in the course of this series of applications of the new theory, conducted with the greatest acumen, Dr. Langmuir has not been obliged to change the theory which I advanced. Here and there he has been tempted to regard certain rules or tendencies as more oniversal in their scope than I considered them in my paper, or than I now consider them, but these questions we shall have a later opportunity to discuss. The theory has been designated in some quarters as the Lewis-Langmuir theory, which would imply come sort of collahoration. As a matter of fact Dr. Langmuir's work has been entirely independent, and such additions as he has made to what was stated or implied in my paper should be credited to him alone.

G. N. Lewis' main contribution to chemistry was the idea that the chemical bond (named the covalent bond by Langmuir) is at all times a pair of electrons held jointly between two

THE GEORGE FISHER BAKER
NON-RESIDENT LECTURESHIP IN CHEMISTRY
AT CORNELL UNIVERSITY

THE NATURE OF THE CHEMICAL BOND

AND THE STRUCTURE OF MOLECULES AND CRYSTALS

An Introduction to Modern Structural Chemistry

LINUS PAULING
Professor of Chemistry in the
California Institute of Technology

SECOND EDITION



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1945

atoms. Lewis also, after having placed the eight electrons of what Langmuir called the octet (s^2p^6) at the corners of a cube, suggested that the electrons are in pairs at the corners of a tetrahedron. In this way he could ascribe to the acetylene molecule a structure with a triple bond, three shared electron pairs lying at the corners of the common face of the two carbon tetrahedra. Lewis discussed the partial ionic character of covalent bonds by writing that the electron pair is midway between two identical atoms but may be shifted toward one or another of a pair of non-identical atoms.

Langmuir (6) contributed the important idea of the electroneutrality principle—that atoms in a molecule hold electrons to such an extent as to keep the electric charge of each atom close to zero. In applying the electroneutrality principle he did not, however, make any correction for the shift of electric charge resulting from partial ionic character. He showed, using the electroneutrality principle, that a transition metal may have high covalence, such as 8 for nickel in nickel tetracarbonyl, to which he assigned a structure with a double bond between the nickel atom and each of the carbon atoms of the carbonyl groups. He introduced the concept of isosterism, pointing out that molecules with an equal number of nuclei and an equal number of total electrons in general have very nearly the same structures. He concluded that CO₂, N₂O₃ NCO-, NNN-, and other such molecules are linear. The linearity of the trinitride ion and the cyanate ion was shown later hy Sterling Hendricks and me through our X-ray diffraction studies of potassium trinitride, sodium trinitride, and sodium cyanate. Langmuir also reached the remarkable conclusion that the nitrous oxide molecule has the linear structure NNO rather than NON. In his discussion of the Heusler alloys. which contain manganese, copper, and small amounts of arsenic, aluminum, or other elements and are ferromagnitic, he stated that "Copper has too many electrons. It gives one to manganese to make the atom like the iron atom." This statement shows remarkable insight.

Langmuir, however, was wrong in some of his ideas. He regarded quartz as containing SiO_2 molecules similar to the molecules of carbon dioxide, and said that the hardness is the result of the leaking of residual silicon-silicon forces. Lewis, in fact, had made a similar suggestion in his 1916 paper. Only in 1923 did Lewis realize that the silicon atoms are held together by bridging oxygen atoms.

Langmuir also assigned to the P_4 molecule a ring structure containing alternating single and double bonds. He overlooked the possibility of a tetrahedron with only single bonds between the phosphorus atoms. Similarly, his structure for P_4O_8 involves a square of phosphorus atoms held together by single bonds, with two oxygens attached to each of two phosphorus atoms and one to each of the other two—not a very sensible structure.

In his 1923 book Lewis discussed early suggestions about the electronic structure of molecules that had been made by Kossel, Stark, and others, especially A. L. Parson, a student who in 1915 published an interesting paper entitled "A Magneton Theory of the Structure of the Atom." Parson considered the electron as a rotating ring of negative electricity that accordingly possessed a magnetic moment and could be called a magneton. Lewis says that it was he who suggested to Parson that the magnitude of the magnetic moment to be assigned to such a spinning electron was constant, whereas Parson had considered it to be variable, Parson and Lewis thus anticipated by 25 years the discovery that the electron has a spin and a magnetic moment. Lewis, however, then rejected the idea, writing, "This idea has not proved fruitful, and it seems unlikely, although perhaps not impossible, that an electron possesses any magnetic properties except when it is a part of an atom or a molecule.'

Lewis felt an indebtedness to Werner, writing that "His 'Neuere Anschauungen auf den Gebiete der anorganischen Chemie' (1905) marked a new epoch in chemistry; and in at-

tempting to clarify the fundamental ideas of valence, there is no work to which I feel so much indebtedness as to this of Werner's." However, in his discussion in 1923 of the types of coordination postulated by Werner (octahedral, tetrahedral, square planar), Lewis did not make any mention of the results of the study of crystals containing these coordination complexes that had been published during the preceding two years by Roscoe G. Dickinson and R. W. G. Wyckoff, who had verified the octahedral arrangement in crystals such as K2SnCl6 and K2PtCl6, the square arrangement in K2PdCl4 and K₂PtCl₄, and the tetrahedral arrangement in K₂Zn(CN)₄ and K₂Cd(CN)₄. No X-ray work was being done at that time in the College of Chemistry at Berkeley, and Lewis seems not to have been following the developments in X-ray crystallography.

G. N. Lewis was remarkable in his originality. I was much impressed in the early 1920's when I read his paper announcing the discovery of the O₄ molecule. He had asked why the paramagnetism of oxygen dissolved in liquid nitrogen decreased as the concentration of the oxygen increased. He was able to show that he could account for the experimental values of the magnetic susceptibility of solutions of oxygen in nitrogen by the assumption that there is an equilibrium between paramagnetic molecules of dioxygen and the diamagnetic molecules of tetraoxygen, O4. From the values of the paramagnetic susceptibility he was able to evaluate the standard Gibbs free energy change and the enthalpy change for the reaction.

As I think about the history of the chemical bond, I ask myself why some of the discoveries that were made in the quantum-mechanical era of the 1930's were not discovered earlier. The electronegativity scale of the elements is an example. It was formulated in 1933 through the analysis of the decrease in enthalpy accompanying reactions in which single bonds between like atoms are converted to single bonds between unlike atoms, such as $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$. The basic idea, attributed to quantum mechanics in 1933, is that the partial ionic character of a bond makes it more stable, with lower energy, than a pure covalent bond between the unlike atoms. This idea is, in a sense, not a quantum mechanical idea; we might well have concluded before quantum mechanics was developed that if the actual bond is a covalent bond with partial ionic character it must be more stable than the pure

covalent bond, because if it were less stable the molecule would have a structure involving pure covalent bonds between the unlike atoms. The necessity for making a correction in the heats of formation of compounds involving reaction of dioxygen or dinitrogen $(O_2 \text{ or } N_2)$ with single-bonded elements to form single-bonded products is a complication, but chemists knew even before quantum mechanics that the bonds in these molecules are not single bonds and that the molecules might have greater stability than single-bonded molecules have. Langmuir formulated the electroneutrality principle, but did not make much use of it, and Lewis ignored it. The reason may well be that the principle does not work very well unless the partial ionic character of bonds is taken into account, and until the electronegativity scale was developed it was not possible to discuss the partial ionic character in a satisfactorily quantitative way. Moreover, Lewis did not make use of the theory of resonance, which had not yet been formulated in 1923 but which might have been proposed, as was done by Robert Robinson and C. K. Ingold in 1926, in the theory that Ingold called mesomerism. Lewis in 1923 expressed some concern that a structure of the carbonate ion in which one oxygen atom is held by a double bond and two by single bonds seems, as had been stated by Latimer and Rodebush (in Berkeley) three years before (7), to be in contradiction with the apparent trigonal symmetry of the ion in calcite as shown by X-ray diffraction. The idea that the double bond resonates among the three positions apparently did not develop in Lewis' mind at that time.

Gilbert Newton Lewis showed himself to be one of the great chemists of the 20th century through his work in chemical thermodynamics and other fields, as well as through his formulation of the basic principle of the chemical bond—the idea that the chemical bond consists of a pair of electrons held jointly by two atoms.

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Publications on Environmental Analysis and Ground Water Available from ACS

"Principles of Environmental Analysis," published in the December 1983 issue of Analytical Chemistry, is now available as a separate brochure from the American Chemical Society. Developed by the ACS Committee on Environmental Improvement's (CEI) Subcommittee on Environmental Monitoring and Analysis, this publication identifies elements needed to obtain reliable data as well as factors that have been shown to produce unreliable measurements. Its intent is to aid in the evaluation of the many options available in designing and conducting analytical measurements of environmental samples and in the intelligent choice of those that will meet the requirements of the situation at hand. These situations range from semi-quantitative screening analyses to those involving strict quality assurance programs intended to document the accuracy of data for regulatory enforcement or legal purposes. Discussion focuses on planning, quality assurance, and quality control, verification and validation, precision and accuracy, sampling, measurements, and documentation and reporting.

While the "Principles" brochure is meant as an aid to those working in the field, the ACS has also produced the third in its series of informational pamphlets that discuss science-related regulatory issues and that are geared to the general public. The "Ground Water Information Pamphlet," also written under the auspices of CEI, focuses on what ground water is, where it occurs, and its volume and quality. Due to the extensive use of ground water, the pamphlet also outlines the scientific aspects of ground-water depletion and degradation. It is not meant to formulate answers to the complex questions inherent in ground-water management. It does, however, present fundamental concepts concerning the chemistry of ground water and begins to build a basis from which citizens can evaluate information about ground-water problems, construct plans of action, and gauge the implications of that action. The pamphlet is written in clear, concise language that educators will find useful in the classroom for high school and college students alike.

Single copies of the pamphlets are free. Multiple orders can also be accommodated. To obtain a copy, call 202/872-8725 or write to Ms. Jean Parr, Department of Public Affairs, American Chemical Society, 1155 16th Street, NW, Washington, D.C. 20036.

The Triplet State

An Example of G. N. Lewis' Research Style

Michael Kasha

Department of Chemistry and Institute of Molecular Biophysics Florida State University, Taliahassee, FL 32306

In the last two years of his life, between the ages of 68 and 70, Gilbert N. Lewis brought to fruition and focus his long-germinating ideas on the triplet states of molecules. I had the great fortune to be his collaborator in this research. These researches, published in two papers in the Journal of the American Chemical Society in 1944 and 1945, were destined to have a profound effect on the course of the subsequent development of molecular spectroscopy and photochemistry. However, the influence was not instantaneous, since more than a decade was required to overcome the negative pressure of prestigious opponents (Franck, Teller, Livingston, Rabinowitch) and to unravel the complexities and misunderstanding of earlier research.

In this presentation I shall examine in retrospect the background of ideas against which Lewis' last researches were done, report my personal interactions with him in the hope of revealing his personality and joi de vivre, reflect on some general observations and views of Lewis on the conduct of scientific research, give an analysis of a unique habit of Lewis' writing of research previews, and indicate through his personal research memoranda to me his intensity of research interest and activity in the last years of his life.

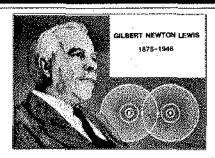
Historical Perspective on Molecular Triplet States

A spectroscopist today is easily baffled by any indication that observing triplet states of organic molecules constitutes in any way a difficulty or a mystery or puzzle. The evolution of the observations and understanding of polyatomic molecule singlet-triplet transitions took a quite different path than the development of atomic and diatomic spectroscopy. The knowledge of the latter subjects led Sponer and Teller (1941) (1) to the view

As in the case of atoms we have, in first approximation, the selection rule that only stetes of the same multiplicity combine with each other. Intercombinations occur with appreciable intensity only if the molecule contains some heavier atoms.

Such a background sets the stage for the expectation that in molecules with low Z (or "light") atoms, such as C, N, O, and H, no singlet \leftrightarrow triplet transitions are to be observed. Here we can state at once the origins of the dilemma

- (1) Radiationless transitions are essentially absent in atoms and diatomic molecules and are known today to be simply the common phenomenon in polyatomic molecules; thus, in polyatomics a prevalent mode of excitation of highly forbidden states (e.g., triplets) is abundantly available.
- (2) The terms "high intensity" and "high transition probability" carry an implication of a direct correlation. But "intensity" of emission is measured by quantum yield, so that "forbidden" triplet state of low transition probability (measured by long mean lifetime) can be observed with high "intensity" (meaured by high quantum yield) in polyatomic moleculee.
- (3) The original observations on phosphorescence emission of organic molecules were made for rigid glass solutions (organic solvent mixtures frozen to glass at 90 K or 77 K). Most of the early interpreters of the phosphorescence phenomena of organic molecules were preoccupied with "clamping of unusual conformations (tautomers) by the rigid glass medium"—which in those days seemed so essential to the observation of the long-lived luminescence.



Confusion concerning the three items just mentioned abounds in the literature before 1944 and had a considerable momentum afterward. We shall examine some of the key contributions to the general background in the various authors' own words and diagrams to indicate the gradually developing tapestry of uncertainty against which the work that Lewis and I published in 1944 was hung.

G. N. Lewis on Triplet Ethylene and Singlet Oxygen

Lewis began to think about electron arrangements in ethylene and molecular oxygen on the basis of electron pairing long before any other researcher, as a consequence of his early electronic structure models. Because ethylene triplet and oxygen molecule singlet states are so intertwined with general thoughts about the triplet states of molecules and their quenching (involving singlet molecular oxygen), it is of interest to cite Lewis' developing ideas on these species.

In his 1916 paper, "The Atom and the Molecule" (2), Lewis states in considering interactions of oxygen and ethylene

These two forms of oxygen (which of course may merge into one another by continuous graduations) can be represented as

:Ö::Ö: and :Ö::Ö:

and the two forms of ethylene as

H.H. H.H. :H:C::C:H and H:C:O:H

These are clear Lewis electron-dot representations of singlet and triplet arrays for the molecules. A later statement (1924) clarifies the issue of their representing discrete states

The enormous difference in magnetic properties between the oxygen molecule and other molecules to which we attribute double bonds seems to support the idea that the change from a non-magnetic to a magnetic molecule is not a gradual process, but that the molecule must possess at least one unit of magnetic moment or no magnetic moment at all.

This paper (3) is titled "The Magnetochemical Theory" and was the first to present in effect an electron spin restriction on molecular interaction, a topic very much alive today. Lewis did not speculate on the spectroscopic implications of his normal and "diradical" configurations.

H. Kautsky; Sensitization Mechanisms by Molecular Metastable States and by Singlet Oxygen

The German photochemist Kautsky wrote a long series of qualitative papers which reported ingenious experiments deacribing metaatable excited states involved in photosensitization processes.

Metastable states of molecules were cited in one series of papers (4) in which Kautsky, et al. demonstrated effectively that sensitization of molecules (energy transfer) by dyes is facilitated by aggregation of the dye molecules. Kautsky mistakenly thought that aggregation was a necessary precondition for metastable state excitation, failing to distinguish between intrinsic metastable state excitation and induced

metastable state excitation. The nature of the metastable state of dyes adduced by Kautsky was not alluded to. His diffuse writings, merging many discrete phenomena and interpretations, had no diagrams or quantitative data.

Singlet molecular oxygen was cited by Kautsky et al. (5) in another series of papers in which the excited singlet molecular oxygen species, generated by energy transfer from metastable states of dyes, were considered the active intermediate in photooxidation. This interpretation was lost until its recent belated and fiery revival (6-8).

Singlet-Triplet Spectrum of Ethylene

In an early paper (9) C. P. Snow and C. B. Alsopp presented a seemingly authentic weak absorption spectrum of various ethylenes, interpreted as representing the singlet-triplet absorption. This observation escaped particular attention at the time and proved to be ten times too intense to be genuine (10). The singlet-triplet absorption was found by C. Reid in 1950 (11), the extraordinarily weak absorption observed from 31,000 to 37,000 cm⁻¹ at 120 K requiring a 1.4-m path of liquid ethylene.

Robert Mulliken visited Berkeley sometime in 1942 and gave a talk about molecular orbitals of ethylene. G. N. Lewis told his research student Jacob Bigeleisen¹ afterwards, "You know, those triplet states that Mulliken was talking about in ethylene are probably the phosphorescent state." So Lewis had triplet states of organic molecules like ethylene very much on his mind.

Jabionski Diagram for the Lowest Metastable State of Dyes

Jablonski, the Polish theoretical physicist, published an interpretation (12) of some of the Kautsky observations on the metastable states of dyes and other known physical observations on dye-phosphors (dye molecules dissolved in sugar glasses and boric acid glasses). He ignored the aggregation phenomena which confused Kautsky and treated only the intrinsic properties of dye molecules. A replica of his diagram

is labelled I in Figure 1. His states are labelled N, normal; F, fluorescent; M, metastable. Jablonski could never accept the M state as a triplet state, and even as late as 1958 (13) he still tried to account for this state as a singlet excited state of low probability! Key quotations from his first papers (12) clearly reveal the concepts of (1) an intrinsic electronic metastable state, and (2) attempts to interpret the forbiddeness of transitions by multipole or other than singlet-triplet mechanisms:

We assume in the case that an "energetically isolated" dyemolecule is phosphorescence-capable, then there must exist in this molecule at least one metastable level.

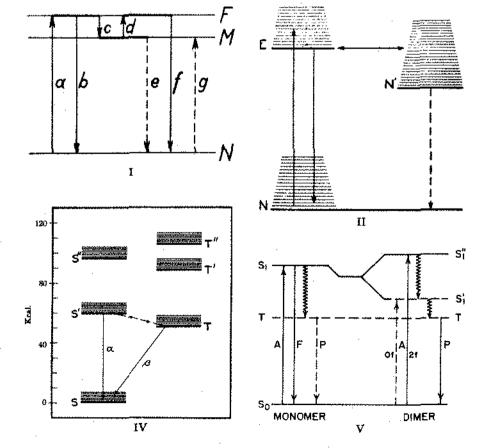
The transition between the ground level N and the metastable level M can occur only with small probability (as for example hy forced dipole radiation or quadrupole radiation). If there exists somewhat above the level M and unstable level F, which combines with the ground level N (only this case will be discussed in detail here), then will the level M in greater part he reached by a detour through F.

Jablonski was entirely concerned with the mechanism of photoluminescence processes of dyes, stressing a kinetic derivation of the thermal activation of the F (fluorescent) level from the M (metastable) level. It could be said that his treatment would not apply to polyatomic (non-dye) molecules in general, since the large excited singlet-triplet energy gap would preclude Jablonski's kinetic treatment, aside from his failure to accept the triplet designation of the metastable state of molecules. Later use of the "Jablonski Diagram" fails to recognize the limitations of his interpretations.

Franck and Livingston Tautomeric Metastable Model

The use of glassy media and adsorbed states in the study of the phosphorescence of dye molecules was a major preoc-

¹ Personal communication.



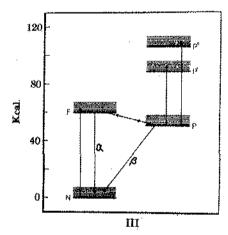


Figure 1. Various energy diagrams for dye mole-

- Jabionski diagram for the lowest metastable state of dyes (12).
- Franck and Livingston tautomeric metastable model (14).
- Lewis, Lipkin, and Magel's energy diagram of fluorescein in boric acid (17).
- IV. Lewis and Kasha's energy level diagram for acid fluorescein (19).
- Kasha and McRae's energy level diagram for a dye molecule versus a dye-dimer (22).

cupation of all authors writing on the subject before 1944. Thus in 1941 James Franck and Robert Livingston (14) presented the idea of a tautomer of the normal molecule rigidly clamped by the environmental medium:

Many of the apparently conflicting facts of the photochemistry as well as of the phosphorescence and the fluorescence quenching of dyes can be given a rational and unified interpretation if it is assumed that an electronically excited dye molecule can go over, by a process of internal conversion, to the electronic ground state of a reactive energy rich tautomer.

The Franck and Livingston diagram is reproduced as II in Figure 1. A potential curve model later given by Förster (15) for the Franck-Livingston model suggests the seemingly unsurpassable difficulty of generating a radiative phosphorescence by their scheme. Later experiments that I performed (16) on perchlorinated aromatics, which can experience no tautomerism but still possess phosphorescence, did not persuade Franck and Livingston to ahandon their scheme.

Lewis, Lipkin, and Magel Study of Fluorescein Phosphorescence

In 1941 a general study of the phosphorescent state of acid fluorescein dye was published by G. N. Lewis and his colleagues (17). One of the main themes of this paper was the quantitative corroboration of the Jablonski thermal activation scheme for the $M \to F$ decay path. Their diagram is reproduced as III of Figure 1 and was labelled "Energy diagram of fluorescein in boric acid." The Lewis, Lipkin, Magel paper presents ambivalent interpretations of the P (phosphorescent) state

There seem to be but two reasonable assumptions as to the nature of the phosphorescent state.

The first assumption is that a molecule in the F state changes from a state of electronic excitation to a very highly excited vibrational state of the N state.... The new molecule could now be regarded as a geometrical isomer of the normal molecule....

The second reasonable assumption is that in the P state the atomic configuration is approximately the same as in the N state, but that one is an electromer of the other, such as a triplet state (biradical), which now has a low probability of returning to the normal state because of quantum inhibitions.

Lewis, like his contemporaries writing on the subject, was also preoccupied with the rigid glass environmental effects, and he wrote (17) colorfully on this aspect:

We could think of the P molecules as held by the rigid medium in their unstable configuration, as though by the jaws of a powerful tran.

The Lewis, Lipkin, and Magel research (17) contained two experimental observations which were to have a powerful effect on later researches.

- (1) The saturation curve for phosphorescence of fluorescein dye in boric acid glass was to prove fundamental to later studies of photomagnetism, since triplet state population inversion with respect to the ground state was demonstrated.
- (2) The absorption spectrum of the P state was observed, opening the door to many later triplet-triplet absorption spectral studies and to the triplet state flash-spectroscopy kinetic techniques.

Terenin on Photochemical Processes in Aromatic Compounds

Terenin, the Russian photochemist, wrote a long descriptive review interpreting and correlating previous researches in photochemistry and luminescence studies in dyes and simpler aromatics (18). This paper heavily depended on the Lewis, Lipkin, and Magel (17) study and generously references the latter. Terenin presented no spectra of phosphorescences of organic molecules, and his paper gave no energy level diagram for metastable electronic levels of a molecule. His words show some of the same ambivalence as Lewis, Lipkin, and Magel:

Several suggestions have been so far advanced as to the nature of this metastable state in dyea, viz.

(a) a highly endothermic and reactive dye tautomer, formed by the transposition of a "labile" hydrogen atom;

(b) a geometrical isomer or distorted dye molecule formed as a result of a strong vibration, imparted to the molecule in its radiationless transit to the ground state, the abnormal configuration being stabilized by the environment, acting like "jaws";

(c) an electromer of the dye, in particular, a triplet state or biradical, from which the transition to the ground level is being prohibited by selection rules.

Terenin rules out tautomerism on the basis of energy consideration and then states

It is, in our opinion, the alternative, mentioned under (b), which, supplemented by the viewpoint (c), can account for the main facts.

Terenin, like his predecessors, was preoccupied by the rigid glass environment problems, and concludes

The molecular modification of abnormally long life, which we have denoted Γ , should correspond to a definite electronic configuration of the compound, differing from that of the excited state ${}^1\Gamma^*$. We assume, furthermore, that it is stabilized by the formation of hydrogen bonds with the environment. The rigidity of the medium, emphasized by G. N. Lewis and co-workers $\{(17)\}$, has, in our opinion, not only a purely mechanical meaning [emphasized by Lewis], but alsu a chemical implication, viz. the formation of "hydrogen bridges," participating to some extent in the resonating structures of the compound and "smoothing" the way from ${}^1\Gamma^*$ to Γ ; we should rather speak of an "incipient tautomerism" of the molecule, in this connection.

Terenin's appraisal (18) seems to be at about the same status of uncertainty as that of Lewis, Lipkin, and Magel (17). Although apparently taking geometrical isomerism, triplet assignment, and tautomerism with H-bonding in concert, Terenin did start seriously discussing electron spin configurations of triplets. His discussions of triplet aromatic molecules together with singlet and triplet oxygen configurations show unusual prescience.

Lewis and Kasha Molecular Triplet State Assignment

In our first paper in 1944 Lewis and I (19) made the unambiguous jump to assign the lowest excited metastable state of organic molecules as an intrinsic triplet electronic state. Our broad study of spectra of 89 molecules reported the great generality of the phosphorescence phenomenon, and we established the independence of the triplet-singlet emission from the nature of the medium hy using a variety of rigid glass solvents. The detailed story of the personal interaction between myself, a young graduate student, and Lewis, who was doing his last piece of major research, to produce both the data and its theoretical interpretation will be told in a later section of this paper.

The energy level diagram which we proposed is reproduced as IV of Figure 1, with explicit labelling of singlet and triplet manifolds. This diagram is an explicit relabelling of the Lewis, Lipkin, Magel diagram, III. Since the latter diagram was for data on acid fluorescein in boric acid glass, we unwittingly performed a disservice to the literature by labelling IV as "Jablonski diagram for fluorescein in boric acid glass," intending to stress the α -phosphorescence (thermally activated T—S' \rightarrow S) versus the spontaneous β -phosphorescence (T \rightarrow S) (the primes also not corresponding properly to excited configuration singlets!). In view of the relation of Jablonski's contribution, this diagram should be properly labelled "Energy level diagram for acid fluorescein."

McRae and Kasha Exciton Intersystem Crossing Diagram

We return in concluding this section to the Kautsky dilemma: intrinsic metastable states of dyes versus dimerization-induced metastable states. Theo Förster in 1946 accepted the gauntlet thrown down by the Kautsky experiment and showed (20) that by dipole-dipole coupling of parallel-transition-moment dimers a forbidden (metastable) singlet-state for the dimer should arise. He assumed this to be the metastable level ascribed by Kautsky to both phosphorescence and photosensitization (our 1944 paper was still not available to Förster because of World War II dislocations). Förster later (21) adopted our triplet state model for the metastable state.

McRae and I (22, 23), pursuing Szent-Györgyi's experiments on dye phosphorescence enhancement in frozen water versus frozen alcohol glass, approached the dye-dimerization problem by molecular exciton theory. Our diagram is given in Figure 1 as V, showing that for a dye molecule singlet-singlet fluorescence dominates the luminescence, whereas in the dye-dimer (in water) the metastable singlet exciton state radiationlessly goes over completely to the triplet state, giving phosphorescence dominance in the dimer. Thus, we effectively explained the Kautsky dilemma, and in effect, combined Förster's two diagrams into one.

Research with G. N. Lewis²

First Contacts

When I came to Berkeley in Fehruary, 1943, G. N. Lewis was 68 years old and had recently stepped aside as dean of the College of Chemistry; I had just turned 22. I had come as a graduate student determined to work with Lewis, as he was certainly the best known physical chemistry professor then at the University of California at Berkeley. The chemistry graduate students were required to select a professor before the end of their first semester and to commence research in that term. I went through the obligatory list of interviews in proforma routine, saving Lewis for the last. My first hour with Lewis was impressive. I must have appeared nervous, for Lewis said, "Now don't think I'm going to embarrass you by asking you a lot of detailed questions about physical chemistry. I would just like to tell you about some of the interesting research which we have been thinking about recently."

Lewis then proceeded to talk with excitement about the phosphorescence studies done with David Lipkin and Theodore Magel and the absorption and photochemical studies just then being completed with Jacob Bigeleisen, who overlapped with me for the month of May of 1943. Lewis and Calvin had developed earlier a semi-classical theory of light absorption in dye molecules, and Lewis and Bigeleisen had done both some elegant polarization studies of x-band and y-hand molecular coordinate resolution of the electronic transitions as well as related photochemical studies.

Lewis had his mind on a new class of dye molecules, the large polycyclic quinones (like pyranthrone, violanthrone), and suggested that I measure their absorption spectra carefully. Bigeleisen gave me a master's introduction to what was probably the Chemistry Department's sole electronic instrument, the battery-operated Beckman DU Spectrophotometer, housed in the Old Chemistry Building. Having learned its operation (and idioayncrasies), I proceeded to measure absorption curves of my dyes. The instrument acale started at 2000 nm (then mu!), and so did my readings.

An Intensive Month of Spectrophotometry

I measured several curves one week from 2000 nm (hardly knowing that I was in a forhidden region of the infrared), to 200 nm, the other limit of the instrument. No one in the laboratory had done this before (as all sensible operators started at 750 nm—the visible limit), and Lewis was astonished to see,

that in addition to a strong absorption band expected in the visible region, I had found an *unexpected* characteristic strong band in the middle of the near infrared for each dye I had studied.

Lewis began to speculate: what could this new electronic band be? He soon had an explanation. The polycyclic quinone dyes which we were studying could be described as large planar oval or round molecules. Lewis thought: "Could it be that we have found the low-energy circular oscillation of electrons, in addition to the higher energy x and y Cartesian oscillation of the previous type?" The test was then to study as many linear absorbing molecules as could be found: a carotene or lycopene. Special samples were obtained from Professor Zechmeister of Cal Tech. While waiting a week or two, I added to our list of new spectra.

The absorption curves for the "linear" electronic systems (carotenes) revealed once again strong electronic bands in the near infrared region, characteristically mimicking the visible absorption bands of the molecule, as in previous "round molecule" casea. Each molecule showed a typical vibrational envelope, band width, and spectral position, analogous to its strong characteristic visible absorption.

When Lewis saw that the Beckman Spectrophotometer gave these results on linear molecules as well, he said,

"Take Me To Your Spectrophotometer!"

Lewis asked me to explain the various components and their operation. He had me unscrew the phototube and cell compartments, exposing the exit slit of the spectrometer.

Then he said.

"Set the mounth-mator dial for 550 m μ ," and poised himself in line with the exit beam. He said,

"I see GREEN."

Then,

"Set the monochromator for 600."

He said,

"I see YELLOW."

Then,

"Set the monochromator for 700."

He said.

"I see RED."

Then,

"Now, set the monochromator for 1,000 m μ ."

With excitement,

"Aha! I am the first man to see the INFRARED. And it is

Lewis had suspected that the monochromator was misbehaving, and we quickly saw that the whole of the visible spectrum could be seen on this instrument by scanning the near infrared from 750 to 2,000 mµ. Thus, any visible dye would show an illusory absorption spectrum on the background of this scattered light, apparently reflected off the instrument wall. There are probably some false curves in the earlier literature based on this error. Lewis taught me to be wary of instrumental performance.

Phosphorescence and the Triplet State

Lewis held a daily research conference with me at 11:00 a.m., usually lasting an hour. Each session launched major plans to be carried out that very afternoon and evening. By the end of such an hour, a whole strategy for the day was mapped out. No apparatus was too complicated to be assembled that day, at least in a preliminary form. Of course, I had an enormous advantage over other graduate students since

² This and the sections of this report designated with an asterisk are taken from Kasha, M., "Four Great Personalities of Science—G. N. Lewis, J. Franck, R. S. Mulliken, and A. Szent-Györgyi," Scientific Essays, Tokyo Science University Lectures, 1979, to be published.

Lewis could call on any and all shop men for instant service

After the month's debacle with the dye spectra, Lewis and I both wanted a refreshing change. I suggested phosphorescence had many puzzles to resolve. Lewis agreed, and said, "Have the shop huild a phosphoroscope." Lewis then left for a month's vacation. It was the first day of June 1943, and Bigeleisen had two or three days left in Berkeley. "Jake, what is a phosphoroscope?" I asked. He was furious that I had not used the library. "Look it up!" was his answer. I studied the idea of the Becquerel phosphoroscope, and designed one with parallel discs and had it built the next day. Bigeleisen's parting suggestion to my question "What shall I study?" was: "Try carbazole, it seems to have a very long-lived blue-violet phosphorescence." This suggestion proved to be worth its weight in gold. In the Lewis inner laboratory, where the old brass-tube and mahogany-wood-boxed Medium Hilger Quartz Spectrograph was housed, was a score of large desiccators containing boric acid and dextrose glass phosphor slabs made with various dyes as solutes (from the 1941 work of Lewis, Lipkin, and Magel). All of these dye "phosphors" exhibited broad-structureless phorphorescence. If I had also studied only dyes, our work may never have developed the direction and significance that it did subsequently.

The carbazole molecule spectrum was astonishing, even to me as a beginning spectroscopist. The spectrum consisted of numerous marvelously detailed "sharp" bands. I don't know how I contained my excitement. I probably showed my spectrographic plates to everyone in the building. Jacob Bigeleisen had left before I got a spectrum. Lewis was away for a month. I was the only graduate student in his laboratory. Having just finished Harvey White's Atomic Spectra and Structure course in the Physics Department, the excitoment of spectroscopy was in me. That month I ran through several dozen molecular samples: naphthalene, benzophenone, anthraquinone, benzaldehyde, nitronaphthalene, etc. Every molecule showed characteristically "sharp" banded structure. All of these were studied in EPA glass at 90 K (we had only liquid air as a coolant). The bands observed were very numerous and highly structured compared with any of the dye spectra which had been obtained in the laboratory before.

Lewis was delighted and excited by the result when he returned. Our work was now turned fully to a broad exploration of the phosphorescence of organic aromatic molecules in rigid glass solution at low temperature. My phosphoroscope, vacuum sublimers, and vacuum stills ran 24 hours a day for the year. At the end of that first summer I was allowed to give a research seminar on the preliminary observations. Admittedly, the presentation was somewhat repetitive in that I tried to show how virtually every molecule we studied showed a characteristic low-temperature phosphorescence—especially if the molecules were non-fluorescent. The rest of that year was spent in an intensive study of the phosphorescence of over 100 different molecules.

In July of 1944 our work was ready to be written up. The procedure used in writing this long paper is worth recording—as it at first startled me. Lewis seated me comfortably in the wide-armed, high-backed wicker chair which greeted all his guests, with pad and paper in my hand, and dictated the paper in perfect flowing English from beginning to end! I was allowed little interruptions here and there, with an occasional slight change of perspective, but on the whole that first paper (entitled "Phosphorescence and the Triplet State (19)) was already in Lewis' mind. How could he do it? I wondered. Then I realized that everything had been discussed endlessly in the laboratory, and finally, as Lewis puffed his cigar and paced up and down Gilman Hall and across campus, the perfect phrasing of each thought was developed. And when we sat down together, he was ready!

It is odd in retrospect that "Phosphorescence and the Triplet Stete" should have to come as late in 1944 as a secure

molecular correlation. In atomic spectroscopy and diatomic spectroscopy there was no difficulty with assigning multiplicities and observing forbidden transitions. I believe that one of the retardations on the understanding of polyatomic triplet states was the fact that the techniques used for observation of molecular phosphorescence, solid solutions in rigid glass matrices, impinged on the doped-inorganic-impurity phosphors, and the suspicion carried over that the strange rigid-glass media those Berkeley chemists were using could involve analogous solid state phenomena. It is hard to helieve today the general negativism and even hostility which greeted the presentation of this work. It took 10 years to overcome early prejudices before the phosphorescence of molecules assigned as the lowest triplet → singlet transition became universally accepted as it is today. Certainly the Lewis and Kasha study showed that phosphorescence was an intrinsic molecular characteristic, independent of the medium or solvent used. Probably, aside from the novelty of the spectroscopic technique, the lack of comprehension of the role of radiationless processes in polyatomic molecules was the other source of diffidence.

In the second year of my work with Lewis, World War II was in its intensive final stages, and I was permitted to remain in Berkeley only if I joined a wartime research project. I easily made the timely decision to take on the heavy extra burden in order to continue with Lewis. So in this second year, Lewis and I saw each other each evening and Saturdays, and frequently on Sundays. We averaged six hours a day together in our whole period of two and one-half years of contact. Our first paper was written in July and August 1944 in the evening hours between 7 and 11 p.m. Meanwhile, our attention had turned to singlet-triplet absorption studies, and a paper was published in June 1945 entitled "Phosphorescence in Fluid Media and the Reverse Process of Singlet-Triplet Absorption" (24). In February 1945 I had completed my PhD degree on the basis of these two researches.

G. N. Lewis Daily Research Memoranda

In June 1943 the research on phosphorescence of organic molecules in low-temperature rigid glass solvents had started in earnest. It may not be out of place to give some indications of the intensity of this research and the pressures which produced such a concentrated effort. The world was at war and academic research in universities was under severe restriction from every side. In 1943 I was still eligible for deferment from Army conscription since I was a teaching assistant in general chemistry, teaching especially the large groups of Navy Medical Corps students. There was a realization that all of the few graduate students of chemistry would rather soon take up war work of one kind or another. Perhaps that contributed to the pace of work as much as anything.

In interviewing me a few months earlier, Lewis gave a fair, thoughtful appraisal of our future relationship. He said, "You don't know me, and I don't know you. Let us say you start an apprenticeship, and in a month or so, for any reason, if you don't like working with me, or I don't like working with you—then we can part freely without friction on either side." We immediately worked so well together that the apprenticeship was never mentioned again.

Lewis had asked no questions about my background, but two of my past experiences prepared me especially well for the intensive period ahead. In my teen years I was in effect the apprentice of a Pennsylvania carpenter and cabinet maker of unusual skill. I was his "man Friday." Every evening I was his instant assistant, knowing every tool, knowing every piece of stock in his shop. I could tell hy his glance what he wanted next, hardly more than a nod being necessary. In working with Lewis, I developed the same relationship. In our many hours together each afternoon, I knew his favorite optical filters, his favorite optical accessories. Our work went swimmingly, and we had much good humor between us.

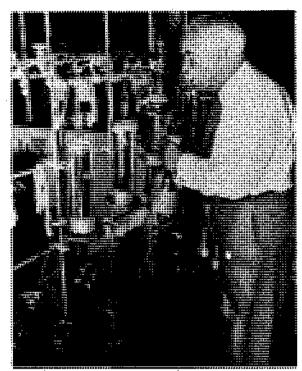


Figure 2. Lewis at vacuum line in laboratory on the third floor of Gilman Hall at the time in 1940's when he was conducting research on color and the triplet state.

My second experience of which Lewis had no inkling was my two and one-half years employment at the Merck Research Laboratories in Rahway, N. J. While going to The Cooper Union Night School of Engineering in New York City, I worked first with the famous chemist Karl Folkers on erythrina alkaloid extraction from poison heans, and fractionation of the alkaloid components. My triumph was the separation of 1.5 g of crude alkaloid into 14 pure alkaloid components by microcrystallization techniques. In my second year I did microbioassays for the entire research laboratory, whose staff was in hot pursuit of a then unknown vitamin, pantothenic acid. I worked on every aspect of this (at the age of 18-19): pilot plant isolation, synthesis of intermediates, and the daily bioassays (Lactobacillus casei growth curves). The excitement of pursuing an elusive research goal, and the pressure of the responsibility of the daily bioassay coupled with night school engineering studies tuned my working habits to the intense regime tacitly demanded by Lewis.

Our daily routine started when Lewis appeared in his office at 11 a.m. for our 1-hr lecture-discussion at the blackboard. The afternoon's work now outlined, he went to the Faculty Club, with the expectation that upon his return at 2 p.m. the new experiments would be ready. Quite often this meant a major feat of glassblowing, metalwork, carpentry, electrical wiring-especially if apparatus had to be moved into the building corridor as it occasionally was. Several shop people would be working furiously to get things ready. From 2 until 5 or 6 p.m. wild, rough experiments would be done. (Figure 2 shows Lewis doing vacuum line work from this period.) Then Lewis would take his departure with the comments: "Very Good! Very Interesting! Just polish up the measurements a bit and we'll study them in the morning." After a quick dinner I would return to the lab and frequently work until midnight on the expected polishing of the afternoon's work. In the morning, with a lot of neat curves, spectral plates, tables of data laid before him, Lewis would say: "Well, we did very well yesterday afternoon, didn't we?!"

Lewis would scribble notes to me if we somehow missed each other. I saved these in a file so that I would not forget to carry out any requests. Then later I realized they could be of historical interest, so I still possess what I recall to be the complete set. They are scribbed in soft pencil on yellow paper. Unfortunately, most are undated, but the research they describe allows their sequential arrangement. The few that I dated at the moment are indicated. They tell a fascinating story of Lewis' intense interest in our rapidly evolving project.

Our first molecule of special interest was carbazole because of its "sharp" bands. By the strangest coincidence the two strongest vibrational peaks of the phosphorescence of carbazole coincided almost exactly with the 4047 and 4358 Å lines of our 1-kW AH6 high-pressure, mercury-exciting light. Lewis at first thought we had some super-enhanced Raman scattering. In a rather dramatic experiment using a powerful Mg-cored carbon arc, with the beam transported across 5m of laboratory and with our phosphoroscope flashing (everyone in Gilman came to see the big experiment), we quickly found that even with fartber UV excitation the same carbazole phosphorescence bands resulted. We did every kind of experiment to prove that our previously unobserved carbazole bands were unique, real, and characteristic. Lewis left me the following message.

It will the ment important mest thing is t get the fluorescene of contageling in higher air - It may the a norgeling of the planth meaning is to far away to fother.

I think the most important next thing is to get the fluorescence of carbazole in liquid air—it may take a very long exposure but the overexposure of the phosphorescence is too far away to bother.

GNL

We then began systematically to study all sorts of typical organic structures:

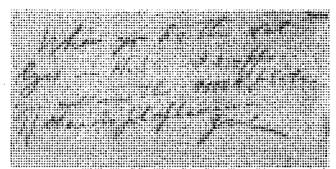
After dime the while still, should be it worm ton fait our fait and grant of the maft the and reflect investigation of the garden grant of the garden

After dinner the whole still should be at room temperature Remove inner part--scrape off what you want of the naphthalene---and replace inner part in still

GNL

We began to recognize quickly that we could tell purity of our compounds from the simplicity and beauty of the phosphorescence bands. Naphthalene usually showed a ghost spectrum to higher frequency, which I could only get rid of by crystallization from ethanol, whereas sublimation seemed to concentrate the impurity. I later diagnosed the volatile impurity to be benzothiophene.

The very large polycyclic quinone vat dyes were still on Lewis' mind, but running concentrated H₂SO₄ as a glass solution of the polycyclic quinones at 90 K gave very complex hands



7/6/43

When you do the vat dyes in H₂ SO₄ I suppose you will use the 9000 A plates if there is phosphorescence

GNL

Lewis got very interested in the vibrational structure and had Linus Pauling pay a visit. Pauling then wrote a communication for the Journal of the American Chemical Society at Lewis' suggestion using our data.



Can I have the first 4 values of β -chlor- β -Brom β -Iodo and α chlor for this evening, GNL

We began to study molecules with unsaturated functional groups (nitro-, carbonyi-, etc.) and began to observe the uniquely short lifetimes and simpler spectra of their phosphorescences (they were later recognized as n,π^* triplet emissions).

I think I would like one photograph of 2-nitro-fluorene

GNL

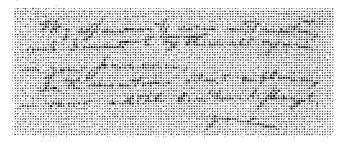
Lewis was toying with ideas of O2 perturbation, but we did not succeed in accomplishing any definitive work on this, since when our solvents were frozen in glass, the perturbation effects were negated. (This dilemma plagued me for several years until I thought of the singlet-triplet absorption experiment in ethyl iodide solvents.) The data of this memorandum reminds me that I had Christmas day off from research that month, but it was very lonely hecause my family was 3000 miles away and my hrother was fighting tanks in Europe.



I think this is the filter we want-511, with a vellow filter on the other side. CuSO₄ should also be used.

Perhaps, when I come in tomorrow we will try the effect of O_2 . We shall want fluoresein and eosin in slightly alkaline alcohol

We kept up the oxygen quenching experiments; we continued extending our repertoire of spectral types of phosphorescence.



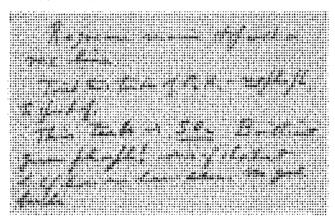
12/28/43

GNL

My experiments were interesting, and I want to try them all again in your presence.

In the meantime start subliming in vacuo a little dinitro-di-

We spent quite a bit of time looking at simple molecules, discussing literature ideas on triplet ethylene especially. The ethylene experiment was done badly, since we did not check if any light was absorbed. The high-pressure arc probably was unsuitable as an excitation source.

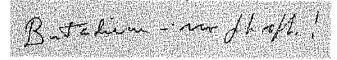


Regrease main stopcock on voc line.

Tried two tubes of C_2H_2 —no phosph. to speak of.

This tube is SO_2 Brilliant green phosph! one of the shortest half lives we have seen. No good bands

We were aware of the wavelength problem, hut bad no better luck with the next larger polyene.



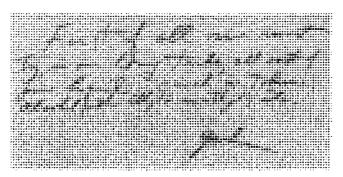
Butadiene—no phosph.!

Polyenes turned out to be elusive for a long time afterward. In about February 1944, a big personal decision loomed: join the U. S. Army, go to Central America on a Signal Corps project, or join the Manhattan District (Plutonium Project) in Berkeley, Lewis expressed his hope that I would do the last, and I did without hestiation, as I could continue working with him evenings, Saturdays, and Sundays. The Plutonium Project work was very demanding, and was also emotionally driven, since we were able to secure secret German war reports on their project. Consequently, we were dedicated to this work, and I remember 60–65-hour workweeks being normal. Then I worked with Lewis from 7 until 10, 11, or 12 p.m. (and he

came in regularly each evening) and every Saturday morning and afternoon. On Sundays I worked alone.

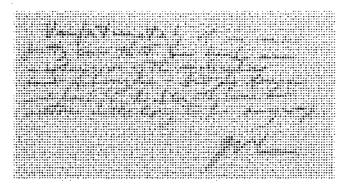
At the end of our first year of research on phosphorescence I had recorded the spectra of more than 100 molecular species. Eighty-nine of these were published, and very few proved to be erroneous—in spite of the lack of refined techniques of chromatography, VPC, IR, NMR, mass spectrometry, etc. available today.

In about July 1944 we began to write our first paper, and we started exploring singlet-triplet absorption. Looking at the long-wavelength edge of dye spectra proved difficult and futile. We began to look at the absorption spectra in long tubes, first in a 1-m cell, then in a 5-m optical cell rigged up in the corridor in front of our spectrometer.



First of all we must try, in our long tube, all sort of pure liquids—such as toluene, alcohol (either ethyl or methyl) etc.

Otto Redlich, of the Redlich-Teller vibrational frequency product rule, was living in Berkeley, and was called in for expert advice. I believe it was he who suggested to Lewis that the weak bands we were finding in 5 m of liquid benzene in the visible and near UV (!) were really IR overtone bands.



Unfortunately it is now pretty sure that our bands are an extension of the molecular bands of benzene—but do benzene and perhaps dichlorethylene and acetone in the long tube anyway.

Nevertheless, the observation of the IR overtone bands gave us confidence that the 3400 Å region weak absorption bands found in liquid benzene were indeed electronic bands, which could be correlated with our triple-singlet emission bands found for benzene commencing in the same region.

Lewis knew Otto Redlich on two grounds. First, Jacob Bigeleisen had got his MS degree with Redlich at Washington State in Pullman for a Raman study of the dissociation of nitric acid—then he came to Berkeley and proved to be one of Lewis' best students Lewis ever had. The second was an instance which occurred when I was in the laboratory and a dark-haired, robust Austrian gentleman appeared at my door and said with a heavy accent, "Where may I find the Herr Doktor Professor Lewis?" As it happened, Lewis was sitting on the floor with a hucket containing dry ice chips within

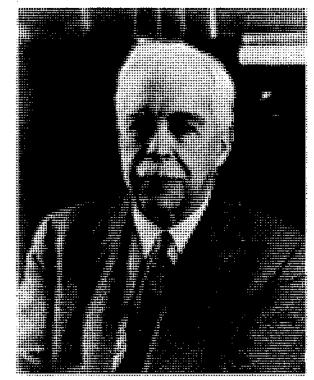
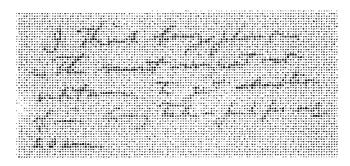


Figure 3. G. N. Lewis on his 70th birthday. Photo by author.

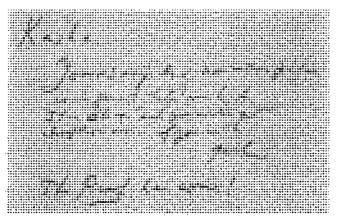
which he was opening an ampule of β -carotene obtained from Zechmeister ("Open in an O_2 -free atmosphere"). So I said, "This is Professor Lewis," pointing to Lewis in a frog-like pose on the floor. Redlich was visibly embarrassed but introduced himself. Lewis exclaimed to me, "Oh, this is the man who improved my book!" Redlich had added a chapter on statistical thermodynamics to the German edition of Lewis and Randall. Redlich again blushed with embarrassment.

As we began to think harder about singlet-triplet absorption and to develop the Einstein A/B relationship, we initiated a study of shorter-lived phosphorescent molecules for their correspondingly enhanced singlet-triplet absorptions



I thinh benzophenone is the most important substance to get absorption of in long tube—perhaps anly 20 cm.

In November 1944 we were well into our singlet-triplet absorption studies, and Lewis personally began preparing some nitrosoalkanes, which had a beautiful blue color. The absorption we thought to be singlet-triplet, but this has proved to be wrong. I believe that the phosphorescencea (IR) are, however, triplet-singlet.



Kasha.

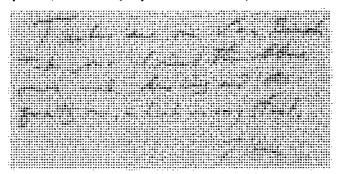
Your sample of bromnitrosopropane is in quartz tube in L.A. [liquid air] It is clear and you could get absorption curve if you wish

G.N.L

The Proof has come!

The proof of our first paper was very thrilling to receive. In December 1944 after the paper appeared in the Journal of the American Chemical Society Sam Weissman took the trouble to write Lewis a congratulatory letter on the paper. Lewis esteemed Weissman very highly, and his letter, stating that the phosphorescence and triplet state paper was "like a breath of fresh air," gave Lewis immense joy and satisfaction. He went around Gilman Hall with a fresh new smile for a week.

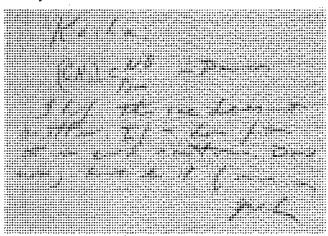
I am sure that Lewis was very fascinated by the color effects in optical phenomena. He loved making the nitrosocompounds, and the deep sky blue color was very beautiful.



Tubes are on Vac Bench Take your choice of the blue ones and disregard the quartz one, which is my stock

GNL

In about January 1945 our work on singlet-triplet absorption was coming to an end, and we began to write our second paper. Nitroso compounds' absorptions are displayed prominently in this work.



Kasha: $(CH_3)_2 C_{g_r}^{NO}$ in Dewar

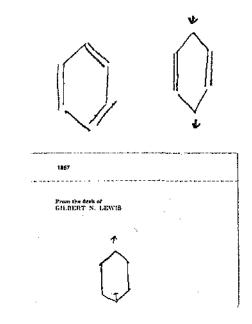
I hope the ice does not matter. If it does put it in cold acetone. Don't worry about lack of meniscus

GNL

The singlet-triplet absorption paper (24) was a landmark paper in correlating absorption spectroscopy with phosphorescence as a further spectroscopic proof of the intrinsic electronic character of the phosphorescent state as a triplet state. Although later research revealed far better examples of singlet-triplet absorption bands (we were hindered by lack of knowledge of spin-orbital Z-effects, which never entered our discussions), this work initiated the direct spectroscopic study of triplet states.

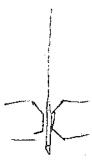
By the end of February 1945 my work with Lewis was completed, my dissertation accepted, and all my energies were devoted to an intensive phase of the Plutonium Project for the rest of 1945.

Lewis began thinking about the consequences of triplet state spin properties quite early. His sketches of the spin orientations for the triplet state began popping up in the laboratory, one on his personal note pad.



A dated sketch (July 18, 1944) shows that at a time near completion of our first triplet state paper, in discussing the expected magnetic properties of the triplet state he had sketched a Guoy balance.

July 18, 1944



Starting in March 1945, Melvin Calvin as our local paramagnetism expert worked with Lewis on an attempt to measure the paramagnetism of acid fluorescein in its phosphorescent state. A communication was submitted by them June 16, 1945 and published in the *Journal of the American Chemical So-*

ciety (25). They indicated a qualitative deflection into the magnetic field in the right direction for the illuminated half of the sample, but immediately afterwards observed a contrary deflection. In January 1946, the main part of my plutonium research completed. I was able to join Lewis full time on this photomagnetism determination. Lewis died shortly afterwards (March 23, 1946), and I, with Melvin Calvin's occasional overviewing, was able to complete a quantitative determination. The mathematical analysis was due almost entirely to Lewis, but it took a major effort on my part, with cogent help from William Gwinn and Harrison Shull at two points, to bring the calculation to a conclusion. Also, it took me two years of meticulous physical experimentation to unravel the side effects, eliminate them, and to refine the laborious quantitative steps in the measurement. In our final day at the 20,000 Gauss magnet, the reproducibility of the Theorell boom displacement in the beam, its dependence on light intensity, and return to zero displacement in the dark, made Calvin exclaim, "G. N. would have loved to be here today! He would have loved this experiment!" I wrote up the paper, and it was submitted in 1949 to the Journal of Chemical Physics, as a joint paper by Lewis, Calvin, and Kasha (26). An elegant refinement of this work was published in 1964 by Joussot-Dubien and Lesclaux (27).

Glibert Lewis' Research Style

Mathematical Prowess

At the blackboard during our conferences, at first in our morning sessions and later in the evening sessions, Lewis' powerful analytical and intuitive scientific prowess shone through. There were two rather detailed mathematical problems that we worked on, one being the derivation, from the Einstein A and B coefficient relations, of the integrated absorption-lifetime equation used in our second paper (we did not know that R. C. Tolman had done this earlier). The other was laying the analytical groundwork for a detailed photomagnetism study which I completed with the overviewing and help of Melvin Calvin after Lewis' death (26). I was at the blackboard groping with a difficult step a couple of times, and Lewis seized the chalk and quickly showed in a few powerful steps a way to its resolution. Although Lewis had published some highly mathematical papers in his career (e.g., on relativity theory with Edwin Bidwell Wilson; statistical thermodynamics with Joseph Mayer), his later years were spent on rather qualitative experimental studies. But the old ability was very much in evidence, hiding just beneath the surface.

Overcoming Logical Barriers

A special trick was used by Lewis when we got boxed into a logical impasse, and it proved to be very effective. It did happen quite frequently that our series of logical steps in some argument or development carried us seemingly to a stone wall: $A \rightarrow B \rightarrow C \rightarrow D \rightarrow \parallel$. Lewis would realize this, and he would say, doing almost a little dance around a semi-circle—i as if to look at an object from behind: "Let's look at it backwards!" So the argument was dissembled $D \rightarrow C \rightarrow B \rightarrow A$, and then suddenly it seemed clear that the steps should have been $A \rightarrow B \rightarrow C \rightarrow D' \rightarrow E \rightarrow$ solution, the blind alley becoming magically revealed by unraveling and reexamining the steps in the logic.

A Delayed Love Affair with Organic Molecules

Lewis died of a heart attack working one Saturday morning in the spring of 1946 at his favorite place in the laboratory, the vacuum bench. He had just passed his 70th birthday. Lewis loved to vacuum distill liquids from one flask to another, to sublime materials into reaction vessels, to watch color changes as reactions took place. The turning of the stopcocks, freezing samples with liquid-air Dewars, warming up a solution with a water bath, or even with a match which had just lit another

cigar, these were all part of the visual physical chemistry that Lewis enjoyed most. He confessed to me that organic molecules had been his special joy in his later years, and how, because he had failed a course in organic chemistry at Harvard as a student, he had developed a lifetime dislike of organic molecules—much to his later regret and chagrin.

Cautions on Heavy Instrumentation

Lewis had strong feelings against a researcher becoming too attached to a large instrument or heavy research machinery. Although he admired and made use of heavy instrumetation at times, he felt that someone who developed such instrumentation was inclined to become a slave to and an exponent of the instrument or machine. He preferred to be free to wander among available techniques and to wonder about ideas and not be tied to one technique. For somewhat analogous reasons he was prejudiced against complicated chemical syntheses as an aid to physical chemical research. He admired researchers who could make molecules, but he preferred to leave this to others so that he could devote himself maximally to developing and testing physico-chemical theories. He believed that if a theory was general enough, there should be ample scope for the physical chemist to select a suitable sample from the chemical storerooms to test it.

Gilbert Newton Lewis' Last Day

I was working with G. N. Lewis on the Saturday afternoon, March 23, 1946, when he died, and I find it worth recording the events of the last day of his life, particularly because there has been misinterpretation of the circumstances of his death.

The Saturday morning was a particularly sunny one scientifically speaking. We had an unusually fruitful discussion, and I especially remember being filled with so many ideas on research that they seemed enough to sustain a year of work. I had some new ideas on triplet-triplet absorption, and Lewis described more of his ideas on photomagnetism which I was then to undertake.

Lewis had a particular experiment he planned to do by himself at the vacuum bench that afternoon. A few days before, he had read in the latest issue of *Transactions of the Faraday Society* a paper which he showed me containing a graph indicating that the dielectric constant of liquid hydrogen cyanide changes hy a factor of over 100 in a certain accessible temperature range. Lewis said, "That would be a very interesting medium in which to test the effect of dielectric constant on the color of dyes!" He planned that experiment for late Saturday afternoon.

Lewis went to lunch with a distinguished guest and returned at 2 p.m. It was unusual for Lewis to go to the Faculty Club on a Saturday. When he returned, he went to his vacuum bench lab, which was at the opposite end of the hall from his office, my laboratory being in between.

I was working on the spectrophotometer in my laboratory. About every 20 minutes or so I walked by to see if everything was all right. Around 4 p.m. when I passed the vacuum bench room on my way downstairs, I glanced in and noticed Lewis missing. I began to step into the lahoratory and got a noticeable whiff of HCN. Stepping back into the hall I saw Lewis' feet just visible behind the bench. I gave out a yell to the lab at the end where I knew Daniel Cubiciotti was probably working, and I ran toward the hood with my nose clamped shut with my left hand. I threw a hrick, which we kept as a weight in the fume hood, through the window. Returning to the hall I noticed the bottle of sodium bicarbonate in the hood, and rushed into the lab again, and covered the liquid on the vacuum bench table with bicarbonate, the active bubbling of which suggested that liquid HCN had just spilled out. Shortly afterwards Cubiciotti and I dragged Lewis into the hall and called for medical help. He had a serious welt in the middle of his forehead, indicating that he had fallen forward and hit

his head on a vacuum bench clamp. Lewis was dead on arrival in the University Hospital, and a medical autopsy indicated clearly that he had died of a heart attack. We concluded that many minutes after he had died, the pressure had built up in the container of liquid HCN, from which the Dewar had been removed, and the vessel dropped to the vacuum bench, spilling the contents.

Lewis' death was a very traumatic experience for me, and because that evening I was previously invited to have dinner with Otto Redlich and bis wife, I tried to cancel the visit. Redlich prevailed, and I owe a great deal to him for the warm, considerate, thoughtful conversation that ensued that evening.

Reception and Verifications of Triplet State Theory

The American Chemical Society had planned a research symposium honoring G. N. Lewis to be held December 30 and 31, 1946, at Northwestern University in Chicago, but his death changed the meeting plans. As his last research student to complete work under his direction, I was invited to present the work on the triplet states of molecules.

My presentation was the first of the meeting, and I was allowed approximately 20 minutes. I knew that a very strong challenge was to be presented by James Franck, hut I had not expected that two hours of rebuttal of our work bad been planned by Franck, followed by Robert Livingston, Eugene Rabinowtich, and Edward Teller. Each demonstrated the impossibility of the Lewis and Kasha triplet state interpretation on the basis of his knowledge, and Teller's detailed mathematical development of the theory of spin-orbital interaction seemed particularly devastating. I report in another place3 more details of this interesting confrontation and of Franck's prior meeting and relationship to Lewis. Robert Mulliken, whom I met at this meeting, tried to defend our thesis. The conference committee seemingly was suspicious of my paper, I now realize, for although my paper (16) was presented first in the program, it appeared last in the published volume!

At the Faraday Society Discussion in 1949 I presented (28) my own new work on intersystem crossing, the radiationless transition leading to triplet excitation, and a kinetic analysis of the rates of radiationless processes with and without spin. James Franck, a medalist at that meeting, was there to oppose the triplet state idea again. Often repeated was the criticism voiced by Radinowitch (1956) (29):

The hypothesis of metastable (triplet) electronic states of organic molecules has been revived by Lewis and Kasha (1944); however, it seems that if the rule which prohibits singlet-triplet transitions does not preclude the formation of the triplet state from the excited singlet state within 10⁻⁷ sec., it is unlikely to delay its transformation into the singlet ground state for as long as several seconds or even minutes.

It is obvious that these critics (which included Franck and Teller) had not considered the implications of intersystem crossing, whose kinetic analysis (28) so clearly indicated an answer to the criticism.

Several spectroscopic elements were provided which finally settled all suspicion concerning the validity of triplet state assignment to organic molecule phosphorescence. The main electronic spectral proof lay in the Z-effect, since atomic number of substituents could be used for proof of spin-orbital perturbation. Learning about the quantum mechanics of spin-orbital interaction from David Bohm in Berkeley in 1948, I was able to show the Z-effect in intersystem crossing (28, 30), and Don McClure immediately afterward was able to show the Z-effect on phosphorescence lifetimes (31). A review (32) of "Spin Intercombinations in Molecules" in 1956 revealed that Terenin still believed that external "paramagnetic perturbations" were essential to induce triplet state emission.

Chronology of Key Discoveries in Triplet State Molecular Spectroscopy

Year	Author(s)	Refer- ence	Research .
1944	Lewis end Kasha	(19)	Phosphorescence assigned as T → \$
1945	Lewis and Kasha	(24)	Singlet-triplet absorption
1949	Lewis, Calvin, Kasha	(26)	Paramagnetism of triplet state
1949	McClure	31)	Z-effect on phosphorescence lifetimes
1950	Kasha	(28)	Z-effect on intersystem crossing Kinetics of radiationless transitions Uniqueness of
	·		emitting states
1952	Kesha	(<i>39</i>)	Environmental Z-effects on triplet states
1958	Hutchison and Mangum	(33)	EPR ebsorption of triplet state (crystals)
1959	van der Waals and de Groot	(34)	EPA absorption of triplet state (glasses)

The difficulties of finding a triplet state EPR signal probably delayed full acceptance of triplet state ideas, but they were finally resolved by the work of Hutchison and Mangum in 1958 (!) (33) and van der Waals and de Groot in 1959 (34). The subject of "Magnetic Properties of Triplet States" was reviewed in 1979 by Pratt (35).

Dellinger and Kasha (36) returned recently to the problem of vibrational potential effects which so dominated discussion before 1944 and concluded that only such large amplitude motions as phenyl ring torsion would be inhibited by rigid glass solvent cages. So all of the early preoccupation with specific glass effects (aside from diffusional quenching) seems to have been unnecessary.

Today triplet state studies of molecules have advanced to highly refined stages, as exemplified in symposia (1967) (37) and research treatises (1969) (38). The key historical steps in the evolution of experiments and interpretetion of triplet states of organic molecules are summarized in the table.

Gitbert Lewis' Research Previews*

Gilbert Lewis' career, rich as it was in permanent contributions to the understanding of physical chemistry, also had a most unorthodox pattern, not noted especially by anyone until now, but one which was typical of Lewis and which had a profound effect on his intellectual fertility and freshness through his whole scientific life. Lewis previewed a research field in print, using his own analysis, sometimes without an exhaustive literature review, before embarking upon research in it. Most scientists think of reviewing a subject in print at the end of a long study and research period. Lewis told me he thought that approach could stifle originality. If a scientist got an absolutely thorough knowledge of the literature before doing research, he was likely to acquire many of the prejudices and mental blocs of his predecessors.

For example, in the beginning of his career he wrote a paper, "Outlines of a New System of Thermodynamic Chemistry" (40) in which the physical thermodynamic laws were applied to physico-chemical problems. This was the origin of Lewis' concepts of activity, activity coefficients, fugacity, partial molal free energy, etc.

Lewis told me that not long after completing his PhD at Harvard, he took a two-year appointment in Manila (as head of the Philippine Bureau of Weights and Measures) 1904-5—a most unorthedox start for a scientific career—so that he could think for hunself. He worked his way through Walther

³ See reference in footnote 2.

Nernst's "Physikalische Chemie" ("correcting all of the mistakes"), hiked his way around the volcanos and countryside of Luzon, and acquired a lifelong taste for Philippine cigars. Lewis then published his chemical thermodynamics overview paper and followed this with about 15 years of research on chemical thermodynamics, culminating in the classic work, "Thermodynamics and the Free Energy of Chemical Substances" (41). Publication of this book marked the essential close of Lewis' researches in chemical thermodynamics; he then turned his attention to other areas. His later works on statistical thermodynamics belong to another period of his work.

Lewis did indeed change research fields abruptly through his career, usually prefacing a research period with his characteristic penetrating research-proposal-overview paper. His later interest in isotopes could have been presaged by his paper, "The Chemistry of the Stars and the Evolution of Radioactive Substances" (42). Starting in 1933 he wrote an extensive series of papers on heavy hydrogen and heavy water, a paper on lithium isotopes, and several papers on neutron physics, culminating in "The Genesis of the Elements" (43).

Lewis' interest in valence theory began with a precocious master's thesis, "The Electron and the Molecule" (Harvard, 1898). I saw a copy of this once in Lewis' office, and I have a clear recollection of its title. I never had the chance to examine it, and it is tantailizing to speculate on what it contained. Lewis' copy of it appears to be lost, and the Harvard Chemistry Library and the Harvard Widener Library have no copy. In Lewis' summary book, "Valence and the Structure of Atoms and Molecules," (44) appear replica pages from Lewis' notebooks of the early 1900's, showing his early thoughts on electron arrangement in atoms and molecules. Lewis continued the development of ideas and nomenclature concerning valence theory, especially the role of electron pairs, octets, odd electron numbers, and diradical configurations in a series of papers, with World War I interruptions, in 1913 (45) and then in 1916-17 (2). At a joint symposium of the American Chemical and Physical Societies and the American Academy of Arts and Sciences in 1917 he threw the challenge to the Bohr atom, showing that it could not explain molecular geometry (46). His chemical intuition set conditions on valency interactions for which only Quantum Mechanics was able to provide the basis.

Other research preview papers by Lewis include his paper on the electronic theory of acids and bases (47), preceding experimental work with Glenn Seaborg on the subject. "The Color of Organic Substances," (48) preceded almost a decade of research on the color and photochemistry of dyes.

Perhaps the atypical case was Lewis' work on heavy water. Lewis had discussed the possibility of heavy water (D₂O) apparently before the actual discovery of deuterium as a proven isotope. Urey used the Rydberg isotope shift in the atomic spectrum of hydrogen to prove that a new isotope of hydrogen (deuterium) existed, after an extensive program to concentrate natural deuterium. Lewis then worked furiously to establish his part of a claim to the discovery of beavy water by doing every conceivable measurement. Finally all of this work was reviewed in a comprehensive summary paper (49) uncharacteristic of Lewis' research previews.

Gilbert Newton Lewis typified the physical chemist of great intuition who was able to conceive of beautifully simple models and concepts to explain complex physical and physico-chemical phenomena. His conceptual contributions have made lasting additions to our knowledge, and his aptness for good nomenclature has enriched our scientific vocabulary, viz., Lewis introduced the term photon for light quantum (50).

Gilbert Lewis once defined physical chemistry as encompassing "everything that is interesting." His own career touched virtually every aspect of science, and in each he left his mark. He is justly regarded as one of the key scientists in American history. It would be a great omission not to record the warmth and intellectual curiosity radiated by Lewis' personality. He epitomized the scientist of unlimited imagination, and the joy of working with him was to experience the life of the mind unhindered by pedestrian concerns.

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A Simple Aid for Teaching the Theory of Atomic Structure

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In the course of both high school and undergraduate college chemistry, students are often puzzled by the theory of atomic structure. In order to help them learn this more easily, we have designed a simple demonstration to show the Pauli exclusion principle, Hund's rule, quantum numbers, electronic energy levels, and electron configurations. The exercise involves hanging valence electrons (represented by pieces of rubber) onto a game board which depicts the energy sequence of a given atom.

Materials

1 wooden plate (60 cm \times 40 cm \times 1 cm)

33 iron nails (1.5 cm in length)

2 rubber tubes of different colors (16 cm × 1 cm), cut these into 1-cm pieces, yielding 16 pieces of each color

7 blank index cards

Set-Up

The game board, or orbital plate, is cut from a piece of wood. It is labeled as indicated in Figure 1, where n is the principal quantum number, s, p, d, and f are the suborbits, and the number in parentheses after the suborbital designation indicates the angular momentum quantum number. The spin quantum number will be designated by using differently colored pieces of rubber tubing which should be cut as described above.

Hammer the nails (which will be used as holders for electrons) into position as noted. Each suborbit should have the number of electron nails that corresponds to the maximum number of electrons that can be held in that suborbit.

Seven index cards should be labeled as shown in Figure 2. These n-value cards will provide the players with standard information about the principal quantum numbers.

The Rules

Remember that the goal of this exercise is to fill out the game board with cards and pieces of tubing so that it provides a visual representation of the electron configuration within the atom. Total the number of electrons within the given atom and compare to the electron totals on the n-value cards. The n-value card with a total that is either less than or equal to the number of electrons in the atom of interest is then chosen and hung onto the upper left nail.

If the number of electrons is equal to the n-value card, you are done. If it is not, determine how many more electrons are present. Take that number of pieces of cut rubber tuhing and hang them, as representatives of valence electrons, on the nails according to the following energy sequence. Use differently colored pieces of tubing to represent electrons with opposite spin. The energy sequence of the suhlevels with the same nvalue is:

ns < (n-2)f < (n-1)d < npif n < 6, then (n-2)f is absent if n < 4, both (n-1)d and (n-2)f are absent

Example: 24Cr

The student would choose the fourth card, because 24 is smaller than the 36 required by the fifth card. There are 18 electrons on the fourth card, thus the remaining six electrons of Cr will distribute themselves in the fourth energy level according to the rules. Rule one

$$ns < (n-2)f < (n-1)d < np$$

translates to

Because 2f does not exist, the aix electrons would be distributed into the lowest available levels; two being placed in the 4s level and the remaining four into the 3d level.

Thus, the configuration of ${}_{24}\text{Cr}$ is shown to be (Ar) $4s^23d^4$ (see Fig. 3). With this the instructor can speak to the special stability of a half-filled sublevel and can show the students that, with 3d sublevels close to those of the 4s sublevel, the effect is large enough to allow "promotion" of a 4s electron to the 3d sublevel, giving Cr five 3d electrons. Thus, the accepted configuration of 24Cr should be shown to be (Ar)4s13d5.

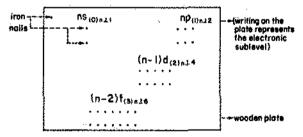


Figure 1. Construction of the game board.



Figure 2. The seven index cards representing the principal quantum num-

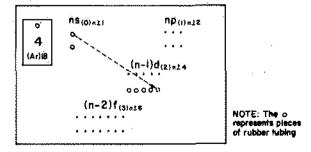


Figure 3. The completed game board for 24Cr.

Photoelectrochemical Solar Cells

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We receive an enormous amount of solar energy from the sun; the solar energy falling on the earth in a fortnight is equivalent to the energy contained in the world's initial supply of fossil fuels (1). Since the 1950's, much attention has been given to the possible use of photoelectrochemical effects to convert solar energy directly into electric power or synthetic fuels, and, as a result of the energy crisis, the study of photoelectrochemical phenomena has become increasingly more popular and important (2). This introduction to photoelectrochemical cells will review topics pertaining to solar energy conversion as well as demonstrate the ease with which a working photoelectrochemical cell can be prepared.

There are numerous ways to convert the solar radiation directly into electric power. The silicon solar cell is the most efficient in this respect, but its use is limited to the more energetic portion of the solar spectrum. Such solid state photovoltaic cells have been quite useful in the space program and now appear promising for terrestrial uses. Endothermic, photochemically driven reactions which produce stable (or isolatable) products (synthetic fuels) are an alternate method of solar energy conversion. Although no economically practical, large-scale photoelectrochemical (PEC) cell has yet been discovered (3), a system of this type could provide a useful source of energy.

A photoelectrochemical effect is defined as the production of a change in electrode potential (on open circuit) or current (on closed circuit) in an electrode/electrolyte system as a direct result of irradiation. The effect is caused by either a photochemical reaction producing electroactive products in the bulk solution or the presence of a photosensitive membrane or electrode. Solar irradiation produces PEC effects on most, if not all, surfaces. PEC effects at clean metal electrodes are very small, usually measured in mV and nA ranges, and are due to such processes as photoelectric emission from the metal surface or thermal effects of the radiation (2). Semiconductors. on the other hand, which may or may not be coated with a sensitizing dye, bave been found to produce pronounced PEC effects. Semiconductors therefore appear to be likely candidates for use in the conversion of light energy into electrical energy. This is reflected in the recent interest in this area (1-5).

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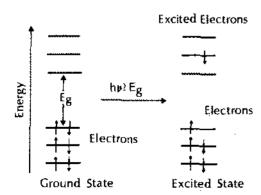


Figure 1. Orbital energy diagrams showing the formation of an excited species when the ground state molecule is irradiated with light of energy greater than the energy gap.

The conversion of light to electrical or chemical energy in PEC cells results from light in the visible region acting as an electron jump (4). The absorption of a photon by an atom (or molecule) results in the pumping of an electron from its ground state orbital to a higher energy orbital. The wavelength of light required for such a transition must have an associated energy greater than or equal to that of the energy difference between the two orbitals. This energy, usually called the energy gap, E_{x_1} is illustrated in Figure 1.

Light absorption within semiconductors occurs in a similar fashion. In semiconductors, the most energetic ground state electrons are located in the valence band and higher energy levels are available in the conduction band. These two energy bands are separated by an energy band gap, $E_{\rm BG}$, in which no electron energy levels are available. Photons with energy greater than $E_{\rm BG}$ are able to stimulate electrons from the valence band to the conduction band. Photon absorption by semiconductors results not only in promotion electrons to the conduction band but also in vacancies or holes in the valence band (left by leaving electrons) as shown in Figure 2.

The result of this process in the production of an electronhole pair (e⁻, h⁺) which may be denoted by the excited state S*. The light may then be stored chemically if S* reacts by one of the two following paths:

$$S^* + A \rightarrow S^+ + A^-$$

 $S^* + D \rightarrow S^- + D^+$

where A and D are suitable acceptor and donor species, respectively. However, unless the back reaction between S^+ and A^- or S^- and D^+ is slow, the energy associated with the pair will be lost almost immediately as heat

$$S^+ + A^- \rightarrow S + A + \Delta$$

If the energy is to be stored in chemical form, either the energy of activation for the back electron transfer must be large thereby retarding this reaction, or the two components of the

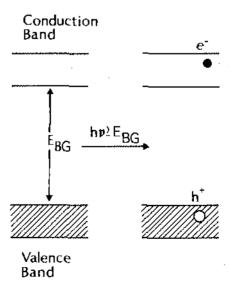


Figure 2. Effects of fight absorption within semiconductors. Electrons are promoted to the conduction band and holes are formed in the valence band.

redox couple must be formed at some distance from each other as in a two-compartment cell. Unfortunately, excited states (electron-hole pairs) are very short-lived and frequently recombine with a total loss of the captured energy into heat. Rapid separation of the electrons from the holes, such as might be promoted by an electrical field, must be achieved in order to use the light efficiently.

Conversion of light energy to the highly desired electrical form has been one of the basic goals of solar energy research. In order to achieve this goal, it is necessary to produce a flow of electrons in an external circuit. Such a condition requires the formation and efficient separation of oppositely charged species (i.e., electrons and holes) which results in charge flow in the external circuit. Semiconductors are ideal candidates for use in such systems due to their ability to separate photogenerated charged species efficiently. A review of some of the basic semiconductor principles may help explain their function in PEC cells.

Intrinsic or undoped semiconductors, like silicon and germanium, are essentially small band gap insulators. Such substances have completely filled valence bands and totally empty conduction bands with bands separated by a few electron volts. A semiconductor such as silicon, a group IVA element, can be doped (impurity added) with a group VA element with one more electron, such as nitrogen, phosphorus, or arsenic, or with a group IIIA element with one less electron such as boron, aluminum, or gallium. The group VA atom with its extra electron fits into the crystalline array of silicon atoms. This extra electron is not required for bonding and is relatively free to migrate through the crystal. This produces an n-type semiconductor where the n denotes negatively charged mobile carriers. Doping silicon with a group HIA element produces a p-type semiconductor containing mobile vacancies as positive holes in the crystal.

Although the doping process retains electrical neutrality, since the dopants are neutral atoms, both mobile and stationary charge carriers are provided. For example, when silicon is doped with nitrogen, an n-type semiconductor results. The extra electron from the nitrogen is relatively free to move throughout the crystal and can participate in charge conductance. Nitrogen, however, also has one extra proton in the nucleus, which when introduced into the silicon array is rigidly bound by the bonding mechanism and cannot participate in charge conduction. Doping of semiconductors results in the production of both stationary and mobile charge carriers; only the mobile carriers can participate in charge conduction. A similar treatment could also be given for p-type semiconductors which have mobile holes and bound negative sites. These charge carriers are responsible for the use of semiconductors in a variety of electrical devices such as diodes, photovoltaic cells, light-emitting diodes (LED), and PEC cells.

When an n-type semiconductor is immersed in a solution, a number of the mohile electrons migrate from the solid surfaces to the solution in order to lower the chemical potential

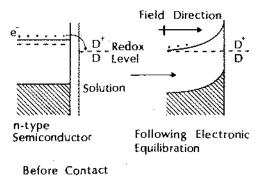


Figure 3. Electron transfer from re-type semiconductor to the solution with redox couple D/D* producing an induced electric field.

of the system. This charge transfer results in a negatively charged liquid surface layer and a positively charged solid surface and an electric field is thus established (Fig. 3).

When light of the proper energy impinges on an n-type semiconductor/liquid interface, electrons are promoted from the valence band to the conduction band of the semiconductor. The induced electric field, shown by the curvature of the bands in Figure 4, drives the photoseparated electrons to the bulk of the semiconductor and the hole to the surface. If the solution contains an electroactive species, D, whose redox potential is above that of h⁺, then electron transfer can occur in the following fashion

$$D + h^+ \rightarrow D^+$$

The excited electron can be transferred away from the bulk semiconductor assisted by the induced field, and if the device is connected by a wire to a second electrode, it is possible for the light-energized electron to reduce a suitable acceptor

$$0 + e^{-} \rightarrow 0^{-}$$

Therefore, the overall process may be summarized by the following equation

$$O + D \xrightarrow{h\nu} O^- + D^+$$

If both O and R were water, the above equation would represent the photolytic decomposition of water

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

The solar spectrum does not possess the required energetics for efficient water splitting, at least not hy a single photon mechanism. However, several other fuel-forming reactions requiring less energy for conversion have been studied (5). Unfortunately, many commercially attractive reactions require too much energy to use the solar spectrum effectively (see table). A band-gap energy equal to 1.1 eV or less is required for the most efficient use of the sun's energy (2). Only the oxidation of $\rm H_2O$ by molecular oxygen approaches this ideality. Although no practical, large-scale system of this type exists at this time, the outlook appears promising.

The basic principles behind the operation of photovoltaic cells is quite similar to that described for semiconductor-liquid interfaces. Both systems require irradiation of a semiconductor junction from which efficient charge separation occurs due to an induced electric field. In the case of the solid state photovoltaic cells, the junction potential is obtained by doping the surface with a foreign material. This process, although quite efficient, is expensive and has limited the use of such devices. Semiconductor-liquid interfacial devices, on the other hand, are prepared quite simply by dipping a semiconductor into a solution containing electroactive species. Their sim-

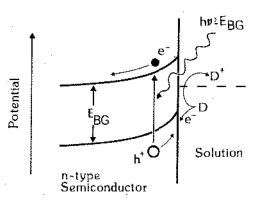


Figure 4. Electron-hole flow upon irradiation of an n-type semiconductor immersed into solution with redox couple D/D⁺.

plicity (and moderate cost) make them attractive candidates for future use in solar energy conversion.

The major hurdle associated with semiconductor-liquid junctions involves the kinetics and energetics of the electron transfer. The semiconductor itself becomes susceptible to oxidation if electron transfer from the donor species is too slow. An example of this type of anodic decomposition is shown for CdS (an n-type semiconductor)

$$CdS \xrightarrow{2h\nu} Cd^{2+}_{(aq)} + S + 2 e^{+}$$

Stabilization may be obtained by adding reducing agents that can scavenge the photogenerated holes at a rate that prevents anodic decomposition. An alternative approach to this problem has been to attach stable electroactive species directly to the surface of semiconductors via surface functional groups. Ferrocene has been used to modify n-type silicon chemically and thereby suppress the growth of SiO_x and bring about a dramatic improvement in the photoanode stability of aqueous solutions (5). In addition, the derivatized silicon is able to oxidize anything oxidizable by ferricenium.

The attachment of visible-light-absorbing dyes to the surface of a semiconductor is another possible solution to the problem of photolytic decomposition. Such a procedure involves sensitizing a larger band gap semiconductor with an absorbing dye. Thus the dye, rather than the semiconductor, is the light absorber and the semiconductor is not susceptible to decomposition. The thickness of the sensitizing layer must be controlled very carefully. Too thick a coating results in the

Typical Photochemical Reactions

R. Raw Materials	eaction Fuel Mixture	Standard Free Energy Change, eV/molecule
H _Z O →	H ₂ + ½ O ₂	2.46
	∩2 T 72 U2	2.40
CO ₂ →	CO + 1/2 O2	2.66
N ₂ + 3 H ₂ O →	$2 \text{ NH}_9 + \frac{3}{2} \text{ O}_2$	3.51
$H_2O + \frac{1}{2}O_2 \xrightarrow{n_F}$	H _Z O ₂	1.24
CO ₂ + 2 H ₂ O →	CH₃OH + ¾2 O2	7.26
CO ₂ + 2 H ₂ O →	CH4 + 2 O2	8.48

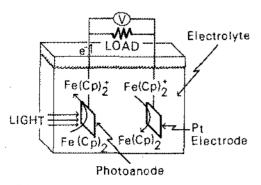


Figure 5. Schematic representation of a photoelectrochemical cell for converting light energy into electricity using n-type silicon as the photoenode and platinum as the reversible counter electrode. Both electrodes are immersed in a ferrocene/ferricenium electrolyte.

insulation of the semiconductor properties and the tendency for back electron transfer increases; too thin a layer results in inadequate absorption. There are several chemical methods available to modify surfaces including chemisorption, covalently binding reactive compounds to surface functionality, and redox polymerization. Carefully controlled experimental conditions must be employed to attain the optimal thickness of the insulating absorbing blanket.

A workable photoelectrochemical cell demonstrating many important aspects of these devices can be prepared quite easily. A stable liquid junction photocell using n-type silicon as the photoanode and platinum as the counter electrode in an ethanol solution of ferrocene can be used to demonstrate the utility of such systems. A schematic diagram of such a system is shown in Figure 5. The functioning of this system is based on the following: Immersion of the n-type silicon in the solution results in charge transfer of the mobile electrons from the silicon to the solution forming a negatively charged surface layer and leaving the semiconductor with a positive surface region. Light of sufficient energy impinging on the negatively charged surface can cause the promotion of an electron from the valence band to the conduction band, leaving a hole where the electron once was. The induced electric field, spontaneously formed at the semiconductor/ liquid interface, forces the promoted electron away from the surface into the bulk and the hole towards the surface. At this point a ferrocene molecule donates an electron to the vacancy and returns to the solution in the form of a ferricenium ion. Meanwhile, the photoseparated electrons pass through an external circuit to the platinum counter electrode and reduce the ferricenium back to ferrocene, as shown in Figure 6.

Experimental

Materials. Single-crystal, n-type silicon wafers (0.25 mm thick, 100 face) doped with Sb and having resistivity of 4–5 Ω cm were donated by Signetics Corporation, Cupertino, CA. Ferrocene and absolute ethanol were used as received from commercial sources.

Electrode and Cell Configuration. Electrical contact to the silicon electrode was made by depositing indium metal on the back side of the semiconductor using a soldering iron. A copper wire was attached to the back with silver epoxy and the whole device was encased in a glass rod. All metallic surfaces were insulated with regular epoxy so only the silicon was exposed to the electrolyte (~ 0.13 cm²). In all experiments a platinum counter electrode was utilized, positioned as close as possible to the silicon photoanode. A one compartment cell with a capacity of approximately 50 cm³ of electrolyte was assembled from Plexiglas®. The electroactive solutions were composed of 0.07 M ferrocene and the amount of ferricenium appropriate for each experiment dissolved in ethanol. Concentrations were determined from optical density measurements (ferrocene: $A_{\text{max}} = 450 \text{ nm}$, $\epsilon_{450} = 90 \text{ l mol}^{-1} \text{ cm}$; ferricenium: $A_{\text{max}} = 618 \text{ nm}$, $\epsilon_{618} = 450 \text{ l mol}^{-1} \text{ cm}$). All electrodes

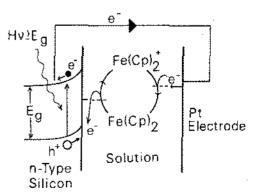


Figure 8. Conversion of light into electrical energy for n-type allicon photosnode immersed in ferrocene/ferricenium (Fe(Cp)₂/Fe(Cp)₂⁺).

were etched in concentrated hydrofluoric acid and rinsed with ethanol immediately before the experiments. A 0.1 M ferricenium sulfate stock solution was prepared by adding 3.3 ml of concentrated sulfuric acid to 1.86 g of ferrocene, then diluting to exactly 100 ml with ethanol.

Experiments. Stability of the silicon photoanodes was determined in ethanol solutions containing 0.07 M ferrocene and 0.001 M ferricenium sulfate. Input light intensities of \sim 25 mW/cm², obtained from a simple spectrophotometer light source and simple lenses, were utilized throughout these experiments. The voltage was measured with a strip chart recorder. Current, in series with the recorder, was measured with a digital multimeter.

Kinetics of SiO₂ formation. A SiO₂ layer spontaneously forms on the surface of the semiconductor. This oxide layer was electrochemically removed from the semiconductor surface by applying a potential difference of 15 V across the photoanode and the platinum electrode immersed in ethanolic ferrocene solutions. With the negative terminal attached to the silicon electrode and the positive to the platinum, gas evolution (presumably hydrogen) from the reduction of water along with SiO2 reduction to silicon was observed at the silicon electrode, and the oxidation of ferrocene to ferricenium was observed at the platinum surface. Upon removal of the applied potential, the open circuit voltage was monitored as a function of time. A decrease in the output voltage, presumably due to oxide formation, was observed in all experiments. The rate of this decrease was used to monitor the kinetics of oxide formation.

The effects of water content on the rate of oxide formation were determined by observing the voltage characteristics after water (5.5 M) was added to the helium-purged ethanolic ferrocene/ferricenium solution. In a similar fashion, the effects of oxygen were determined following an oxygen purge of the ethanolic solution.

Results and Discussion

Most nonoxide semiconductors used in PEC devices are susceptible to photolytic decomposition. In the case of n-type silicon photoanodes, the semiconductor itself can be oxidized if the photogenerated holes are not quenched prior to electrode decomposition (oxide formation)

$$Si + 2 H_2O \rightarrow SiO_2 + 4 e^- + 4 H^+$$

Oxide formation may also be produced by the reaction of silicon with dissolved oxygen

$$Si + O_2 \rightarrow SiO_2$$

 SiO_2 formation has the effect of insulating the surface. As the oxide layer thickens, the photocurrent and voltage levels de-

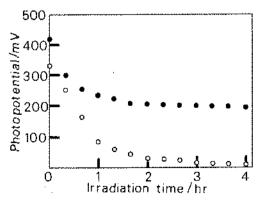


Figure 7. Plots of open circuit photopotential against time for n-type silicon electrode immersed in 0.07 M ferrocene and 0.001 M ferricenium sulfate. For run 1 (•), 0.13 cm² of n-type silicon was kradiated with 25 mW/cm² white light. Run 2 (•) was obtained under dark conditions.

crease significantly. Since rigorous precautions were not taken to eliminate moisture and dissolved oxygen from the system, it was imperative that the oxidation of ferrocene was kinetically favored over oxide formation.

Long-term stability characteristics of the silicon photoanodes was established by irradiating the semiconductor electrode in anhydrous ethanol containing the ferrocene/ferricenium redox couple. Figure 7 shows the electrode potential obtained over the course of several hours. Also shown here for comparison is the electrode potential under dark conditions. Indeed, the ability of ferrocene to capture photogenerated holes preventing SiO₂ formation is quite good as demonstrated by the stability of this device.

 ${
m SiO_2}$ can be removed from the semiconductor surface to restore original activity. This may be accomplished electrochemically or with the use of HF etching. Both methods have proven successful in restoring the efficiency of the system following oxide passivation. The latter method has been used almost exclusively by previous authors, but the former offers insight into the kinetics and energetics of oxide formation. After a negative potential is applied to the photoanode, the efficiency of the device increases significantly. This is most likely due to the reduction of ${
m SiO_2}$ to free silicon

$$SiO_2 + 4 H^+ + 4 e^- \rightarrow Si + 2 H_2O$$

Following reductive treatment of the photoanode, the open circuit voltage decreases exponentially, gradually leveling off at an equilibrium value as the passivating oxide layer reforms.

The results of the three experiments testing effects of oxygen and water on the rate of oxide formation have been summarized in Figure 8. Oxygen content was found to have little effect on the rate of oxide formation, showing photopotential characteristics similar to the O_2/H_2O free reference. Solutions containing water, on the other hand, showed signs of increased oxide formation.

In summary, a PEC cell demonstrating many important aspects of the chemical solar cells can be easily assembled with n-type silicon as the photoanode and a platinum counter electrode, both immersed in ethanolic ferrocene/ferricenium solutions. A system of this type can be used to convert solar power directly into electrical energy for an extended period of time. Unfortunately, such systems are plagued with photolytic decomposition of the photosensitive electrode which limits their efficiency. This is the major scientific hurdle associated with these devices. The sun can contribute greatly to our energy needs if an efficient, inexpensive, workable

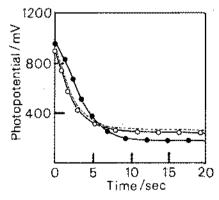


Figure 8. Plots of photopotential against time immediately following electrochemical removal of the oxide layer from the siticon electrode. These plots display the rate at which oxide reforms on the siticon electrodea under various conditions, noted by the decrease in the photopotential as the passivating oxide reforms. Run 1 (O) exhibits the kinetics obtained with a helium-purgad anhydrous electrolyte; run 2 (—), with an anhydrous oxygen-asturated electrolyte; and run 3 (•), with a solution containing 5.5 MH₂O. Each run was performed in ethanoi containing 0.07 M terrocene and 0.001 M terricenium sulfate with incident light intensities of ~25 mW/cm².

system can be devised. The present work suggests that such a system may soon be developed.

Acknowledgment

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Thermodynamic Inefficiency of Conversion of Solar Energy to Work

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It might be thought that photon energy should be pure energy, that is, should have no entropic content, and hence that solar energy should in principle be entirely convertible into useful work. A more conservative guess might be that since solar energy relates to radiation from a 6000 K source. a Carnot efficiency factor of about $((6000 - 298)/6000) \approx 0.95$ might apply. Neither of the preceding statements is correct for a quantum or threshold solar device, but it is true that there is a thermodynamic limitation to the efficiency with which light energy can be converted into work. The limitation depends on the intensity of the radiation and its wavelength and can be substantial.

Chemists practicing in the solar energy field seem generally not to pay much attention to this limitation. Its treatment is not new (1-4), but analyses seem not to have appeared in easily accessible chemical literature. A useful review, however, is by Bolton and co-workers (5). In addition, the various treatments have been couched in terms of black-body radiation fluxes or semi-conductor solar cell analyses, and the language has been more that of physics than of chemistry. In this paper, we present a more chemical and less sophisticated approach.

Einstein Dld Us In

The thermodynamic limitation is usually mingled with another kind of efficiency limitation, and it seems well to separate the two aspects. This other limitation is a consequence of the quantum aspect of nature, as embodied in Einstein's law of photochemical equivalence (6, 7). Light energy comes in quantum packets of value $h\nu$, where h is Planck's constant and ν is the frequency. Photochemistry involves putting a molecule in an excited state of some definite energy E^* above the ground state. (In the case of a semiconductor solar cell, there is a minimum energy E^* of promotion of an electron into the conduction band.) Einstein's law affirms that unless the energy $h\nu$ is at least equal to E^* there can be no absorption of light energy.

Pursuing this last aspect, suppose that we have the photochemical system

$$A \xrightarrow{h\nu} A^* \tag{1}$$

where the electronic excited state A* is to be the source of chemical or electrochemical energy. Nowadays, for example, many inorganic photochemists are exploring the case of

$$\mathrm{Ru}(\mathrm{bpy})_3^{2+} \stackrel{h_F}{\longrightarrow} [\mathrm{Ru}(\mathrm{bpy})_3^{2+}]^* \qquad \Delta G^{\circ}_{208} \simeq E^* = 2.1 \mathrm{V} \qquad (2)$$

where bpy denotes 2,2'-bipyridine, and G° is standard free

energy. The approximation of equating energy and free-energy differences is discussed later in this paper. As we discovered some years ago (8), [Ru(bpy)32+]* is a good reducing agent, good enough to reduce water. The product, Ru(bpy)₃3+, is a good oxidizing agent, good enough to oxidize water. The simple scheme,

$$[Ru(bpy)_3^{2+}]^* + H_3O^+ \rightarrow Ru(bpy)_3^{3+} + \frac{1}{2}H_2 + H_2O$$

 $-\Delta G^{\circ}_{298} = \epsilon^{\circ}_{298} \simeq 0.84V$ (3)

$$Ru(bpy)_3^{3+} + \frac{3}{2}H_2O \rightarrow Ru(bpy)_3^{2+} + \frac{1}{4}O_2 + H_3O^+ -\Delta G^{\circ}_{298} = \epsilon^{\circ}_{298} \simeq 0.03V \quad (4)$$

gives, in combination with eqn. (2), the net reaction

$$\frac{1}{2}H_2O \xrightarrow{h_V} \frac{h_V}{2}H_2 + \frac{1}{4}O_2 \qquad -\Delta G^{\circ}_{298} = \epsilon^{\circ}_{298} \simeq -1.23V$$
 (5)

(the potentials are from ref. (9)). In effect, Ru(bpy)₂²⁺ acts as a catalyst whereby light energy is used to split water. The produced hydrogen could be used as a fuel to run an engine. There are many difficulties with the simple scheme above, but a more complicated version has shown some success (10). The system is cited here merely to illustrate how the energy contained in an excited state may be used to produce useful work. We do not concern ourselves here with the many complexities and inefficiencies of actual conversion schemes. Rather, we are after some basic limitations upon which no scheme can

Returning to the type reaction of eqn. (1), if the transition wore between two specific states, we would see a single sharp line absorption spectrum of A. In this case, only light of frequency corresponding to $h\nu = E^*$ would be absorbed, neglecting line broadening inherent in the uncertainty principle. In practice, however, we are dealing with at least diatomic and usually with polyatomic molecules and the electronic excited state A* will have a different bond length in the diatomic case, and different bond lengths and bond angles in the polyatomic one. Thus, A* will be geometrically distorted relative to the ground state A. The situation is illustrated in Figure 1.

The Franck-Condon principle tells us that no appreciable nuclear motion occurs during the absorption of a light quantum, that is, that the transition is a "vertical" one. The consequence, shown in Figure 1, is that light absorption produces a distribution of vibrationally excited A* molecules. The experimental observation is that the absorption bands are broad, as illustrated for the case of Ru(bpy)32+ in Figure 2. Our energy E^* is now actually that of the transition from the v=0level of A to the v = 0 level of A*, or of the so-called zero-zero transition (where v denotes vibrational quantum number).

This transition is not totally forbidden by the Franck-Condon principle and can, in fact, sometimes be seen as a weak feature on the long wavelength tail of an absorption band. In the case of $\text{Ru}(\text{bpy})_3^{2+}$, E^* is about 50 kcal mole⁻¹, corresponding to a λ^* of 570 nm.

Einstein's law tells us that light of wavelength longer than λ^* will not be absorbed (neglecting the small tail of the absorption band beyond λ^*). Now, however, light of wavelength shorter than λ^* will be absorbed because of the broad nature of the absorption band (for example, 450 nm radiation in the case of Fig. 2). The produced A^* is vibrationally excited, but this vibrational energy is ordinarily very quickly lost to the solvent medium (within picoseconds). We thus end up with non-vibrationally excited, that is, A^* species. Moreover, this is apt to be the situation even if we are populating some higher excited state by using light of yet shorter wavelength (such as light of below 300 nm in the case of Fig. 2). Usually (although not always), crossing from one excited state system to another occurs so that we still end up with A^* .

A further, and important point is that we actually are dealing with a collection of A* molecules in thermal equilib-

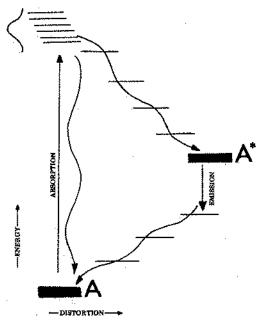


Figure 1. Energy level diagram showing the effect of excited state distortion. Straight arrows represent a radiative process and wavy arrows non-radiative processes.

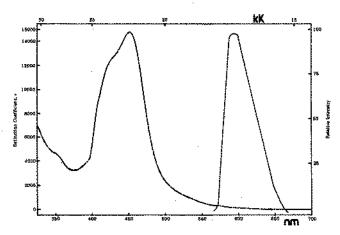


Figure 2. Room temperature absorption (---) and emission (----) spectra of aqueous $Ru(bpy)_3Ci_2$.

rium with their surroundings. This collection is, in effect, a thermodynamic ensemble having entropy and hence free energy as well as energy. This excited state ensemble has been called a thermally equilibrated excited state; we have used the special term thexi state (11). A thexi state is a good chemical species; it is, in effect, an isomer of the ground state. Thexi states, as noted above, have well-defined energy, entropy, and free energy. They have standard oxidation and reduction potentials; they have a definite structure, reaction chemistry, absorption spectrum, etc., all of which may be different from the corresponding ground state properties. One special feature of a thexi state is that it may be able to return to the ground state A by emission of light. This is true for [Ru(bpy)₃²⁺]*, for example, and the emission spectrum is included in Figure

We are now at the point where the limitation imposed by Einstein's law can be examined. The problem is that solar light covers a wide energy spectrum, being essentially black-body radiation. A standard intensity spectrum for light incident on the earth's surface is shown in Figure 3. The situation is that all light of wavelength greater than λ^* is wasted since it cannot be absorbed at all. Because of the typical broadness of absorption bands, we can assume that all light of smaller wavelength can be completely absorbed. However, the energy content in excess of E^* per mole of light quanta is also wasted. This excess energy goes into vibrational excitation of A^* , an excitation which is promptly lost as heat to the surroundings. We will limit ourselves to the case of an isothermal system, so that this heat is unavailable to do useful work.

The above qualitative exposition can be made quantitative in the form of the integral,

$$f_E = \frac{E_0^* \int_0^{\lambda^*} I(\lambda) d\lambda}{\int_0^{\infty} I(\lambda) E(\lambda) d\lambda}$$
 (6)

where $I(\lambda)$ is the intensity of solar radiation in incident quanta per wavelength interval and $E(\lambda)$ is given by hc/λ . The coefficient f_E is the efficiency factor resulting from this working of Einstein's law. This integral has been evaluated as a function of E^* (see Ref. (5), for example). It maximizes at $f_E=0.44$ for λ^* about 1100 nm. (There is a second-order dependence on whether we are talking about the solar spectrum reaching the earth's surface, or that just outside the earth's atmosphere.)

It is probably no coincidence that the chlorophyll of plants absorbs in the red, so that f_E is relatively large. An interesting point is that while f_E is thus made large, light of such long wavelength does not carry enough energy per quantum to do the needed photochemistry. Plants solve the problem by means of a complex chain of molecular events whereby two or more photons are used to provide the energy needed for the

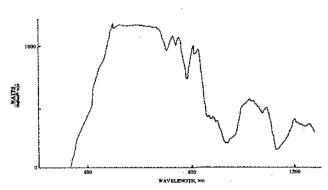


Figure 3. The spectral distribution of solar energy with the sun at 60° from the zenith (12). (The dips in the spectra are due to absorption by various atmospheric and solar atmospheric species.)

reduction of CO₂. Man-contrived chemical solar energy conversion systems, however, are more likely to take the mechanistically simpler route of doing the job with just one photon per primary reaction event. There is a trade-off, however, in that the required photon energy is increased, with a corresponding reduction in f_E . To take the Ru(bpy)₃²⁺ system as an example, λ^* , is now 570 nm, and f_E has dropped to 0.20.¹

The Thermodynamic Limitation

We come now to the additional limitation that is the focus of this paper. Any means of reversible generation of work would do, but for convenience of exposition, let us assume the following. We have the cell

Pt/C(s) Solution of AX concentrations are (A+eq) and (A+eq)
$$\begin{vmatrix} h\nu \\ \text{Solution of AX under} \\ \text{irradiation. Concentrations} \\ \text{are (A+) and (A+*).} \end{vmatrix}$$

We take species A as actually to be a cation, A⁺, so we can be dealing with an electrolyte; the anion, X⁻, is purely a spectator species. C is a one-electron-reduced form of A⁺. We suppose that the couple C(s)/A(solution) is reversible at a Pt electrode, and that the electrode M is such that the couple C(s)/A⁺(solution)/M is reversible while the couple C(s)/A⁺(solution)/M is not, that is, that electrode M is polarized with the respect to the second process.² The dashed vertical line in the cell denotes a liquid junction.

The right-hand solution is under steady irradiation of wavelength λ^* , and is of sufficient concentration that the incident light is completely absorbed by A^+ . The irradiation builds up a concentration of A^{+*} to some value (A^{+*}) and at this point the cell is allowed to operate, drawing just sufficient current to maintain (A^{+*}) at a steady state value. The whole system is at constant temperature and, under the steady state condition, light energy is being converted to useful work.

A potential problem is that A^{+*} can in general disappear by other processes than the cell reaction. A^{+*} can, for example, return to A^+ by light emission or by non-radiative relaxation. These are first order processes with rate constants k_r and k_{nr} , respectively, and the sum, $k = k_r + k_{nr}$, determines the rate at which A^{+*} would ordinarily disappear. The requirement here is that the cell reaction must keep (A^{+*}) small enough that $k(A^{+*})$ is negligible compared with the rate of the photochemical reaction (see Example below).

We want our idealized cell to be one which can operate under steady state conditions. To accomplish this, suppose that essentially all of the current across the liquid junction is carried by $A^{+,3}$ The cell processes per faraday are as follows. The right-hand compartment gains one mole of A^{+} by transference, loses one mole of A^{+} by photoexcitation to A^{+*} , and this mole of A^{+*} is reduced to C(s). The left-hand compartment gains one mole of A^{+} by oxidation of C(s) and loses one mole of A^{+} by transference. There is thus no net change in either compartment.

The net cell reaction is just $A^{+*} = A^+$, and the corresponding emf is

$$\mathcal{E} = \mathcal{E}^{\circ}_{C(s)/A(solution)} - \mathcal{E}^{\circ}_{C(s)/A^{*}(solution)} - \frac{RT}{2} \ln(\alpha_{A^{+}}/\alpha_{A^{+*}}) \quad (7)$$

where a denotes activity. In the left-hand solution A^{+*} is in equilibrium with A^{+} , and for the process $A^{+*}_{eq} = A^{+}_{eq}$, we have

$$\Delta G^{\circ} = G^{\circ}_{A^{+}} - G^{\circ}_{A^{+}} = -RT \ln K, K = a_{A^{+}_{eq}}/a_{A^{+}_{eq}}$$
 (8)

Further, $\Delta G = -\mathcal{F}\mathcal{E}$ and $\Delta G^{\circ} = -\mathcal{F}\mathcal{E}^{\circ}$, and we can replace ΔG° by its equivalent from eqn. (8). We thus obtain

$$w_{\text{rev}} = -\Delta G = RT \ln \frac{a_{\text{A}^{+} = 0} a_{\text{A}^{++}}}{a_{\text{A}^{++} = 0} a_{\text{A}^{+}}}$$
 (9)

where $w_{\rm rev}$ is the reversible work. The activity coefficients of A^{+*} and A^{+*}_{eq} can be taken to be the same (both solutions will be very dilute in A^{+*}), as can those of A⁺_{eq} and A⁺ (the total concentration is the same in the two compartments). eqn. (9) simplifies to

$$w_{\text{rev}} \approx RT \ln[x^*(1-x^*_{\text{eq}})/(1-x^*)x^*_{\text{eq}}]$$
 (10)

where x^* is the fraction present as A^{+*} .

For any system likely to be of interest, x^*_{eq} will be very small, and likewise x^* (see Example below). Equation (10) reduces to

$$w_{\text{rev}} = RT \ln(x^*/x^*_{\text{eq}}) \tag{11}$$

Equation (11) is essentially eqn. (16) of Ref. (5) and eqn. (6) of Ref. (2), obtained by a more general route,

The simple assumption is that the excited state energy, E^* , is entirely available for work, and we now want to compare this amount of work to w_{rev} . We can structure this assumption more specifically as follows. First, we say that A^+ is converted entirely to A^{+*} so that the energy producing process $A^{+*} \rightarrow A^+$ is between species at the same concentration, that is, there is no entropy of dilution difference. We can take the conditions of A^+ and A^{+*} to be their respective standard states. Next, we neglect any internal entropy difference between A^+ and A^{+*} , that is, we take ΔS° to be zero⁴ and equate energy and enthalpy. With these assumptions, $E^* = -\Delta G^\circ$.

The thermodynamic efficiency factor, f_T , can now be written as

$$f_{\rm T} = w_{\rm rev} / -\Delta G^{\circ} = \ln(x^*/x^*_{\rm eq}) / \ln K$$
 (12)

or

$$f_{\rm T} = 1 - \ln(x^*) / \ln(x^*_{\rm eq})$$
 (13)

(We have approximated $a_{A^+eq}/a_{A^{+*}eq}$ by $1/x^*_{eq}$.)

A Numerical Example

We can build an example around the Ru(bpy)₃²⁺ case. We take λ^* to be 570 nm or $E^* = 50$ kcal per mole of light quanta.

³ The condition of near unitary transference number for A⁺ might be achieved, for example, by using a cation exchange membrane to separate the two compartments.

⁴ This could be a dangerous assumption. One might guess that ΔS^o is apt to be negative on the grounds that some bond weakening should occur in the excited state, with concomitant reduction in I_T .

 $^{5}\,\mbox{This amounts to neglecting any partial molal volume difference between <math display="inline">\mbox{A}^{+}$ and \mbox{A}^{+*} .

¹ in reading articles on solar energy conversion, it is well to remember that authors generally do not include f_E in their efficiency statements. Rather, the efficiency reported is that for complete absorption of light of optimum wavelength, or around λ^* . (For example, Graetzel and co-workers report this type of efficiency as \sim 0.1 for their Ru(bpy)₃2+ system (10).) Such an efficiency statement is useful, of course, in evaluating the chemical performance of the particular system; it is misteading, however, in that if the f_E factor were to be included, the practical interest of the system might be greatly diminished.

² Remember that A^{+*} is an isomer of A^{+} which can have quite different properties from those of A^{+} . As an example, A^{+} and A^{+*} might have acidic protons, but the pK_a of A^{+*} might be very different from that of A^{+} , so that in a given solution, the degree of dissociation would be very different. This difference might allow electrode M to be polarized with respection to the reduction of A^{+} but reversible with respect to that of A^{+*} . Such selectivity is a matter of kinetics, and while the condition might be difficult to achieve in practice, it is a thermodynamically permissible one.

If this is taken also to be $-\Delta G^{\circ}$, then 1/K at 25°C is 2.13 \times 10^{-37} . This is also the value of $x*_{eq}$.

The average solar power at noon in the general latitude of the U.S. is about 750 watt m⁻² (12). With $f_E = 0.20$, about 150 watt m-2 might be available to produce [Ru(bpy)32+]*. The molar extinction coefficient of Ru(bpy)32+ is quite large (note Fig. 2), and we can suppose that a layer 1 mm thick of 0.001 M solution will be totally absorbing. One liter of solution will thus cover 1 m² and in this solution (150)/4.184) (50.000) = 7.17×10^{-4} mol sec⁻¹ of [Ru(bpy)₃²⁺]* will be produced.

We can now estimate a practical value of x^* . The rate of production of [Ru(bpy) $_3^{2+}$]*, is 7.17 × 10⁻⁴ mole/liter-sec, and is also to be the rate of its removal in our hypothetical cell. This rate must comfortably exceed the combined rate of the various dissipative processes. That is, we want $7.17 \times 10^{-4} \gg$ $k(A^{+*})$. The minimum value of k is given by $1/\tau$, where τ is the emission lifetime in the absence of specific quenchers or excited state reactants. This lifetime is about 600 nsec at 25°C and in an aqueous medium, giving a minimum k value of 1.67 \times 10⁶ sec⁻¹. Our requirement is that (A^{+*}) \ll (7.17 \times 10⁻⁴)/ (1.67×10^6) or $\ll 4.29 \times 10^{-10}$. We can take $1 \times 10^{-11} M$ as a reasonable maximum value for (A+*), and a corresponding maximum value for x^* of $(1 \times 10^{-11})/(0.001) = 1 \times 10^{-8}$.

Returning to eqn. (13), we obtain

$$f_{2} = (1 - \ln(1 \times 10^{-8})/\ln(2.13 \times 10^{-37})) = 0.78$$
 (14)

There is thus an additional 22% loss of efficiency due essentially to the difference in entropy of dilution of A^{+*}_{eq} and A^{+*} . The efficiency f_T varies with light intensity. If the intensity were reduced one-hundredfold, so that $x^* = 1 \times 10^{-10}$, then $f_T = 0.73$. Conversely, one might think of focusing sunlight so as to increase the intensity. The sun is not a point source, and it turns out that the maximum factor by which the intensity can be so increased is just $1/\omega^2$ where ω is the solid angle subtended by the sun's disk, assuming a perfect f 1 lens. Since ω is about 9.3×10^{-3} , this factor is 1.16×10^{4} , giving a new x^* value of 1.16×10^{-4} . The new f_T now has the fairly respectable value of 0.89. The combined efficiency $f_R f_T$ is 0.16, 0.15, and 0.18 for the three cases.⁷

We might, alternatively, consider a system of smaller E^* value. For example, if we take the λ^* of maximum f_E , or 1100 nm, E^* becomes 26 kcal mole⁻¹. With the same x^* value of 1 \times 10⁻⁸, f_T is now only 0.58. The combined efficiency $f_E f_T$ hecomes 0.26. Thus, the gain in f_E is largely offset by the loss in f_T . Other, more sophisticated analyses, give the maximum $f_E f_T$ value as about 0.34 (5).

Conclusion

The above has been presented as an interesting exercise in an uncommon area of first and second law thermodynamics. The result has also some importance in that it tells us that no single chemical system converting solar energy into useful work, can be very efficient. By contrast, if solar energy is absorbed as heat for heating purposes then it is almost completely used (13). To the extent that we use fuel for heating purposes it should be far more efficient to release that fuel by using solar heating than to replace it by solar energy conversion devicea.

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Division of CHEMICAL EDUCATION

American Chemical Society

Joint Great Lakes/Central Regional ACS Meeting

The Division of Chemical Education has organized a stellar program for the Joint Great Lakes/Central Regional ACS Meeting being held in Kalamazoo, MI, May 23-25, 1984. The following symposia are planned: Coping With CPT Guidelines, Derek A. Davenport, Chair; Using Computers Creatively, John W. Moore, Chair; The Analytical Curriculum, Roland Hirsch and Harry L. Pardue, Co-Chairs; Environmental Update: Problems of the Great Lakes Region, John W. Moore, Chair; Chemistry for Allied Health Sciences, Anne Deckard, Chair. Spirited discussions are expected on incorporation of descriptive inorganic chemistry and computer literacy into the curriculum; how and whether the current analytical chemistry curriculum ought to be changed; the problems of Love Canal, PCBs, dioxin, and hazardous materials; and appropriate courses for those aiming at health-related careers.

In addition there will be a high school chemistry teachers' day with a program on chemical demonstrations appropriate for the high school classroom. Those presenting the demonstrations will be: Glen Dirreen, Douglas Halsted, Doris Kolh, and David Tanis—two college teachers and two high school teachers. The high school symposium will take place the morning of Friday, May 25. All teachers are invited to attend, whether or not they are members of ACS or DivCHED.

For more information about meeting registration, accommodations in Kalamazoo, other divisions' programs, etc., please contact Dr. Lydia E. M. Hines, General Chair, The Upjohn Company 7284-126-6, Kalamazoo, MI 49001, (616) 385-7818.

⁶ White 2.13 X 10⁻³⁷ is unimaginatively small as a laboratory number, it represents a perfectly good alternative thermodynamic statement to that of 1/K.

⁷ A typical nuclear or coal-fired power plant might put out 1000 megawatts of power (for example, one of the San Onofre units in California). At 16% efficiency, the ideal Ru(bpy)32+ device could deliver about 0.16 X 750 or about 100 watt m⁻². For 1000 megawatts, one would need 1 \times 10⁷ m² or 10 km² of 1-mm thick solution, or 1 \times 10⁷ liters of 0.001 M solution, corresponding to about 1 X 104 moles or 7 tons of a salt of the complex. At the current price of about \$10 per gram, this amounts to a cost of \$65 million (assuming that there is that much ruthenium around!)

The Evaluation of Empirical Resonance Energies as Reaction Enthalpies with Particular Reference to Benzene

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The knowledge that the absence of double-bond reactivity in benzene is associated with an enhanced thermochemical stability dates back to the 1890's. Stohmann (1) showed that in the three successive hydrogenation steps wherehy benzene is converted into cyclohexane, and terephthalic acid into hexahydroterephthalic acid, the first step is far less exothermic than the other two, if not endothermic (see Table 1). Furthermore, the second and third steps have reaction heats much more like those for simple acyclic olefins, e.g., ethylene —31.9 and propylene —32.5 kcal mol⁻¹ (1). In later, more accurate experiments, Kistiakowsky et al. found that the first step for benzene was also endothermic (3).

With the advent of valence-bond theory in the 1930's this stabilization was accounted for in terms of quantum mechanical resonance, involving in the main the two equivalent Kekulé structures (4) and an empirical resonance energy of 37.3 kcal mol $^{-1}$ was calculated as the difference between the experimental energy of atomization of behzene and a value calculated using bond energies $E(C_-H)$, $E(C_-C)$, and $E(C_-C)$ derived from thermochemical data for paraffins and olefins (5). To meet the requirement that the single valence bond structure used as reference should be a distorted 1,3,5-cyclohexatriene structure in which all the carbon-carbon bonds are equal in length, 1.39 Å, and not a structure with alternating long single bonds of 1.54 Å and short double bonds of 1.34 Å, a "compressional energy" correction factor was subsequently introduced (6).

The present article deals with the nature of this empirical (i.e., experimental) resonance energy—how its magnitude depends upon the choice of reference molecules from which the bond energies are derived, and how, in fact, it can be evaluated much more simply, without recourse to bond energies, as the enthalpy change for a reaction predetermined by the choice of reference molecules. As a corollary, reference molecules can be chosen so as to minimize contributions to the reaction enthalpy arising from structural changes that have nothing to do with aromatic stabilization. Since reaction enthalpies are phenomenological in nature and not dependent on any theoretical approach, the more general term "stabilization energy" will be used in the later discussion.

A clear distinction can be made between empirical resonance energies and theoretical resonance energies (7) based

Table 1. ΔH° for the Three Successive Hydrogenation Steps, in kcal mol⁻¹ (data (a) from Sichmann (1), (b) from Kieliakowsky et al. (2, 3)).

Molecule	First Step	Second Step	Third Step
Benzene	(a) ~0.8	(a) -25.0	(a)27.8
	(b) + 5.6	(b) -26.7	(b) -28.6
Terephthalic Acid	(a) + 2.8	(a) -28.9	(a) -23.5

on the properties of individual bonds inferred from calculations using, for example, the π -electron approximation, or calculated using model structures with idealized bonding or hypothetical reference structures such as an infinitely large cyclic polyene. Empirical resonance energies can be calculated theoretically simply as the difference between the energies of product and reactant species. Ab initio calculations are well suited for this purpose because all electrons are taken into account.

Stabilization Energies Calculated from Bond Energies

 $\Delta H_{\rm f}^{\, o}$ for the gaseous molecules at 298 K, in kJ mol⁻¹, have been taken from a computer-analyzed revision (8) of thermochemical data (9). However, to maintain continuity with the older literature, the results are reported in kcal mol⁻¹, 1 kcal ≈ 4.184 kJ. All the calculations have been carried out to two decimal places and rounded off to one decimal place. $\Delta H_{\rm a}^{\, o}$ is used to denote enthalpy of atomization, and for a hydrocarbon, $C_m H_n$.

$$\Delta H_a^{\circ}(C_m H_n) = m \Delta H_f^{\circ}(C) + n \Delta H_f^{\circ}(H) - \Delta H_f^{\circ}(C_m H_n)$$
(1)

where $\Delta H_f^{\circ}(C)$ and $\Delta H_f^{\circ}(H)$ are the enthalpies of formation of the carbon atom from graphite and the hydrogen atom from H_2 , 170.9 and 52.1 kcal mol⁻¹, respectively (8).

Following Pauling and Sherman (5) the stabilization energy, SE, for benzene is given by the expression

$$SE = \Delta H_a^{\circ} \text{(benzene)} - 6E(C-H) - 3E(C-C) - 3E(C-C)$$
(2)

E(C-H), E(C-C), and E(C-C), calculated for various sets of reference molecules by the usual procedure, equating ΔH_a^c for each molecule to the appropriate sum of bond energies, are given in Table 2 along with stabilization energies for benzene calculated using eqn. (2). The very wide range of values for SE, from a high of 64.2 to a low of 4.4 kcal mol⁻¹, will be commented on later.

Stabilization Energies Equivalent to Reaction Enthalples

The particular reaction that underlies the calculation of SE from a given set of bond energies can be identified by carrying out the following steps.

- Express ΔH_a° for the paraffin(s) and olefin(s) in terms of E(C—H), E(C—C), and E(C=C), and solve for the bond energies.
- Express ΔH_a° for benzene as the function of bond energies and SE according to eqn. (2).

¹Using the rounded-off bond energies in Table 2, the multiplication factors in eqn. (2) for calculating *SE* lead to round-off errors of 0.1–0.3 kcal mot⁻¹ in some cases.

3) Substitute the bond energies from step 1 in eqn. (2) and collect like terms. SE then appears as a sum and difference of ΔH_a values for benzene, the paraffin(s) and the olefin(s) which is ΔH° for the particular reaction.

The calculations of SE using the bond energies derived from the sets of molecules 1-10 in Table 2 are thus found to be equivalent to ΔH° for reactions 1-10 in Table 3 evaluated directly as the difference between ΔH_f° for the product and reactant species.

The procedure introduced by Kistiakowsky et al. for the calculation of SE, namely taking the difference between ΔH° for the hydrogenation of benzene to cyclohexane and three times ΔH° for the hydrogenation of cyclohexene to cyclohexane, i.e., $-49.8 - 3(-28.6) = 36.0 \text{ kcal mol}^{-1}(3, 10)$, is, in effect, the determination of SE as ΔH° for the reduction of benzene by cyclohexane,

benzene + 2 cyclohexane → 3 cyclohexene

i.e., reaction 7, Table 3.

The Matching of Structural Elements in Reactents and Products

Dewar and Schmeising (11) criticized this procedure on the grounds that there were energy contributions to SE arising from the stabilizing influence of C_{sp^2} — C_{sp^3} bonding in the cyclohexene that was not matched in the benzene and cyclohexane, which would serve to diminish the value, from the ring strain in the cyclohexene, which would serve to enhance the value, and from hyperconjugation effects. To avoid these irrelevant energy contributions, they proposed that the hydrogenation heat of ethylene be taken as reference. This is equivalent to evaluating SE as ΔH° for the reduction of benzene by ethane.

i.e., reaction 3, Table 3. But this reaction also has mismatched bonding. The C_{sp^2} — C_{sp^2} bonds are not matched in the products, nor are the various kinds of C-H bond (12).

Table 2, Values for the Bond Energies E(C-H), E(C-C), and E(C-C) Obtained Using Different Sets of Reference Molecules, and the Corresponding Values of SE for Benzene in kcai mol⁻¹ at 296 K.

Reference Molecules *	E (C—H)⁵	E(C—C) ^b	E(C—C) ^b	SE
1) CH ₄ , CH ₃ CH ₃ , CH ₂ =OH ₂	A/4 = 99,3	C 3A/2 ≠ 76.8	B - A = 140.6	64.2
2) CH ₉ CH ₉ , CH ₃ CH ₂ CH ₉ , CH ₂ CH ₂	C/2 - E/4 = 96.6	3E/2 - 2C = 82.8	B + E - 2C = 143.2	48,4
3) CH ₃ CH ₃ , cyclohexane, CH ₂ ·····CH ₂	C/4 - L/24 = 96.6	L/4 - C/2 = 62.8	B + L/8 - C = 143.3	48.4
4) CH ₄ , CH ₃ CH=CH ₂	A/4 = 99.3	sum ≈ <i>D</i> 3/	4/2 * 224.6	48.1
5) CH ₄ , CH ₃ CH ₃ , (CH ₃) ₂ C=CHCH ₃	A/4 = 99.3	C - 3A/2 = 78.8	$I + 2A - 3C \approx 156.3$	17.0
6) CH ₄ , CH ₃ CH ₃ , (CH ₃) ₂ C==C(CH ₃) ₂	A/4 = 99.3	C 3A/2 == 78.6	J + 3A - 4C = 160.5	4.4
7) [CH ₄], cyclohexane, cyclohexene	A/4 = 99.3	L/6 - A/2 = 81.5	K = 5N/8 = 147.4	35.6
8) [CH ₄], CH ₅ CH ₃ , trans-CH ₃ CH=CHCH ₃	A/4 = 99.3	C - 3A/2 = 76.8	H + A - 2C = 151.5	31.7
9) [CH ₄], CH ₂ —CH ₂ , trans-CH ₂ —CH—CH—CH ₂	A/4 = 99.3	F + A/2 - 2B = 93.1	B - A = 140.8	21.6
10) [CH₄], CH₂—CH₂, 90° CH₂—CH—CH—CH₂	A/4 = 99.3	G + A/2 - 28 = 85.9	B - A = 140.6	43.0

^{*} The reference molecules in square brackets have been added in order to solve the simultaneous equations for the band energies. Their enthalpies of atomization do not, however

Table 3. Various Reactions Whose ΔH° Values, in kcal mol $^{-1}$, at 298 K can be Taken as a Measure of the Stabilization Energy of Benxene, SE, Together with Their Specification as to Whether There is Matching between the C-H, C-C and C-C Structural Elements in Reactants and Products. 4

			CHS	tructurał E	lements		C	⊸CandC≔CSI	ructural Eleme	nts
Reaction	ΔH^{o}	C[4]H ₄	$C[4]H_3$	$C[4]H_2$	C[3]H ₂	C[3]H	C[4]—C[4]	C[4]C[3]	C[3]C[3]	C[3]=C[3
1) benzene + 6CH₄>	64.2 ± 1.7	по	กด		по	по .	no		по	yes
3CH₃CH₃ + 3CH₂CH₂		(24:0)	(0:16)		(0:12)	(6:0)	(0:3)		(3:0)	(3:3)
2) benzene + 9CH₃CH₃ →	46.5 ± 1.8		no	no	no	no	no	• • •	na	yes
$6CH_3CH_2CH_3 + 3CH_2 - CH_2^b$			(54:36)	(0:12)	(0:12)	(6:0)	(9:12)		(3:0)	(3:3)
 benzene + 3CH₃CH₃ → 	48.4 ± 1.2		ПO	กอ	no	กอ	na		no	yes
cyclohexane + 3CH ₂ =CH ₂			(18:0)	(0:12)	(0:12)	(6:0)	(3:6)		(3:0)	(3:3)
4) benzene + 3CH ₄ -+	48.1 ± 0.7	no	no	, , ,	no	no		กด	กด	ye8
3CH₃CH==CH₂		(12:0)	(0:9)		(0:6)	(6:3)		(0:3)	3:0}	(3:3)
5) benzene + 6CH ₂ CH ₃ >	17.0 ± 1.1	nο	по			по.	no	no	no	yes
3CH ₄ + 3(CH ₃) ₂ C—CHCH ₃		(0:12)	(36:27)			(6:3)	(6:0)	(0:9)	(3:0)	(3:3)
6) benzene + 9CH₃CH₃ →	4,4 ± 1,7	no	na			no.	no	no no	no	yes
6CH ₄ + 3(CH ₃) ₂ C==C(CH ₃) ₂		(0:24)	(54:36)	•		(6:0)	(9:0)	(0:12)	(3:0)	(3:3)
7) benzene + 2 cyclohexane>	35.8 ± 0.6	(,		ves		ves	no	no	по	yes
3 cyclohexene ^c	00.0 = 0.0		• • • •	(24;24)		(6:6)	(12:9)	(0:6)	(3:0)	(3:3)
8) benzene + 3CH ₃ CH ₃ >	31.7 ± 0.6		yes			yes	กด	no	no no	ye8
3 trans-CH ₂ CH=CHCH ₃ d	· ·	• • •	(18:18)	• • •	• • • •	(8:6)	(3:0)	(0:6)	(3:0)	(3:3)
9) benzene + 3CH₂≠=CH₂ →	21.6 ± 1.5	. , .			yes	yes	,0.0,	(0.0)	ves	yes
3 trans-CH ₂ CH CH CH ₂	# 1.0 T 1.D	.,.		• • • •	(12:12)	(6:6)	•••	•••	(3:3)	(3:3)
	43.0 ± 3.6									, ,
10) benzene + 3CH ₂ CH ₂	43.0 ± 3.0	• • •	• • •		yes (********	yes	* 1 *	* * *	yes	yes
3 90° CH₂CHCHCH₂					(12:12)	(8:6)			(3:3)	(3:3)

a C[4] and C[3] denote carbon atoms to which four and three other atoms, respectively, are bonded. C[4]H4, C[4]H5, C[4]H5, C[4]H5, and C[3]H denote a carbon-hydrogen bond in product (y) molecules.

benzene +
$$3(n+1)C_nH_{2n+2} \rightarrow 3nC_{n+1}H_{2n+4} + 3CH_2 = CH_2$$
.

CH==CH₂; H, trans-CH₃CH==CHCH₃; I, (CH₃)₂C==CHCH₃; J, (CH₃)₂C==C(CH₃)₂; K, cyclohexene; and L, cyclohexane,

The general equation for this type of reaction is

 $^{^{\}circ}$ Correcting for the ring strain energy associated with cyclohexene, 1.32 kcal mol $^{-1}$ (9), ΔH° becomes 31.9 kcal mol $^{-1}$.

^d With cis-2-butene, which is 1.05 kgal mol⁻¹ less stable (8), ΔH° becomes 34,8 kgal mol⁻¹.

In fact the very wide range of SE values in the tables is due to contributions to the reaction enthalpy arising from structural changes other than those responsible for the aromatic stabilization in the benzene. To trace these changes, the bonding state of the carbon has to be taken into account, C[4]tetrahedral and C[3] trigonal (so there are C[4]—C[4], C[4]—C[3] and C[3]—C[3] single bonds²), as well as the number and kind of nearest neighbor atoms around each kind of carbon. Nearest neighbor bonding can be specified conveniently in terms of the number of bonded hydrogens.

The results of this analysis are set out in Table 3, where it can be seen that the majority of the reactions fall into one of three categories. In reactions 1-6 only the C=C bonds are matched; in reactions 7 and 8 the C-H bonds are also matched; and in reactions 9 and 10 the C-C bonds are matched as well.

Closer examination shows that finer distinctions can be made. Although the mismatch in the C-C bonding is the same in reactions 1 and 2, the mismatch in the C-H bonding is quite different and the SE values differ by 16 kcal mol⁻¹. In reactions 1, 4, 5, 6, in which the ethylene is unsubstituted, mono-, tri- and tetra-methyl substituted, respectively, the mismatch is different in both the C-H and C-C bonding, and at the extremes the SE values differ by 60 kcal mol⁻¹. On the other hand, in reactions 7 and 8, not only is the C-H bonding matched, but the mismatch in the C—C bonding is the same. If ΔH° for reaction 7, which is the reaction that underlies the procedure of Kistiakowsky et al. is corrected for the ring strain energy of the cyclohexene, it becomes 31.9 kcal mol⁻¹, which is identical to the value for reaction 8 within experimental uncertainty. Although in their entirety the structures of the reactants and products in these reactions are very different, this very close agreement is in accord with more recent assignments of bond energy terms which take into account the bonding state of the carbon and the number and kind of nearest neighbor atoms (9, 13, 14), and with corresponding group additivity schemes (15, 16).

In matching the C—C bonding in reaction 9, C[3]—C[3] is identified with the central bond in the planar trans-1,3-butadiene molecule (14). But this amounts to assessing the stabilization in benzene relative to three times whatever the stabilization is in the aliphatic diene. It has been argued, rather convincingly, that the stabilization is quite small, at most only a few kcal mol⁻¹ (17), and recent ab initio calculations strengthen the case (18). There is no way it can be evaluated from thermochemical measurements, because there is no appropriate stable molecule with a C[3]—C[3] bond to serve as reference. An alternative approach is to use the rotomer of 1,3-butadiene in which the H₂C_i-C_{ii}H-plane is twisted 90° with respect to the -C_{iii}H=-C_{iv}H₂ plane as the reference molecule (19). In such a molecule π_x -delocalization energy is absent, but there would be some hyperconjugation exerting a small stabilizing influence (20). A recent study (21) of the torsional potential function, using Raman spectrophotometry and a high-intensity argon-ion laser source, finds the energy of the 90° rotomer relative to the stable planar trans structure to be 7.16 kcal mol⁻¹, which would lead to an SEvalue for benzene of $21.56 + (3 \times 7.16) = 43.0$ kcal mol⁻¹.

At first sight it might seem contradictory that the SE value based on reactions 7 and 8 is less than that using 90° 1,3butadiene in reaction 10, since the elimination of a mismatch in the structural elements might be expected to lower SE. But this is not necessarily so because a mismatch can make either a positive or negative energy contribution to SE depending upon the direction in which the structural change occurs.

All the reactions in Table 3 are of the type called isodesmic. i.e., there are equal numbers of formal single and double bonds between the carbon atoms in reactants and products (22). Reactions 9 and 10 belong to a special subgroup called homodesmotic (23) to emphasize the sameness in the character of the bonding in reactants and products over and above the equality in the number of bonds of each formal type, i.e., there are equal numbers of each kind of carbon-carbon bond—C[4]—C[4], C[4]—C[3], C[3]—C[3] and C[3]-C[3]—and equal numbers of C[4] and C[3] atoms with one, two, and three hydrogen atoms attached. Since homodesmotic reactions minimize energy contributions arising from changes in the bonding state of the carbon and changes in the bonding of the hydrogen they are the reactions of choice for the evaluation of stabilization energies from thermochemical data, e.g., for polycyclic benzenoid hydrocarbons and other cyclic conjugated hydrocarbons (24). Similar reactions, in which nitrogen-carbon bonds are matched according to the bonding state of the nitrogen together with the number of hydrogen atoms attached to each kind of nitrogen atom, can be set up for the evaluation of stabilization energies for aromatic nitrogen heterocycles, e.g., pyridine, pyrrole, and porphine (25). The stabilization of aliphalic acyl compounds

with respect to reference molecules containing C=O and C-X bonds, and compounds of the type

with respect to molecules containing C=O, C-X, and C-Y bonds, can also be treated in the same way.

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²This notation is purely descriptive in nature and in the present context preferable to C_{sp^2} — C_{sp^3} , C_{sp^8} — C_{sp^2} , etc., which can be taken to imply a particular theoretical approach.

a place for chemists

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Analytical Chemistry

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It is important to realize that in the practice of his or her profession the analytical chemist uses a wide variety of experimental procedures. The field of chemistry has traditionally been divided into the major disciplines of analytical, inorganic, organic, physical, and biochemistry. Today, however, there is a large amount of overlap among the various disciplines as seen by job descriptions for chemists in areas such as physical-organic, environmental, analytical, bio-inorganic, organometallic, as well as medicinal, clinical, and polymer chemistry. In view of such a multidisciplinary marketplace, it should be understood that an effort to describe the activities of the analytical chemist is meant only to be suggestive and by no means limiting.

What is Analytical Chemistry?

Analytical chemistry basically deals with the qualitative and quantitative identification, characterization, and measurement of the chemical species present in a sample. The measurement process can range from standard techniques for routine quality control to state-of-the-art techniques used for fundamental studies. However, regardless of the measurements made, the actual experimental determination of a given chemical species is only one aspect of a much more comprehensive analytical procedure which takes into account:

- definition of the problem and the manner in which chemical analysis will be relevant to its solution,
- identification of the appropriate chemical species to be measured,
- 3) collection and preliminary treatment of the sample,
- selection of a suitable measurement technique with respect to species concentration, accuracy, precision, cost and time,
- separation of the desired species if interfering components are present.
- 6) measurement of the concentration of the species
- 7) evaluation of the data, and
- 8) communication of the results.

A closer look at each of these individual operations will provide an idea of the diversity and challenges involved with the problem-solving aspect of analytical chemistry.

The first three of the above operations will often not be under direct control of the analytical chemist, but will be the responsibility of the person, or client, requesting the chemical analysis. This, however, does not mean that these operations can be neglected. The analytical chemist should obtain as much information as possible about the client's problem, the way in which the chemical data are to be used and interpreted, the general composition of the sample, and the manner in

This feature surveys the diversified careers which are available to chemists or which require some chemical training. We are all career consultants to some degree. This feature may supply some new insights as to what is available.

which the sample was collected, stored, and treated. This overall understanding of the problem and the sample is a necessary prerequisite for choosing a measurement process which will provide both the desired information and the required level of reliability in terms of accuracy and preciaion.

Choice of the optimum experimental procedure is a decision for which the analytical chemist is uniquely qualified. The wide variety of problems encountered by the analytical chemist requires the use of methods which range from traditional wet chemistry to modern instrumentation. Compendia of analytical methods provide ideas as to what techniques may be most applicable, but it is up to the analytical chemist to organize creatively the appropriate methods into a procedure which works well for the samples at hand. The method selection and experimental design must be based on previous experience, general knowledge of the chemical reactions involved, the desired accuracy and precision of the data, and the suitability of various instrumental and wet chemistry procedures. In situations where more than one type of procedure is capable of providing the requisite precision and accuracy, the analytical chemist must use cost/benefit considerations in choosing the least expensive way of obtaining the desired information. For example, the benefit associated with an expensive, highly accurate, and very precise quantitative analysis of drinking water for a component which may affect human health is worth the cost, but the henefit of an equally expensive, accurate, and precise analysis for a component which only imparts a slight odor to the water may not justify the cost when a less expensive, less accurate method can provide the required information. Analyses which are more accurate than the situation warrants can be costly and wasteful in both time and resources; while, on the other hand, analyses that lack the necessary accuracy are of little use.

Other factors which enter into the cost/benefit consideration are the time required for a single determination and the total number of determinations to be performed. The overall impact of these two factors is often reflected in the choice between wet chemistry and instrumental procedures. While wet chemistry procedures such as titrations and gravimetric methods offer low cost with good accuracy and precision for high concentrations of selected components, they may be lengthy if many samples are analyzed. Instrumental procedures, on the other hand, are generally more expensive in terms of initial cost, offer lower detection limits with some loss in precision, and require less analysis time per sample, which can make them cost effective for large numbers of samples. The experienced analytical chemist will realize that the proper use of both instrumental and wet chemistry methods complement each other and will make extensive use of both.

Since most samples are really complex mixtures they often require some type of clean-up procedure in order to isolate effectively the component of interest, or analyte, from other components which may interfere in the analysis. In order to avoid time, expense, and possible loss of any analyte due to lengthy isolation procedures the analytical chemist should develop efficient separation schemes. The separation may require the combination of several standard methods into a unique procedure for the matrix of interest. For example, the vanadium content in a new alloy may be critical to its physical properties. While methods for determining vanadium exist, none of them may be suitable for the new alloy. Thus, the analytical chemist would need to develop a procedure which would be suitable for this new matrix.

After the appropriate collection and separation steps have been taken, it is the measurement process used in the laboratory which finally provides data on the analyte concentration. The quality of the experimental data will ultimately depend on the ability of the person performing the measurements. In many cases the data will not be obtained by the analytical chemist, but rather by personnel trained specifically for that purpose. These technical personnel, or analysts, need not be concerned about the overall scope of the problem, but should focus on the quality of data, ensuring that it is acquired with the best possible accuracy and precision inherent to the method. The position of analyst is one frequently filled by bachelor degree chemists, since a general background in chemistry is needed to learn effectively and understand the specific experimental procedures used in any given laboratory. Although the job of analyst is not as involved as that of the analytical chemist, it is very demanding and requires a high degree of proficiency.

After the data have been acquired they must be converted to a form which is relevant to the problem, such as absorbance readings heing converted to the weight percent of analyte present in the original material. For many routine experiments acquisition of the raw data and conversion to meaningful results is automatically carried out by computers, but the fact that a result is calculated to 12 digits does not mean that it is correct. The analytical chemist should have some intuitive, common sense feeling for the quality of the data based on past experiences. Thus, he or she should be able to identify those results which may indicate erroneous procedures. In addition to calculating the final result, it is essential that the analytical chemist calculate the reliability of the result in terms of precision and accuracy. The random errors associated with precision will tend to cancel one another when a large number of measurements are made, but determinate errors such as operator, instrumental, or procedural bias which affect accuracy do not cancel and will offset the experimental results from the true results. By proper use of statistical procedures the analytical chemist can determine the extent of random and determinate errors and consequently design or re-design experimental procedures which maintain the required accuracy and precision. The degree of uncertainty indicated hy the accuracy and precision must also be communicated to the client. This allows the client to arrive at an interpretation of the data which is consistent with the experimental procedures and which also takes into account any limitations associated with the data.

The analytical chemist must oversee a large number of operations in the process of performing a chemical analysis. The task of selecting the best procedure for a given analysis can be compared to selecting the best path through a maze. In selecting a path through a maze, there are many directions in which to proceed and one may encounter many wrong turns and dead ends. The task however becomes much easier if one has an overview of the entire maze and clearly knows in which direction to proceed to find the end. Similarly, for a chemical analysis, there are many procedures which may be used to obtain the desired information, but selection of the best procedure becomes easier when the problem is clearly defined and the requirements for the date well established.

Career Planning

Students interested in analytical chemistry should realize that the discipline is both applied and fundamental in nature. The applied concept uses established procedures to obtain information about a specific problem, while the fundamental concept is concerned with overcoming problems associated with the development of new tools and techniques with which to better investigate the physical and chemical properties of materials. The new knowledge which is obtained as a result of fundamental studies has the potential to improve the applied aspects of the discipline. While the applied studies are generally found in industrial settings and the fundamental studies in academic settings, there are no fixed dividing lines and both applied and fundamental studies are carried out in both settings. Regardless of the setting or the type of work, the analytical chemist will be presented with challenging opportunities to investigate new and interesting areas, to overcome unforeseen technical and chemical difficulties, and to gather original information in response to unique questions. With the rapid development of computer technology, opportunities for analytical chemists promise to be even more exciting and demanding. In a special report on the future of analytical chemistry1, Thomas Isenhour comments on the future of computers in analytical chemistry, "It looks great. The table has been set for a feast of new analytical chemistry."

To prepare for a career as an analytical chemist or an analyst, students should take as much math, chemistry, and physics as possible in high school. At the college level the student should take courses required for a chemistry major, as well as courses in statistics, electronics, and computer science. Courses which deal specifically with analytical chemistry, instrumentation, or separations should be taken if they are not included in the chemistry major requirement. Independent research should be part of the student's program if it is at all possible, because it is through this type of activity that the student learns how to define a problem and to develop a systematic approach for obtaining the data needed to address the problem. While the formal training offered at the undergraduate level cannot turn out students ready to attack every type of problem (and is not intended to), it can provide students with both a sound background of fundamentals on which to base decisions and a confidence in one's ability to gather accurate, reproducible data.

Education at the undergraduate level will, in most cases, be appropriate for a student to seek employment as a technician. For students who wish to seek positions with a broader range of reponsibilities and to develop self-directed research programs it will be necessary to obtain a master's or, preferably, a doctoral degree. Many graduate programs are structured such that the student can proceed directly from the bachelor's degree to the PhD without earning a separate master's degree. In graduate school, the student will generally take courses which have a strong emphasis on analytical methods, such as separations, spectroscopy, electrochemistry, electronics, or solution equilibria, although many other specialized courses are offered. The PhD is a research degree, so that a major portion of the student's activity will be involved with a unique research project under the direction of a professor who serves as the student's mentor during the course of the studies. Students who are thinking about attending graduate school should also be aware that there are a reasonable number of graduate teaching assistantships available which pay stipends.

Upon completion of the PhD the analytical chemist may proceed into a variety of governmental, industrial, or academic positions. An extensive survey of salaries for chemists is given in the July 11, 1983 issue of Chemical and Engineering News.

¹ Isenhour, Thomas, Anal. Chem., 55, 824 (1983).

While the job descriptions will vary greatly, the activities of the analytical chemist most often will involve answering questions which deal with various aspects of the overall analytical procedure outlined at the beginning of the article. To provide the best answer to these questions, the analytical chemist must have a critical attitude toward the techniques and procedures which are used and the results which are obtained.

report of the polymer core course committee

Inclusion of Polymer Topics into Undergraduate Inorganic Chemistry Courses

Inorganic Core Course Committee¹

Inorganic Core Content Related to Polymer Science

Inorganic chemistry core courses typically focus on the relationships of structure and reactivity in compounds of all the elements except catenated carbon (organic chemistry). Included as integral parts of these courses are discussions of polymers and polymeric structures since many inorganic substances lack discrete molecular species and have chemistry inextricably related to their extended structures. Notable examples of these substances would be metals, metal salts, oxides, silicates, nitrides, etc. These and even the more classical inorganic polymers such as siloxanes, boranes, silanes, phosphazenes, polyphosphates, etc. often do not have isolable monomeric units typical of classical organic polymers, so the actual "polymer science" content in the core courses has somewhat different format. Practical applications of polymeric inorganic substances likewise extend beyond the usual purview of polymer chemistry concerns, which are largely organic in nature. It is safe to conclude, nevertheless, that no study of inorganic chemistry is intelligible without an understanding of its intrinsically "polymeric" structural con-

It does seem appropriate that chemistry of the more traditional inorganic polymers be included in the core along with discussions of mechanisms and syntheses of substances capable of forming linear or branched polymers. Additionally, the chemistry of inorganic species that catalyze organic polymerizations or the synthesis of important monomers should be presented. A listing of important inorganic topics of current interest to polymer science would thus reasonably include:

- a) Notable linear and branched polymers: silicones, phosphazenes, polysulfides, (SN)_x, borazenes, polyphosphates, silicates.
- Catalytic systems important to condensation processes of organic monomers: Ziegler catalysts, organolithium reagents, organometallic catalysts, and anchored metal catalysts.

 Polymeric solid state structures: oxides, chlorides, sulfides, carbon (graphite and diamond).

d) Important polymers (but not necessarily in commerce): aluminum hydride/alkoxide, (SO₃)_x, metal alkyls, SbF₅, sulfur, phosphorus.

 e) Concepts useful to the understanding of polymerization reactions; structure and chemistry of organometallics, metal carbonyl chemistry, and olefin complexes.

These topics are, in fact, considered in current inorganic texts in enough length and detail to please polymer scientists. Where only one course of truly inorganic chemistry is in the curriculum it is impossible for it to include of all polymer science concerns. If the structure and reactivity relationships among the elements are faithfully portrayed, however, the interests of polymer scientists, biochemists, biologists, solid state chemists, physical chemists and analysts, engineers, and nuclear scientists, etc. are being well served. When possible, an additional course can provide for study of organometallic chemistry in a depth more suited to polymer science interests

Resource Information and Illustrations

In order to stimulate student interest and emphasize real world relationships of inorganic chemistry and polymer science, it would be extremely valuable to have, for classroom use, samples of actual commercial materials employing inorganic polymers. Some materials like (SN)_x, boron-fiber-reinforced plastic, ferrocene, and polycarborane polymers would be uniquely and compellingly illustrative but are not readily available. Other materials, such as zeolites, silicones, molysulfide, are available at retail stores. The problems and opportunities related to obtaining these types of illustrative materials are considered in another, associated report that was published on page 161 of the February 1984 issue of THIS JOURNAL.

Other information in this section is provided as examples of resource material for students that: (a) helps them to appreciate the relationships of inorganic chemistry and polymer science; (b) illustrates theory and concept; and (c) points to emerging areas of research and application.

Commercial Materials

The relationship of inorganic materials with polymer science extends to auxiliary uses such as fillers, colorants, opacifiers, antistatic agents, preservatives, processing aids, and reinforcing agents. The table is a partial listing of trade and hrand names of inorganic materials utilized in the polymer industry.

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List of Inorganic Compounds Utilized in the Polymer Industry

Trade or Brand Name	Product	Manufacturer
Acrylacon	Fibrous-glass reinforced polymers	Rexall Chemical Company
Albacar	Calcium carbonate filler	Pfizer Corporation
Absibronz	Wetground muscovite mica	Franklin Mineral Prod. Co.
Aisilate	Clays	Freeport Knolin Co.
Atomite Azdel	Calcium carbonate Fibrous-glass reinforced	Thompson, Weinman & Co. Generic
	ABS sheet	
Barden Bondstrand	Kaolin clay Filament wound fiber glass	Huber, J. M., Corp. Ameron Corrosion Control
DO KISH BIKI	reinforced plastic	Div.
Borofil	Boron filaments	Texaco Corporation
Cab-O-Sii	Colloidal silica	Cabot Corporation
Calwhite	Calcium carbonate	Georgia Marble Co.
Camel-Carb	Calcium carbonate	Harry T. Campbell Sons' Corp
Carboloy	Cemented carbides	General Electric Co.
Carbospheres	Hollow carbon spheres	Versar, Inc.
Celite Celramic	Diatomite filler	Johns-Manville Corp.
Dicalite	Glass nodules Diatomaceous earth	Pittsburgh Corning Corp. Dicalite Grefco, inc.
Eccospheres	Hollow glass spheres	Emerson & Cummings, Inc.
EH	Carbon black	Cabot Corporation
Fibergles	Fibrous glass	Owens-Corning Fiberglas Corp.
Firmex	Carbon black	Columbian Carbon Co.
Flakeglas	Glass flakes for reinforcement	Owens-Corning Fiberglass Corp.
Fluorobestos	Asbestos-Teflon composite	Raybestos Manhattan, Inc.
Gema-Sperse	Calcium carbonate	Georgia Marble Co.
Garan	Fibrous-glass roving	Johns-Manville Corporation
Glaskyd	Glass-reinforced alkyd resin	American Cyanamid Co.
Hi-Sit	Amorphous silica	PPG Corporation
Horse Head	Zinc oxide pigments	New Jersey Zinc Co.
Hydrocal Kadox	Gypsum Zinc oxide	U. S. Gypsum Co. New Jersey Zing Company
Kalite	Precipitated calcium	Diamond Alkali Company
Kalmac	Calcium carbonate	Georgia Marble Company
Kaofill	Coating and filler clay	Thiele Kaolin Company
Kosmos	Carbon black	United Carbon Company
Kronos	Titanium dioxide	Kronos Titan
Ludox Micronex	Coltoidal silica Carbon black	du Pont de Nemours & Co. Columbian Carbon Co.
Mitter	Aluminum silkerte filler	American Nephetine Corp.
Mogul	Carbon black	Cabot Corporation
Powminco	Asbestos fibers	Powhatan Mining Co.
Q-Cel	Inorganic hollow microspheres	Philadelphia Quartz Co.
Santocei	Silica serogel fillers	Monsento Co.
Silastic	Silicone materials	Dow Corning Corporation
Silastomer	Silicones	Midland Silicones, Ltd.
Silene States	Calcium silicate	PPG Corporation
Statex States	Carbon black Fiber glass reinforced	Columbian Carbon Co. Dan Industries, Inc.
Styragias	polystyrene	
Surtyn Thermax	lonomer resins Carbon black	du Pont de Nemoura & Co. Commercial Solvents Corp.
Thornet	Graphite filaments	Union Carbide Corporation
Ti-Pure	Titanium dioxide pigments	du Port de nemours & Co.
Titanox	Titanium dioxide pigments	Tilanium Pigment Corp.
Vicron	Fine calcium carbonate	Pfizer Minerals, Pigments & Metals

Anchored Metal Catalysts

One of the most active research areas in chemistry is the study of chemical reagents and catalysts supported on polymers. A majority of these materials can be considered organometallic polymers. A number of "anchored metal" catalysts offer advantages over "nonanchored" catalysts in terms of efficiency, selectivity, and separation.

Homogeneous metal complex catalysts are known which selectively promote useful reactions under mild conditions. Such reactions include hydrocarboxylation, linear oligomerization, cyclooligomerization, hydroformylation, decarboxylation, and hydrogenation. Through attachment of a homogeneous catalyst to a cross-linked polymer, the catalyst is made "heterogeneous" with respect to the specific reaction environment. Many transition metal complexes have been attached to swellable styrene-divinylbenzene resins.

The wider topic of polymer supports in organic synthesis is covered by a continuing column (since vol. 4, 1977) by Charles Pittman in *Polymer News*.

Polymers Modified or Formed by Coordination

Polymers involving coordination at metal sites have been technologically important before recorded history. For instance, the tanning of leather depends on the coordination of metal ions with the proteins which make up the hide. These protein-metal ion complexes resist bacterial attack, wear, and weathering which befall nontanned animal skins. Similarly, metals bound to other natural polymers, including proteins, affect numerous enzymatic and membrane interactions.

Metals can be coordinated with organic ligands to form a polymer or to form a coordination complex within an already formed polymer. The correlation of product structure with property is more comprehendible when the coordination polymer is designed to contain a repeat unit with one metal ion per unit. Even so, there exists a larger number of synthesized coordination polymers for which the exact structure is unknown and probably varies within a single polymer chain

Bailar has listed a number of principles in designing coordination polymers (1-3): (1) little flexibility is imparted by the metal ion in its immediate environment, so the flexibility must arise from the organic moiety; (2) metal ions only stabilize ligands in their immediate vicinity, thus the chelates should be strong and close to the metal atom; (3) thermal, oxidative, and hydrolytic stability are not directly related, thus, polymers must be designed specifically for the properties desired; (4) metal-ligand bonds have enough ionic character to permit them to rearrange more readily than typical "organic bonds," (5) flexibility increases as the covalent nature of the metal-ligand bond increases; (6) coordination number and stereochemistry of the metal ion determines polymer structure (such as square planar, linear, planar, or three-dimensional); (7) complex formation is favored through use of pure reactants in stoichiometric amounts.

Polymers involving coordination can be prepared by a number of routes, the three most common being: (a) preformed metal complexes polymerized through functional groups, where the actual polymer forming step may be a condensation or addition reaction.

(b) coordination of a metal ion by a polymer containing chelating groups,

and (c) polymer formation via coordination reactions which are condensation-type reactions

Condensation polymers of the latter type which involve organometallic halides (or another organometallic moiety of high polarity) and polyfunctional, potentially anionic Lewis bases can be considered extensions of classic organic condensations.

In fact, research in this area was catalyzed by observation that the organometallic halides behave like organic acid chlorides (3, 4).

Polysiloxanes

Lack of strong single bonds between elements other than carbon has limited the interest in catenated inorganic polymers. Linkage between dissimilar atoms is stronger, for example Si—C (58 kcal/mole) and Si—O (89 kcal/mole) bonds are much stronger than Si—Si (30 kcal/mole) bonds, making heteroatom backbone polymers inherently more stable. Important classes of commercial polymers of this type are those with —Si—O— linkages that are the bases of the diverse technologies of glass, cement, and ceramics dating to antiquity, and more recently to polysiloxanes or silicones (a misnomer arising from a ketone formality proposed in Kipping's work of the 1920's).

By reducing functionality of silicon to two by organic substitution, the spontaneous condensation of silanol groups is used to advantage to make a host of commercially attractive silicone polymers:

$$n R_2 SiCl_2 \xrightarrow{n H_2 O} n [R_2 Si(OH)_2] \xrightarrow{-n H_2 O} [R_2 Si_O]_n$$

Capping the hydroxyl end groups with monofunctional groups derived from trialkylchlorosilane or trialkylalkoxysilane stabilizes the polymers, and addition of trifunctional linking groups derived from alkyltrichlorosilane gives cross-linked silicones. Because of the ease of formation of six- and eightmembered rings, there are many "wasted loop" side reactions, but fortunately, cyclic siloxanes may be removed by distillation and reused in the feed.

Silicone oligomers are used as lubricants and antifoaming agents. Bouncing putty is produced when polydimethylsiloxanes with capped ends are heated with boric acid. Silicone oils are prepared in the presence of hexamethyldisiloxane which produces trimethylsiloxyl capped ends. The viscosity of silicone oils is controlled by the ratio of hexamethyldisiloxane to the dimethyldimethoxysilane used.

Since polymerization of alkoxy- or chlorosilanes takes place in the presence of water, one-package systems are used as room temperature curing (vulcanizing) silicone elastomers. Linear silicones may also be cured by free radical reactions. Cross-linking is also promoted by bubbling oxygen through silicone solutions in order to oxidize the alkyl groups and thus form oxygen linkages between chains.

The characteristic resistance of silicones to degradation at elevated temperatures is related to the siloxane backbone. The lubricity and water repellancy are related to the pendant lyophilic alkyl groups which encase the backbone.

Phosphazene or Phosphonitrilic Halide Polymers

Phosphazenes are very important phosphorus-containing inorganic polymers. Three types of polymers based on the phosphazene structure have been developed: linear, cyclolinear, and cross-linked cyclomatrix.

Low glass transition temperatures, $T_{\rm g}$'s, for most polyphosphazenes indicate low barriers to internal rotation and potential for elastomer applications. In fact, theoretical calculations based on a rotational isomeric model assuming localized π -bonding predict the lowest (~100 cal/mole repeating unit) known polymer barrier to rotation for the skeletal bonds for poly(difluorophosphazene) (5).

From a practical point of view polyphosphazenes are usually soft just above the lowest phase transition, so that compression molding of films can be carried out. This suggests that the lower transition of the two first-order transitions usually observed for organo-substituted phosphazenes represents the upper temperature for most useful engineering applications. Polyphosphazenes are described in greater detail in references (6) and (7).

Heterogeneous Polymerization Catalysts

Prior to 1950, the only commercial polymer of ethylene was a highly branched polymer called high-pressure polyethylene (extremely high pressures were used in the polymerization process). A technique for making a linear polyethylene at low pressure was discovered by Karl Ziegler in the early 1950's. Ziegler prepared high-density polyethylene by polymerizing ethylene at low pressure and ambient temperatures using mixtures of triethylaluminum and titanium tetrachloride. Giulio Natta used these complex coordination catalysts, now known as Ziegler-Natta catalysts, to produce crystalline polypropylene and to study stereoregular polymerization of olefins. Because of these remarkable contributions to polymer science, Ziegler and Natta were honored by the Nobel prize in Chemistry in 1963.

In general, a Ziegler-Natta catalyst may be described as a combination of a transition metal compound from groups IV to VIII and an organometallic compound of a metal from groups I to III of the periodic table. It is customary to refer to the transition metal compound such as TiCl₄, as the catalyst, and the organometallic compound, such as diethylaluminum chloride, as the cocatalyst.

Several exchange reactions between catalyst and cocatalyst

take place, and some of the Ti(IV) is reduced to Ti(III). It is customary to use the purple, α or δ forms, rather than the brown, β crystalline form, of TiCl₃ as the catalyst for the production of stereoregular polymers. Both the extent of stereoregularity and the rate of polymerization are increased by the addition of triethylamine. Thus, at least 98% of the isotatic polymer is produced when propylene is polymerized in the presence of triethylamine, γ -titanium(III)chloride, and diethylaluminum chloride.

It is generally agreed that a monomer molecule

is inserted between the titanium atom and the proximal carbon atom in the growing chain, and that this propagation reaction takes place on the catalyst surface at sites activated by the ethyl groups of the cocatalyst. Recent discussions of mechanisms can be found in references (8) and (9).

Most vinyl monomers with Ziegler-Natta catalysts polymerize to give polymers emphasizing the isotactic form. The degree of stereoregulation appears to be dependent on the amount of exposure of the active site; the more exposed the catalytic site, typically, the less is the isotactic fraction in the resulting chains.

The potential versatility is clearly demonstrated in the polymerization of conjugated dienes, such as 1,3-butadiene, where any of the four possible forms—isotactic 1,2; syndiotactic 1,2; trans-1,4; and cis-1,4--can be synthesized in relatively pure form using different Ziegler-Natta catalysis systems.

Stereoregular polymers are also produced utilizing a number of other organometallic and inorganic catalysts including Philips and Alfin catalyst-systems.

Solubility

Many inorganic polymers become soluble only with accompanying degradation (this is particularly true for threedimensional networks such as sand and diamond). Even the ostensibly more tractable organometallic polymers are soluble in fewer solvents and to lesser extents within these solvents than classical organic polymers. While a few are soluble in typical solvents such as toluene and chloroform, most are either insoluble or soluble only in a few select dipolar aprotic solvents and salt-dipolar solvent combinations. Even where solubility appears to have been achieved, actual polymer integrity in solution may be questioned.

The poor solubilities of organometallic polymers are probably due to a combination of related factors including (a) high cohesive (secondary bonding) forces between chains, (b) the highly crystalline microstructure of a number of products, and (c) a peculiar combination of bonding offered by the organometallic polymers—a combination of both nonpolar (organic) and polar contributions. Attempts to achieve better solubility include (a) use of flexible and/or dissymmetric reagents, (b) copolymerization using two metal-, with one nonmetal-containing reactant(s) or one metal-, with two non-metal containing reactants, (c) use of model compounds (monomers) as a predictor of polymer solubility, and (d) addition of a chain terminator to shorten the chain length.

Applicability

Apart from pure science, the interest in polymers which include metal atoms is related to the enormous and varied chemistry of the metals and the technologies that might he developed around them. For instance, polymers with Cp₂M moieties (M = Fe, Ti, Zr, Hf) are reported to be stable to uv radiation; thus, polymers with such groups might impart to outdoor paint better wearability relative to uv degradation. Similarly, polymers incorporating tin would be expected to have antifungal and antibacterial resistance typical of organotin compounds. Certain metal complexes are exquisitely specific catalysts, so metal-containing polymers might afford this specificity along with selective stereoregulation imposed by constraints of the polymer chain.

More recent research with conducting polymer films on silicon, polymetallophthalocyanines, polyacetylene, and (SN), promise a future in lightweight batteries, better solar cells, conducting fibers, etc., as well as a better understanding of the chemical physics of conduction theory. It is not clear just which applications will prove commercially successful, but it is clear that the potential is enormous, in view of the almost limitless variety of metal-containing polymers and the escalating need for specialty materials.

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Appendix: Questions for Inorganic Core Content Closely Related to Polymer Science

- 1. Contrast the structures in (a) HNO3 and (HPO3),; (b) CO2 and $(SiO_2)_x$; (c) BCl₃ and $(BeCl_2)_x$.
- 2. Sketch the structure of each of the following, showing empirical formula.
 - (a) single chain silicate
 - (b) double chain silicate
 - (c) sheat silicate
- 3. SoNo slowly polymerizes without much change in crystallinity. Suggest a reason and explain the interest in the resulting polymer.
- 4. Show structures for diamond and graphite, and explain why graphite is a conductor and diamond is nut.
- 5. With chemical equations describe the synthesis of high polymers of the type (NPR2)x. What is the critical step which allows for high molecular weight (dagree of polymerization)?
- 6. List advantages and disadvantages for the inorganic polymer classes of silicones and phosphazenes, compared to organic polymers.
- 7. Bonding of inorganic polymers is varied. For the following polymers select the single (best) phrase which describes the bonding.

	Polymer	Bonding	Explanations
(a)	$(PNCl_2)_x$		1. Sheet structure with sigma- bonded network reinforced by # bonding.
(b)	$(\mathrm{Me_2Be})_x$		Lewis acid-base bonded backbone
(c)	$(SN)_x$		 Sigma framework enforced by d-p π bonding.
(d)	$(SO_3)_x$		Shared corners, edges, and/or faces of octahedra and tetrahedra.
(e)	PW ₁₂ O ₄₀ 3+		5. Chain structure with one- dimensional metal-like delocalization
(f)	$(BN)_x$		6. Three-centered bonding in bridges

8. (a) Outline a mechanism for Ziegier-Natta polymerization of ethylene, CH2=CH2, by heterogeneous Ti(IH) catalyst.



(b) Why is this type of polymerization significant?

Multiple Choice.

Circle single best answer for:

9. The heating of sulfur is a complex process.

(a) Rings break primarily to form aggregates of S₄ chains.

(b) Rings break to form polymers with radical ends.

(c) Chains break to form Sa rings.

(d) Two of the above are correct.

10. Molybdenum disulfide is a lubricant because it is

 (a) a viscous liquid from below room temperature to elevated temperature.

(b) a solid composed of microspheres when precipitated from solution.

(c) a layer structured solid with weak interplane bonding.

(d) none of the above.

 Oxygen, sulfur, nitrogen, and phosphorus form homo-catenated compounds,

(a) such as ozone, hydrazine, red phosphorus, and dithionite.

(b) such as hydrogen peroxide and pyrophosphates.

(c) such as the various allotropes of nitrogen and phosphorus.

(d) Two of the above are correct.

12. For the transformations

$$L_{3}NiH^{+} + CH_{2} \longrightarrow L_{3}NiH^{+} (2) + L$$

$$L_{3}NiH^{+} + CH_{2} \longrightarrow CH_{2} \longrightarrow L_{3}NiH^{+} (3)$$

$$CH_{2} \longrightarrow CH_{4}$$

$$\longrightarrow L_{3}NiCH_{2}CH_{3}^{+} (4);$$

 $L = PR_3$

- (a) Species (2) and (4) are "16 valence electron" complexes.
- (b) Species (1) and (3) are "16 valence electron" complexes.
- (c) Species (1) and (3) are "18 valeoce electron" complexes.

(d) Two of the above are correct.

 Some solid metal chlorides have discrete molecular units as exemplified by

(a) CdCl₂ and Hg₂Cl₂.

- (b) AlCl₃ and AuCl₃.
 - (c) NaCl and KCl.
 - (d) none of the above.
- 14. Ferrocene, like benzene,

(a) has 6 π electron six-membered rings.

(b) is a colorless liquid.

(c) has aromatic character.

(d) Two of the above are correct.

15. Silicate, borate, or phosphate glasses

(a) unlike organic vitreous materials have sharp melting

 (b) differ structurally in that borate glasses have occasional planar triangular arrays of BO₄ as well as the EO₄ tetrahedra.

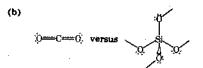
(c) are preparable from giant molecule precursors SiO₂, B₂O₃, and P₂O₃.

(d) cannot be made from melts of basic oxides and the oxides of silicon, boron, or phosphorus.

(Possible) Answers.

1)(a) H-Ö: Ö H-Ö: Ö versus

Nitrogen forms N=O double bonds about as stable as 2 single bonds (good π -orbital energy match) but phosphorus does not. For phosphorus oxyanion acids polymeric structures are possible via P-O-P bridges. Formally, a head-to-tail polymer of the double-bonded monomer results.



Each Si surrounded by 4 oxygens and each oxygen bonded to 2 silicons to form framework (quartz)

Weakness of Si⇒O is obviously a facilitating property.

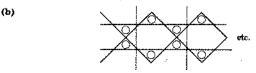
Be, being more electron deficient than B, forms halide bridged polymers.

2)(a) repeat SiO₃²⁻ unit

etc.

pyroxene minerals.

amphibole minerals



repeat Si₄O₁₁⁶ unit

etc.

repeat SiO₁₊₃ = SiO_{2.5}

 Little change in positions of atoms must be responsible for small change in crystallinity during polymerization.

or Si₂O₅²⁻



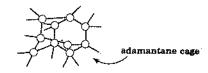
Bond structures difficult to draw because SN unit is "odd" in electron number. π -Molecular orbitals encompassing chain form partly filled conduction bands. Polymer consequently has metal-like conduction and can be considered a one-dimensional metal. It has been used to store electrons in battery systems.

4) Diamond has each carbon tetrahedrally bonded to 4 others. The lattice is the zinc blende structure with C—Zn—S



fcc of carbon with carbon in every other (shaded) smaller cube.

Carbons at face centers and centered in smaller cubes (10 in number) form adamantane cage whose 3-fold axis is coincident with cube diagonal.



Graphite forms bonded layers with little inter-plane bonding. Consequently, graphite is "slippery." Each carbon shares 1 double bond and 2 single bonds with 3 other carbons and is thus $(2+2)/3=1\frac{1}{3}$ bond order. The π orbitals form extensive MO's which are like 2-dimensional metal band structures. Being partly filled (1 π electron per π atomic orbital) the band is conductive

5)
$$NH_4Ci + PCl_5 \xrightarrow{\Delta} (NPCl_2)_{3,4}$$

cyclic structures separated; when highly purified (from cross-linking PCl₅) the trimer thermally polymerizes to

$$N = P$$
 $X \sim 15000$

The linear polymers so obtained are still soluble in organic solvents and a host of substituted polymers are possible, many with physical and chemical properties for practical use.

$$(NPCl_2)_x + Ns^+OR^- \rightarrow NPP_x$$
 $(NPCl_2)_x + NH_2R \xrightarrow{Base} NPP_x$

Strictly organic substituents like Ph or $\overline{\rm CH}_3$ are not accessible from chloropolymer reactions.

Silicones (or polysiloxanes)

and polyphosphazenes,

have strong sigma-bonded backbones (with d-p π bonding in phosphazenes) which impart thermal stability. Hydrophobic organic substituents (R = alkyl, aryl for siloxanes; R = -0-alkyl, -0-aryl, or -NH₂R for phosphazenes) confer a kinetic hydrolytic stability to the polymers. Depending on substituents and crosslinking, polymers range from oils to elastomers.

Phosphazenes are more susceptible to hydrolytic degradation but can be prepared in seemingly limitless classes by substitution reactions on preformed (NPCl₂)X high polymer.

Novel features include a bouncing putty (siloxane polymer) and surgical sutures which hydrolyze to harmless products (phosphazenes with $-NH_2R$ moieties being amino acids).

7) a(3); b(6); c(5); d(2); e(4); f(1)

8) (a)

(b) Polymer grows from Ti site outward leading to strictly linear polymer with high molecular weight and higher stereoregularity than polymers derived by radical initiation. Steric constraints at Ti site require higher olefins to polymerize with stereoregularity (to give isotactic polypropylene, for example).

institute for High School Chemistry Teachers

An Institute for High School Chemistry Teachers will be held July 6–16, 1984 at San Jose State University, San Jose, California. The purpose of the Institute is to provide background in theory through lectures by Ronald Ragsdale, University of Utah; Arthur Campbell, Harvey Mudd College; and George Pimentel, University of California at Berkeley. Special sessions are planned for teachers of advanced placement courses and for beginning teachers. Laboratory experiments, demonstrations, computer workshops, and model building will also be included in the program. Two college credits will be given for successful completion of the Institute.

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Discovering Watson's Crick in High School Chemistry

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The first two weeks of school present a unique blend of the good and the bad, which makes the beginning of school a time of considerable adjustment for both teachers and students. Though many students possess a vibrancy and an eagerness to learn that may well be missing by November, their attention spans have been adjusted over the summer to expect a commercial break every seven minutes. In addition, late arrivals, transfers, and student schedule changes serve to undercut attempts by the teacher to achieve classroom continuity early in the school year. To accommodate these inherent idiosyncrasies best and still to achieve academic progress, I have begun each of the past three school years by assigning to my first year chemistry students "The Double Helix" by James Watson, a very readable account of the events leading to the discovery of the structure of DNA by Watson and Francis Crick

During the first two weeks, I tentatively allocate half of each class period to discussion of "The Double Helix," but I let class interest dictate. Some days the entire hour is consumed by such discussion, while on other days ten minutes will suffice. Regardless of the time spent, dividing the hour hetween text material and "The Double Helix" guarantees a break in discussion. Thus, the students are not forced early in the year to concentrate on one topic for a full hour. In addition, allotting substantial time to "The Double Helix," allows me to establish an academic atmosphere and to reintroduce my students to the discipline of study, without covering so much "fundamental" material that late arrivals will be hopelessly lost only two weeks into the school year. However, the true value of the book is in its content, not just in its ability to buffer the nuisances associated with beginning a new term.

Watson's narrative is illuminating and direct, and students rapidly develop a feel for the human side of science. Reading about Watson, Crick, Pauling, and the others who figure into the account, students come to realize that chemical knowledge is a product of real people with real feelings and real hang-ups as the book removes the shroud of mysticism that the uninitiated sometimes associate with genius. One quickly comes to appreciate the role of the individual and the relations between individuals in striving for scientific achievement.

The reading assignments coincide with start-of-the-year lectures intended to develop an understanding of the scientific method, and the lectures and reading complement one another well. Students find it exciting to follow Watson and Crick as they collect background information, develop hypotheses, test the hypotheses, and formulate new hypotheses. Mapping their progress awakens the students to the fact that scientific achievements are the cumulative results of the contributions and errors of a large number of individuals. To view the blunders, as well as the achievements, is particularly enlightening.

I refer to the book repeatedly during the remainder of the school year. If students are to understand the flow of Watson and Crick's investigations, it is necessary to discuss X-ray diffraction, hydrogen bonding, crystallography, macromolecules, molecular geometry, and acids and bases. Obviously, during the first two weeks of the school year only the most superficial explanations can be made, but when we broach

these topics later, I see the lights come on when reference is made to our earlier discussions of "The Double Helix."

I have found it necessary to conclude our study of "The Double Helix" with a short quiz, in order to present just rewards to those who have pursued the book in earnest, as well as to those who have fallen along the way. I have real misgivings about quizzing my students over factual material from the book, for it is not the facts which make it valuable; however, some students will not invest their time unless they perceive a material benefit for doing so. This is the nature of the beast, and I am certain that the threat of the quiz encourages a number of students to read the book who otherwise would not.

Two or three days prior to the quiz the students are given a list of main characters and a set of questions that are to be asked about the one specific character on the quiz. The identity of the character remains secret, until the name is pulled from a hat just before the students begin the quiz. The quiz is open book, and while the students may not mark in the books, they may use blank bookmarks. The questions asked about the character are

- 1) place of employment,
- one area of scientific expertise,
- one major scientific achievement,
- 4) one distinctive personality trait,
- one error made which hurt his/her chaoces for discovering the structure of DNA, and
- 6) the character's reaction to Watson and Crick's success.

In addition to an answer, the students are asked to cite the pages in the text from which their answers come. The inclusion of the citation insures that the students must become familiar with the book, rather than rely upon their recall of class discussions; and to prepare answers for each of the main characters, the students must understand the book's content.

Each year, as I have read and reread the book and have developed background material, "The Double Helix" has become an increasingly important part of my curriculum. For background information, I recommend volumes 159 and 160 of Science, which contain original reviews, as well as comments of some of the principal characters discussed in the book. Below are some of my student objectives and some sample discussion questions.

After reading "The Double Helix" students should:

- know the steps of the scientific method of research and how they are utilized in the book,
- be aware of the individual differences among ecientists, and how their approaches to the same problem may differ, and
- be aware of the strong influence personalities and politics have on scientific achievement.

Sample questions include:

- Chapters 1-3. What role do personalities and politics play in science? Be able to support your answer with examples from the book.
- Chapters 4-6, What is the difference between inductive and deductive reasoning? Consult a dictionary.
- 3) Chapters 22-25. What was most surprising about Pauling's error? What were Watson and Crick able to determine from Franklin's work that Franklin did not know? How would you characterize Watson's thinking at this point? Organized? Productive? What was Watson's new hypothesis?

¹ Watson, James B., "The Double Helix," New American Library, New York.

textbook forum

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Who is Anti-Markovnikov?

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A common reaction in organic chemistry which is of wide commercial and academic interest is the addition of free radicals to olefins. Naturally all organic chemistry textbooks describe these reactions, and the majority discuss the factors which control the rate and orientation of addition of radicals to unsymmetric olefins. Unfortunately the great majority of textbooks give interpretations which are derived from explanations of the rate and orientation of heterolytic addition to similar olefins. Such analogies are extremely precarious, and they have undoubtedly led to much misunderstanding. The factors which control free radical addition reactions are complex, but this cannot be used as a justification for perpetrating incorrect ideas.

Chemists are usually fairly quick to accept new ideas and are willing to adjust the structure of the subject to accommodate new knowledge. Occasionally, however, new factors are ignored if they appear to challenge accepted belief, in the hope that further work will prove the "new facts" wrong. This phenomenon occurs either when a really major breakthrough is achieved which involves a substantial change in existing outlook, or when the point in question affects a fairly small area of knowledge and the existing incorrect interpretations give predictions which are qualitatively correct in many common cases. It is the latter type problem we are concerned with in this article.¹

The question we are going to consider is: "What are the factors which control the rate and orientation of free radical addition to alkenes?" The addition of alkyl radicals to olefins is usually an exothermic reaction, irreversible at normal temperatures. Addition of atoms (e.g., halogena) or some hetero-radicals (e.g., HS-, CF₃S-, etc.) is often reversible. This article is based primarily on results involving the behavior of alkyl radicals. The arguments to be developed, however, undoubtedly apply to the addition of atoms and hetero-radicals to olefins, though experimental verification is difficult because of the kinetic complications associated with reversible processes.

The problem was first confronted when it was established that the orientation of addition of hydrogen bromide to unsymmetric olefins differed according to the experimental conditions. In the presence of ultraviolet light or in the presence of peroxides the normal orientation of addition was reversed.

UV light or peroxides RCH₂CH₂Br Anti-Markovnikov It was suggested almost simultaneously by Kharasch in America and independently by Hey and Waters in Britain that this reversal of addition was due to a change in mechanism, the normal Markovnikov addition involving ions and the anti-Markovnikov addition involving atoms and radicals.

This occurred at the end of the 1930's, that is, at a time when the electronic theory was having an enormous impact on organic chemistry, and it was natural to invoke similar ideas to explain both ionic and radical mechanisms. Thus ionic addition was believed to yield the intermediate carbonium ion in which the charge was the most delocalized, so similarly radical addition was assumed to yield the initial adduct radical in which the unpaired spin was the most delocalized. This was long before the contribution steric compression makes to bond strengths was fully appreciated.² At that time the relative weakness of a tertiary carbon-hydrogen bond was attributed exclusively to resonance stabilization through hyperconjugation in the incipient tertiary radical. However, even at that time the "resonance explanation" of anti-Markovnikov addition to vinyl chloride was unsatisfactory.

$$: \ddot{\mathbb{C}} \stackrel{H^0}{\longrightarrow} : \ddot{$$

The resonance stabilization of the intermediate carbonium ion is reasonable; we have plenty of evidence that chlorine can act as a donor when attached to a site of high electron demand. In contrast, the corresponding resonance structure for the 2-bromo-1-chloro-ethyl radical is unimportant; it requires the donation of an electron from electronegative chlorine to neutral carbon, and it results in the formation of a dipole. The contribution such a structure can make to the ground state of the 2-bromo-1-chloro-ethyl radical is small. Finally since radical addition is usually a very fast exothermic reaction it would be expected to have an "early transition state," and therefore resonance stabilization of the adduct radical would be unlikely to be a major controlling factor.

The importance of other factors, expecially steric effects was clearly discussed by Mayo and Walling in their seminal review (2). However, the analogy with ionic addition proved too strong and emphasis on "resonance stabilization of the adduct radical" continued to be the popular textbook explanation of the orientation of radical addition.

More than 15 years ago it was discovered that trichloromethyl radicals preferentially attacked the unsubstituted end of vinyl fluoride because attack at the substituted end was retarded (3). Since then this has been established to be quite generally true and similar data is available for vinyl chloride, propene, 3,8,3-trifluoropropene, acrylonitrile, methylvinyl ketone, etc. (4). (At 164°C the rate of addition of trifluoromethyl radicals to the unsubstituted ends of these olefins varies by little more than a factor of two although the rate of addition to the substituted ends varies by several powers of ten.) Radicals attack the unsubstituted end of mono-substituted olefins preferentially, bocause attack at the substituted end is retarded by the substituent. One cannot emphasize too

¹ The present article is based on conclusions derived from fifteen years research aided by numerous collaborators of whose contributions that of J. C. Walton was predominant.

² The importance of steric effects in Free Radical reactions was emphasized by Rüchardt ten years ago (1).

strongly that orientation data by itself without kinetic data cannot be used to elucidate mechanism. The fact that a methyl radical adds to the -CH2 end of vinyl fluoride five times faster than it adds to the --CHF end could be because attack is enhanced at the $-CH_2$ end or because it is retarded at the -CHFend. Kinetic results show that the methyl radical adds to the -CH₂ end of vinyl fluoride at almost exactly the same rate it adds to one end of ethylene. In other words attack occurs preferentially at the -CH2 end of vinyl fluoride because addition to the -CHF end is retarded at this site by the fluorine atom, i.e., the activation energy is greater for addition to the -CHF site. Kinetic data for a wide range of radicals shows that in all the monosubstituted ethenes studied so far, attack occurs preferentially at the unsubstituted end of the molecule, mainly because the substituent inhibits attack at the site to which it is attached. Substituents with π orbitals of the correct symmetry (e.g., CH_2 = CH_- ; $-C_6H_5$, etc.) do accelerate attack at the unsubstituted end, but even here the very large orientation ratios are due more to lack of attack at the substituted end than acceleration of attack at the -CH2 end of the molecule. Similarly vinyl substituents with nonbonding pairs (e.g., F-, Cl-, -CH₃O) have a very small resonance stabilizing effect, which can be completely swamped by the resultant polarity (see above). In ionic addition, cations (especially the proton) add to the unsubstituted ends of propene (CH3CH=CH2) and vinyl fluoride (FCH=CH2) but to the substituted ends of 1,1,1-trifluoropropene (CF₃CH=CH₂) and methylacylate (MeOCOCH=CH₂). In radical reactions the radical invariably adds preferentially to the unsubstituted end of these olefins and kinetic studies confirm that this is attributable to greater activation energies for addition to the substituted

Experiment shows that steric effects are of major importance in determining the orientation of radical addition. Although most radical additions are exothermic the approach of the radical to an olefin carbon atom in the transition state is sufficiently close for the increasing steric compression (i.e., mutual repulsion between the nuclei, their bonding electrons, and adjacent atoms) to be important. It will be expected that bulky radicals are particularly discriminating. Thus, at 164°C trichloromethyl radicals add at approximately the same rate to the -CF2 end of CF2-CHF and CF2-CHCl, but attack the -CHF end of the former olefin approximately 85 times faster than the -CHCl end of the latter olefin.3

$$CCl_{3}CF_{2}CHF + CF_{2}CHFCCl_{3}$$

$$22\% 78\%$$

$$CHX + CCl_{3} \cdot (164^{\circ}C)$$

$$CCl_{3}CF_{2}CHCl + CF_{2}CHClCcl_{3}$$

$$96\% 4\%$$

Fluorine and chlorine have similar electronic properties (i.e., both are electron-attracting donors), but their size is very different. The importance of the size of the radical is well illustrated by the orientation of addition of perfluoroalkyl radicals to vinvl fluoride (cf. Table 1). Notice that although the orientation ratio $\alpha:\beta$ varies 200-fold, the relative rate of addition to the α site and to ethylene varies by less than a factor of two.

Although steric factors are predominant, polarity does influence the rate of reaction (cf. Table 2). Table 2 clearly shows that fluorine atoms in the olefin enhance the rate of addition of methyl radicals, which therefore behave like "nucleophiles," while the same fluorine atoms retard the addition of trifluoromethyl radicals, which behave like "electrophiles."

Steric effects normally overrule polarity in determining the

orientation of addition (cf. the orientation of methyl and trifluoromethyl radicals to vinyl fluoride).

However, in a polysubstituted olefin, steric effects and polarity can be in opposition such that polarity has a decisive effect, i.e., under these circumstances different radicals may add preferentially to different ends of the same olefin.

$$\begin{array}{c} 32\% \text{ CH}_3\text{CHFCF}_2 \\ 68\% \text{ CHFCF}_2\text{CH}_3 \end{array} \xrightarrow{\text{CH}_3} \begin{array}{c} \text{CHF} \longrightarrow \text{CF}_2 \\ \text{164°C} \end{array} \xrightarrow{\text{CF}_3\text{CHFCF}_2 \text{ 95\%}} \\ \text{CHFCF}_2\text{CF}_3 \quad 5\% \end{array}$$

We thus conclude that the rate and orientation of radical addition to olefins is controlled by an interplay of steric and polar effects, while delocalization of the unpaired electron in the adduct radical is only a major factor in special cases such as radical addition to conjugated olefins (e.g., styrene, butadiene, etc.). It is possible to develop some qualitative rules (e.g., in monosubstituted ethenes addition is always preferred at the unsubstituted end), but in alkenes substituted at both ends no single criteria is adequate, and, as we have seen, different radicals may add preferentially at opposite ends.8

These results also illustrate another characteristic of radical additions. When two radicals are compared the more reactive radical is often the more selective. This is quite general for alkyl and fluoroalkyl radicals and represents a direct contradiction of the Reactivity-Selectivity Principle, which implies a decrease in selectivity with increasing reactivity. The reason for this breakdown of the Reactivity-Selectivity Principle when CH3 and CF3 are compared is that the more reactive radical (e.g., CF₃) is also that which leads to the more polar transition state (7).

Radical addition is a very important process by which many polymers are prepared. Mistakenly, it is usually introduced in textbooks as an exception (i.e., anti-Markovnikov addition of HBr), and the explanation usually given is almost always misleading and sometimes wrong. Unfortunately, the true picture is more complicated than the various single alternatives, but nature does not organize herself for our benefit.

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Table 1. Orientation and Relative Rate of the Addition of Perfluoroalkyl Radicals to Vinyl Fluoride CHy CHF (160°C gas phase) (from ref. (3))

Radical	CF3	CF₃CF₂·	(CF ₃) ₂ CF-	(CF ₃) ₃ C-
α:β	1:0.1	1:0.06	1:0.02	1:0.005
2ka/ke	0.5	0.6	0.5	0.5

 $k_{\rm e} = {
m rate}$ constants for addition to ethylene

Table 2. The Ratios of Addition to Tetraffuoroethylene and Ethylene by Methyl and the Fluoromethyl Radicals, (164°C gas phase) (from ref. (3))

Radical	CH ₀ .	FCH _{2*}	F ₂ CH-	F₃C-
KozF4/KozH4	9.5	3.4	7.1	0.1

³ Rules for determining the rate and preferred orientation of radical addition have been given in ref. (θ a) and in greater detail in ref.(θ b).

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Goals

Why Teach Organic Chemistry

Medical schools suggest that calculus and organic chemistry distinguish students who have analytical abilities from those who have cluttered minds. Analytical ability is one quality the medical schools look for in prospective candidates. After teaching organic chemistry at several levels for 42 years I would not quarrel with this view. However, I do doubt whether learning to think analytically in one field transfers to another situation. For example, I can think of more than one famous chemist whose views on political questions were completely prejudiced and unreasoned. In the history of chemistry there are examples of scientists who clung to theories long after evidence was overwhelming against them.

This does not discourage me, however, as I look elsewhere for reasons to learn some organic chemistry. Today a citizen cannot read a newspaper intelligently without some knowledge of organic chemistry. Certainly advertisements for aspirin can be read more critically if one knows that aspirin is a single pure substance. How then, can one brand of aspirin be better than another? Of course one company may have better safety precautions for testing than another, but that is a matter of trust in proceedings, not a property of a substance, and generally not the point of the advertisement.

In the last few years I have taught principally pre-medical students. I have had conversations with former students now practicing medicine who are proud to tell me that they have not used organic chemistry since they left my class. I know that this cannot be true, because what I have tried to leave with them after they have forgotten the mechanism of the Cannizzaro reaction, the utility of a Grignard reagent, and the structure of glucose include the following.

- 1) Some feeling for the limitations of the measurements they get from laboratory technicians. In particular, doctors need to be aware of the limitations of instruments, as, for example, in determining the amount of sugar in a urine sample.
- 2) The use of tracers (D, T, ¹⁸O, ¹³C, ¹⁵N, and others) in following the pathway of a chemical reaction. Such tracers may be used in medicine to follow the pathway of a drug in the body.
- 3) Some appreciation that proteins, carbohydrates, and fats as well as amygdalin (laetrile), ascorbic acid, dioxin, nylon, and cocaine are chemicals.
- 4) Some notion of the problems they may encounter in practicing medicine. A doctor I met in India who had practiced 11 years in this country before returning to his native land said, "The most trying problem I face day-to-day is telling a patient that he could cure his illness by eating better food when I know he can't afford it." What should he say to his patients? Where hetter to think about ethical problems than

The Place of Organic Chemistry in the High School Curriculum

At Detroit Country Day School, approximately one-third of the course time in second-year chemistry is spent on the study of organic chemistry. This is rather unusual because most high school courses tend to concentrate on the physical or descriptive side of inorganic chemistry. If organic chemistry is mentioned at all, it is usually in a brief survey of simple functional groups with a mention of combustion, addition, and esterification reactions. This amounts to a memory exercise and provides the student with no depth of understanding of the molecular interactions so vital to the nature of chemistry. These problems are noted in a recent paper dealing with the inclusion of organic chemistry in the CHEM Study program. The many reasons for our focus on organic chemistry are elaborated upon in the following paragraphs.

Students enjoy organic partly because it is a break from the constant emphasis on the quantitative nature of chemistry. There is an underlying beauty in organic reactions stemming from the predictability afforded by our detailed understanding of reaction mechanisms. This provides an exciting challenge to students and truly tests their understanding of the material. Because natural and man-made products of organic reactions are so common and important in all aspects of life, students take a different view of chemistry and chemists. They come to see that chemists are not people who merely solve problems on their calculators but that they also are involved with exciting synthetic procedures and interesting laboratory experiences.

Our first-year course is a comprehensive one which covers most of the traditional topics: atomic structure, bonding, gases, solution chemistry, thermodynamics, kinetics, equilibria (including acid/base chemistry and solubility), oxidation-reduction reactions, and electrochemistry. Beginning in the fall of the second year, organic chemistry is introduced. One very important reason for this is to review, in a new context, many of the major concepts taught previously. Students need a thorough review of the introductory course (especially if a year has elapsed since their first exposure) in order to place these topics in the proper perspective. Rather than repeating the same examples, reinforcement of important principles comes from using organic chemistry.

The course begins with a discussion of bonding and hybridization, using carbon compounds as examples. Emphasis is placed on the stereochemistry of these compounds, and both structural and stereoisomerism are introduced. Nomenclature and the reactions of various functional groups are then discussed. Oxidation of alcohols provides a review of halancing

About the Authors

Leallyn B. Clapp is Emeritus Newport Rogers Professor of Chemistry at Brown University in Providence, Rhode island. He has had a distinguished career in chemical education, serving as chairman of the Division, as a pertinipant in the Visiting Scientist Program, and as a member of numerous committees concerned with the teaching of chemistry and the preparation of high school teachers. Among the numerous honors accorded him are the MCA Award in College Teaching and the Division's SAMA award. He received his B.Ed. degree from Eastern Illinois State College and his MA and PhD degreess from the University of Illinois.

Mary C. Johnson has taught chemistry for thirteen years in the Detroit area. For the past three years she has been a chemistry teacher at Detroit Country Day School in Birmingham, Michigan, where sha is currently involved in teaching regular and honors first-year chemistry and honors second-year chemistry. Last year 106 students were enrolled in her classes. She received her B.A. degree from Western Michigan University in Kalamazoo, Michigan and her MS degree from Wayne State University in Detroit, Michigan.

¹ Beasley, W., CHEM. EDUC., **57**, 807 (1980).

in the organic class? In 1946, DDT was used to spray for mosquitoes in Sri Lanka, and the death rate from malaria diminished from 30 to 22 per thousand population in one year. Some years later some of the people of Sri Lanka starved to death because there was not enough rice for the extra people who had escaped the ravages of the disease. Was it ethical to

supply DDT in the first place?

Organic chemistry is part of our culture. Culture is what remains when you have forgotten all that you learned. Organic chemists have added to our cultural heritage in a very short time. Even today's 20-year-olds have lived through about one-seventh of the entire history of organic chemistry. In 1828 Wohler synthesized urea (an animal substance) from ammonium cyanate (strictly a mineral substance) and forever removed the mystery which previously had held the synthesis of an organic substance required a "vital force." Citizens, chemistry majors, and pre-medical students ought to appreciate some of the clever thinking and strenuous laboratory work that have highlighted accomplishments in this field in the past—Emil Fischer's proof of structure of glucose and his synthesis of a peptide of 18 units; du Vigneaud's and Tuppy's work that resulted in elucidating the structure of the first proteins, the pituitary hormones oxytocin and vasopressin; Carothers' work on polymers; and Woodward's remarkable synthesis of chlorophyll and many other complex molecules.

As in all young sciences, theories and research in organic chemistry are still empirical in many respects, although quantitative explanations are slowly creeping into the field. The role of catalysts, particularly heterogeneous catalysts, is still a dark corner to be explored.

Students say that chemistry is less "cut and dried" than physics, by which they imply that every phenomenon in physics has already been explained. Instead, what they mean is that in chemistry it is easier to get to the edge of research than it is in physics. In biology it is still easier for a beginner to make a contribution, because many biological problems yield to empirical methods. At the moment chemistry is in the ideal position between these two disciplines.

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The 1984 international Chemistry Olympiad in Frankfurt/Main (West Germany)

The 16th International Chemistry Olympiad will be held in Frankfurt/Main (West Germany) from June 30 to July 10, 1984, with more than 20 countries participating. The four best pupils from each country are given the opportunity to test their skills against those of others. Participants must perform both theoretical tasks (from all spheres of chemistry) and practical laboratory work, these assignments going far beyond what is required in school.

An extensive information and cultural program provides a chance to become better acquainted with the host country and its people. Many students find that the Olympiad allows them to transcend political and ideological boundaries and to establish contacts and make friends; this may well be the most valuable contribution of the International Olympiad.

The Olympiad (as well as some of the requirements for participation) has been described in: Ellis, P. R., Educ. Chem. 20, 208 (1983).

For further information concerning participation in the 1984 International Chemistry Olympiad in Frankfurt/Main contact:

StD Klaus Hagenstein Geschäftsführer der 16. Internationalen Chemieolympiade Brandsbornstrasse 11–15 D-6050 Offenbach, West Germany oxidation-reduction reactions as well as an introduction to aldehydes, ketones, and acids. The study of carboxylic acids affords an opportunity to reemphasize the importance of equilibrium, particularly with respect to weak acid/base chemistry, and the relationship of pK_a , equivalence point, buffers and indicators to the titration procedure. Mechanisms play a vital role in modern organic chemistry, and discussions of S_N1 , S_N2 , E1, and E2 reactions follow directly from a review of kinetics and the orders of reactions. Polymers and medicinal chemistry are other topics which can lead into discussion of many relevant issues facing today's society, and these subjects would be difficult to study without a knowledge of molecular structure.

Organic reactions can be used to introduce many new laboratory techniques. Kinetics experiments such as the oxidation of ethanol (followed titrimetrically)² and the bromination of acetone (followed spectroscopically) are two examples. Of course these experiments could be performed without any knowledge of organic chemistry. However, students have a hetter appreciation of the experiment when they understand the reaction behind the procedure. Each student is required to synthesize and purify a different organic compound and then, using instrumentation available at a nearby university, to verify its structure by NMR and IR spectroscopy. Students enjoy the challenge of searching the literature to find a suitable procedure and then making the proper analysis.

On the more practical side, students have found that a background in organic chemistry is an advantage when they go on to their college studies. Some take survey courses in their freshman year which include organic and biochemistry. The pace of such courses is usually rapid; prior exposure to the subject is of great value. Other students place out of first-year chemistry and go directly into organic, a very challenging course at the university level. Students with some organic background are less bewildered by the introduction of many concepts in quick succession. Also, students from our course are already familiar with refluxing, distillation, recrystallization, and some chromatography techniques and feel much more at ease in a college lab.

Finally, our school follows the curriculum of the International Baccalaureate, a program involving a rigorous course of study over a broad range of disciplines, and organic is a vital aspect of the chemistry covered in this program. However, even if our school were not involved, I still would try to place a major emphasis on the teaching of organic chemistry in either a second-year or a third-semester of high school chemistry. Since a great deal of all chemistry done in industry, including agricultural, pharmaceutical, paint and polymer chemistry, involves organic reactions, it does seem strange to leave such an enormous wealth of material out of the curriculum, even at the high school level.

In previous years, I have taught a one-semester course of organic chemistry to non-honors students, using common high school equipment along with old glassware donated by a university. I have found that we could make a decent attempt at good lab experiments without a tremendous outlay of funds. The course does not have to be a rigorous one, duplicating a college-level course, to be interesting and educational to the student. My only regret is that at present I do not have enough time in the first-year course to offer more than a superficial sketch of organic chemistry for those who will not be going on to the second-year class.

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² Finlayson, M. E., and Lee, D. G., J. CHEM. EDUC., **48**, 47 (1971).

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profiles in chemistry



Neoprene and Nylon Stockings: The Legacy of Wallace Hume Carothers

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What do rubber tires and nylon stockings have in common? They are both made with synthetic substances developed by the brilliant chemist Wallace Carothers. Neoprene was the first successful synthetic rubber developed in the United States. It has a wide variety of uses from tires and life rafts to sealants for space vehicles. Nylon revolutionized the textile industry by ushering in the era of synthetic fibers. In addition to its use as a textile, nylon has many applications as a moided plastic. Today, many well-dressed women would not consider leaving their homes without wearing nylon hose. If Carothers only knew what he had started!

Wallace Hume Carothers was born in Burlington, Iowa, on April 27, 1896. His paternal forebears were farmers and artisans of Scotch origin. His father, Ira, was born on a farm in Illinois but left the farm at age 19 and taught country school. Later, he entered the field of commercial education and was a teacher and eventually vice president of Capital City Commercial College in Des Moines. His maternal ancestors were farmers of Scotch-Irish stock who loved music. It may have been the influence of his mother, Mary Evalina McMullin, that led to Carothers' keen interest in and appreciation of music as an adult.

Carothers was the oldest of four children. He was especially devoted to his sister, Isobel, who achieved radio fame in the early 1930's as Lu in the trio Clara, Lu, and Em. When she died suddenly in 1936 after a short illness, Carothers was greatly shocked, and he never complately adjusted to her loss.

When Carothers was five, his parents moved to Des Moines where he began his education in the public schools. He graduated from North High in 1914. During these years, he displayed an overwhelming interest in tools and mechanical things and spent hours experimenting. Carothers was a perfectionist. He carefully finished every task he started.

Carothers enrolled in the Capital City Commercial College in the fall of 1914 and graduated in the accountant curriculum in July 1915. In the fall he entered Tarkio College in Missouri, where he pursued a scientific course and also accepted a position as assistant in the commercial department. Carothers excelled in his chemistry courses and, after two years, his superior record in English earned him a teaching assistantship in that department. Then, during World War I, Arthur Pardee, head of the chemistry department, accepted a position at another institution. Carothers, who had taken all of the chemistry courses at Tarkio by the end of his sophomore year, was appointed to take over the chemistry instruction. He had been rejected as a soldier because of a goiter condition, so he served as a chemistry teacher during his junior and senior years while he completed his studies.

"Profiles in Chemistry" is a biographical feature, highlighting the contributions of distinguished chemists in the context of their lives. The column is designed for curriculum enrichment, allowing the secondary school teacher to enhance the vitality of chemistry with the sense of scholarship and adventure shared by chemists throughout history.

In 1920, Carothers left Tarkio College with a bachelor of science degree. He began his graduate studies in the chemistry department of the University of Illinois. After one year, he had completed the requirements for the master of arts degree but lacked funds for further study. Carother's former instructor at Tarkio, now chairman of the chemistry department at the University of South Dakota, was looking for a young instructor to teach analytical and physical chemistry. Carothers was chosen for the position and went to South Dakota with the idea that he would make enough money to complete his graduate work. The careful preparation of his courses and his concern for the students demonstrated that he could he a very successful chemistry teacher.

Carothers started to develop some independent research projects while he was teaching. His first contribution to the Journal of the American Chemical Society was "The Isosterism of Phenyl Isocyanate and Diazobenzene Imide" in 1923. His second paper, in 1924, was "The Double Bond," in which he presented the first clear application of the electronic theory to organic chemistry. It became evident that teaching was not his primary interest, and he spent all of his spare time on research projects. His friends urged him to relax, but it was as if he were driven by an inner desire to investigate.

Carothers returned to the University of Illinois in 1922 to complete his studies, and in 1924 he received the PhD in organic chemistry. His thesis research explored the catalytic reduction of aldehydes with platinum-oxide platinum-black, and the effect of promoters and poisons on this catalyst in the reduction of various organic compounds. These studies were completed under the direction of Roger Adams, the legendary Illinois chemist who trained his research students as careful experimentalists and inspired in them an intense interest in chemistry. Adams was strongly oriented toward the chemical industry, and this attitude apparently influenced Carothers. While at the university, Carothers also studied physical chemistry and mathematics. He held assistantships in inorganic and organic chemistry, was promoted to a research assistant, and was later granted the Carr Fellowship, the highest award offered by the chemistry department.

After graduation, Carothers was appointed instructor in organic chemistry at the University of Illinois where he taught for two years. In 1926, he was chosen to fill an organic chemistry position at Harvard University. During his first year at Harvard he taught experimental organic chemistry and an advanced course in structural chemistry. It was here that Carothers began his studies on polymerization. Then in 1928, Du Pont began a new program of fundamental research at the Experimental Station at Wilmington, Delaware. Carothers was asked to head the organic chemistry program, and it was at this time that he permanently left education.

From the time Carothers joined Du Pont until his death, his accomplishments were plentiful and of great value. During the nine-year peried that he was with Du Pont, Carothers not only made numerous contributions to the theory of organic chemistry but also provided inspiration and guidance to the chemists under his direction. His work laid the foundation for several new developments of commercial importance.

The first area which he studied extensively was acetylene polymers and their derivatives. Julius A. Nieuwland, a priest at the University of Notre Dame, had completed the basic research on the synthesis of vinylacetylene and divinylacetylene. When a chemist from Du Pont heard Nieuwland's

presentation at an American Chemical Society Organic Chemistry Symposium in 1925, he realized that Nieuwland's knowledge could be valuable to Du Pont, and an association was formed. Now that vinylacetylene and divinylacetylene were available to Carothers, he completed a detailed study of these substances. Further, he found a way to add hydrogen chloride to monovinylacetylene to form chloroprene. This substance is structurally analogous to isoprene, but polymerizes several hundreds of times faster to produce polychloroprene. The first polychloroprene was named duprene; however, Carothers changed the name to neoprene. Neoprene resembles rubber and is used as an additive to natural rubber to improve its properties. The first large-scale application of neoprene was for the production of gasoline hose which could withstand attack by gasoline and hydrocarbons. Today, Du Pont produces about 175,000 tons of neoprene a year, which results in sales of about \$400 million annually.

While investigating the chemistry of polymerization, Carothers also synthesized some cyclic polymers which possessed a musklike aroma. Du Pont marketed these substances under the trade name Astrotone synthetic musk for the perfume industry.

Carothers' most outstanding scientific accomplishment was his work on linear polymers. He wrote a series of 31 papers in the field of polymerization and held 50 patents. In these papers, he proposed a theory of condensation-polymerization and a terminology suitable for this field. During the 1930's Carothers devoted his attention to the preparation of polymers which were structurally analogous to cellulose and eith. Many compounds were studied; however, the results were disappointing. Du Pont was on the verge of abandoning the project when in 1935, success was attained when nylon was developed. Nylon is a macromolecule obtained as a condensation product from adipic acid and hexamethylene-diamine, with a molecular weight of over 10,000. Nylon has become a fiber particularly suited for textiles.

Carothers' advice was sought by chemists throughout the world. At the age of 33, he was elected associate editor of the Journal of the American Chemical Society. The following year, he became the editor of Organic Syntheses. In 1935, he

spoke before the Faraday Society in London on "Polymers and the Theory of Polymerization." He was the first industrial organic chemist to be elected to the National Academy of Sciences. Apparently Carothers never regretted his decision of research over teaching; he turned down several academic positions during his years at Du Pont.

On February 21, 1936, Crothers married Helen Everett Sweetman of Wilmington, Delaware. She had received her bachelor's degree in chemistry at the University of Delaware and was employed in Du Pont's chemical patent division.

Carothers was an avid reader and especially enjoyed poetry. He also liked to sing, and he found it very relaxing to listen to his many recordings of great composers such as Bach, Beethoven, and Brahms. Carothers was shy and sensitive, and he avoided parties and crowds. His close friends described him as deeply emotional, generous, and modest. In very small groups, he was a brilliant conversationalist.

Carothers suffered from a nervous condition, revealed in his later years, in his poor health. He was plagued by periods of depression which became more and more pronounced. On April 29, 1937, at the age of 41, he checked into a Philadelphia hotel and committed suicide by drinking cyanide. He never saw his daughter, Jane, who was born seven months later. Despite the brevity of his career, Carothers' contributions to organic chemistry are recognized as outstanding, and he is acknowledged as a pioneer in the field.

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The Density of Solids

Dale Burgess

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An experiment to determine the density of a solid usually is a simple one in which the student carefully slides a cylinder of metal into a graduated cylinder partially filled with water in order to determine volume by displacement and weighs the metal cylinder. The student calculates the density from the formula D = M/V and answers a few pertinent questions.

In my experiment, however, I have a large collection of assorted objects. This collection includes rebar, concrete, boards, rocks, gears, hose, pipes, corks, styrofoam, rubber stoppers, and odd pieces of metal.

Each student is given one of the objects and is told that he can use anything in the lab in his determination of the object's density, but that the size of the measuring device must baye an accuracy commensurate with the size of the object being measured. The volume of the object must be obtained both by displacement and by using a ruler to get its dimensions.

The students have the normal chemistry lab equipment and some large pans to be used for large object displacement. There is also a trip balance with no weights. The objects either

do not fit easily into a graduated cylinder or are too heavy to be weighed on the triple beam balances, so the students must think up ways to weigh the objects using the trip balance and to determine the volume with a reasonable degree of accu-

There is generally a short period of student confusion and aimlessness, but then the students start getting ideas and the experiment becomes both challenging and fun for most of them. In my last class a couple of the students found a hox that contained vermiculite that had been used as packing, and they used the vermiculite as a displacement medium and the box as a container to determine the volume of a large board.

Following the experiment I discuss: (1) the comparison of the measured densities with the real densities, (2) the comparison of the results of the two methods, (3) the possible errors introduced by the measuring devices, (4) relative error in the experimental data, and (5) other methods of density determination. The discussion of relative error leads nicely into a discussion of significant figures.

Use of the Computer for Chemistry Instruction



Robert Suder

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In these times of rising costs and decreasing revenues, one must be able to work as efficiently as possible. At the school system where I teach chemistry we have seen a drastic decrease in funds, resulting in many changes. Therefore, the teacher must be able to work smarter, rather than harder.

Several years ago, I purchased an Apple II computer with an Epson MX-80 printer. Since I had programming experience, adapting to the Apple presented little difficulty for me. The personal computer has been the greatest invention for the teacher since the chalkboard. It has allowed me actually to increase my efficiency without compromising quality. However, one must be careful to do only tasks with the computer that actually result in time saving. Too often, the computer is used to accomplish tasks that can be done better without it

Gradebook

In our school system, student grade reports are issued six times per school year. As any teacher is aware, considerable time is needed to determine grades and, hecause of the sheer number of grades being calculated, errors will inevitably result. Therefore, I decided to use the computer as the gradebook. This allowed me to compute the grades for all my students in a matter of minutes. At the end of each week, I spend about fifteen minutes entering scores into the computer. When the grades are due, I simply enter the grade cut-off point and the computer determines the grades. Then I have the grades transferred from the printout sheets to the school's report card sheets by my student assistant. My actual time involved in preparing grades is a few minutes, rather than hours.

Since I have extensive programming experience, I decided to write my own gradebook program, rather than buy a packaged one. In this way, I could design the program to fit my needs exactly. Admittedly, it was a considerable amount of work, but well worth it. My gradebook program will perform the following:

record scores
record absences
determine test score averages
determine total points for each student
determine letter grade for each student
determine the number of each grade given per class
allow for addition or deletion of students
permit either screen or printer display (see Fig. 1)
allow for easy changing of information

The records in the program are stored sequentially on the disk. An added advantage of the program is that a student is able to determine his or her grade at any time during the marking period. Therefore, he or she knows how hard to work in order to improve the grade. Naturally, the program must have a security system that will permit the student to check only his or her grade, not change it. I use a password system that prevents the unauthorized modifying of grade records. The password uses control characters which cannot be seen by listing the program.

Chemistry Laboratory

The microcomputer is also very useful in the laboratory. Too often, the student simply performs the experiment, rec-

NAME	ABSENCES	POINTS	GRADE
ADAMS J	. 0	243	· A-
DGE J	. 0	217	₿
GARY R	2	251	Α
JONES M	1	196	Ē
MILLER R	0	225	В
PHILLIPS F	2	203	C+
SMITH J	3	240	B+
TAYLOR S	İ	198	C
WHITE B	0	211	£+

± ==	====	2282
	A	2
	9	3
	Ç	4
	D	0
	E	0

SUMMARY TABLE

POSSIBLE POINTS -- 263
FAILING POINT --- 60 %

GRADING SCALE

A+	255 - 263
A	248 - 254
A-	241 - 247
₿+	232 - 240
B	222 - 231
₽	212 - 221
C+	201 - 211
. C	190 - 200
C~	178 - 189
D÷	171 - 177
D	164 - 170
D-	157 - 163

FAILING SCORE - 60 %

Figure 1. Sample printout of computer gradebook.

ords data, and has no idea if the experimental results are correct or not. The student generally does not learn whether the experiment has been done correctly until the graded experiment write-up is returned. Therefore, I have written a number of programs that will permit the student to check his

or her experimental data right in the laboratory. The student performs the experiment, enters the data into the computer, and then the computer informs him or her whether the data is good. If it is not, the student knows to repeat the experiment. Since I began using the computer in the laboratory, the work of my students has improved considerably.

I have also attempted to have the student first type his or her name before entering any data. The idea was to record the student's name and data, use the computer to calculate the experimental results, and save all this information on the disk. When checking lab reports I would be able to recall the information from the disk, and then compare their calculations with the computer's. This should make lab report grading very easy. However, it has not worked out that way. The problem is that there is only one computer available and lab periods are only one bour long. Most students have no typing skills or computer experience. A non-typist may require several minutes just to type a name. I was finding that most of the students were not working at their lab stations, but waiting to use the computer. Having more computers available or more lab time would help to solve the problem.

The computer also can be used to simulate experiments. This is especially appropriate in cases that require special, or expensive, equipment or chemicals. One such simulation which I bave written is adapted from the classical pressure-volume experiment. After the student types his or her name, the computer graphics show the apparatus (Fig. 2). Pressing the return key changes the applied pressure, which causes the corresponding volume change. The computer will randomly generate different values for each student; therefore, each will have different experimental data. In addition, the computer will calculate the correct experimental results and record this and the students' names on the disk, making it a simple matter to retrieve the information and compare with the students' results.

Students are required to show their calculations in their lah reports. However, by encouraging them to check their calculations with the computer's, they will be able to investigate their mathematic computations and hopefully remove any errors before submitting their reports. The programs I use do not show the students how to perform the calculations but simply provide them with a computed result.

Because of the very easy access to the Apple's input ports, it is a relatively simple matter to interface it with laboratory instruments. Usually all that is required is an analog-to-digital converter. A-to-D converters that fit directly into the slots can be purchased for about \$100.2 A less-expensive alternative would be to use the analog inputs in the game controls.3 One application of interfacing would be to provide a digital readout of analog devices, such as a Spectronic 20. It is very easy for students to read absorbance incorrectly because it reads backwards on the meter; however, they can check their meter readings with the digital readings displayed on the computer. It is also possible to save the experimental results on disk to check the students' results.

The computer can be used for pre-lah quizzes. I have found that most titration errors involve reading the buret, and, therefore, I designed a quiz that will simulate a buret (Fig. 3). The volumes are selected randomly by the computer. If the student has read the buret and answered two questions correctly, his or her name will be stored on the disk, I can then determine who has passed the pre-lab quiz and is therefore ready to perform the experiment in the laboratory.

A modem allows one computer to communicate with others

using the telephone line, which enables one to contact chemical information services such as CAS ONLINE. A very valuable exercise is to have the student perform a compound search using this facility.

Communicating with the Student

When writing programs for student use, one must realize that very few of them have any computer experience. The simple instruction "ENTER NAME" will confuse many of them. It would be better to use "TYPE NAME, THEN PRESS RETURN." Also, the numbers one and zero are confused with the letters I and o. Numerous error-trapping routines are required. After the students enter their data, one must make provisions for the correction of errors. I use the statement:

CHECK YOUR DATA. IS IT CORRECT (Y/N)?

The problem that arises is that some students will type "Y" and others will type "YES." Therefore, the program should only look for the first letter. Also, some students will type "T" or another letter. The program should be able to handle this problem.

There should be no provision for exiting the program other than by special commands known only to the instructor or by turning off the computer. Assume that a student has finished

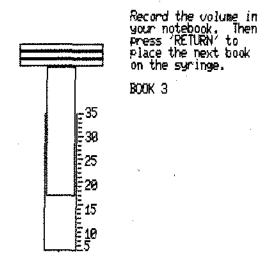


Figure 2. Pressure-volume simulation.

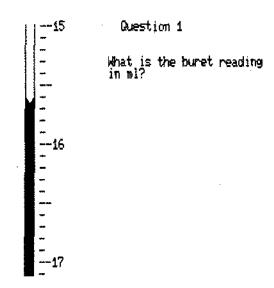


Figure 3. Titration simulation.

¹ Dietz, P., Tellefsen, R., Parry, R., and Steiner, L., "Chemistry Experimental Foundations: Laboratory Manual," Prentice-Half, Englewood Cliffs, New Jersey, 1975.

² John Bell Engineering, Inc., 1014 Center Street, San Carlos, CA 94070.

³ Deininger, R., and Berger, C., inClder, 74 (January 1983).

his turn at the computer, and the following instructions appear on the screen:

- (1) PRESS (RETURN) FOR ANOTHER SET OF DATA
- (2) PRESS (E) TO EXIT PROGRAM

Option (1) should be selected so that another person can use the computer. However, since most students have no idea of what exit means, they will select this option when done. The instructor will have to reload or rerun the program. On the other hand, there are the hot-shot programmers who like to get a listing of the program and then change the commands. Therefore, if possible, disable the reset key.⁴

Database System

A database program is similar to a computerized index card system. It will store information for easy retrieval. There are many database programs available. Examine several before making a decision.

One use for the database program is stockroom inventory. Since we have a large chemical stockroom, computerization seemed the logical choice. One can have information concerning the name of compound, class, amount, etc. One of the features of database systems is their shillity to sort and search. If one wants to know what bases are available in the stockroom, the computer can be instructed to search the base classification and all these compounds will be referenced. Another advantage of the computerized stockroom is that one has instant access to the chemicals that are available. Since I do not have an office in school (it was converted into a classroom), all my reference books are at home. If I find a promising experiment that I would like to try, I can easily check my computer listing to see if the required chemicals are available.

Another use of the datahase program is to record student data, such as home phone number and hook number. If a student leaves his book in class, I simply have the computer do a search to find the owner. Also, one can keep a permanent grade record of the students. One problem with the database program is that a considerable amount of time is needed to record all the information. It is very helpful if one has a student assistant who is able to type.

When selecting a database program, be certain that it uses machine language for sorts and searches. The first program I tried did not, and an hour was required to sort 175 chemicals. My present database program can accomplish this task in a few seconds using machine language.

Word Processing

The term "word processing" is *computerese* for typing. The word processor is probably the most used progam that I have. With it I can write letters, tests, and experiments and edit them as needed. Once satisfied with the document, I can have it printed out. The document can also be saved on disk if I desire.

Since f am not able to purchase textbooks for my organic chemistry class, I must generate most of the written materials used. The word processing capability of my computer has proved to be a valuable resource, especially when I am preparing leb experiments. Once I type them, they are saved on disk and updated as needed each year.

I like to give my students as many practice problems as possible, and it seems they are always asking for more. To handle this demand, I prepare a master worksheet using the word processor, and need only to add new data to produce any subsequent worksheets. For example, if I am writing a molarity practice sheet, I typically vary only the names and amounts of the given substances.

The same technique can be used to write tests. I had found even before I began using the word processor that my tests follow a similar pattern year after year. Thus, with the word processor, I have freed a considerable amount of time that can be used more productively elsewhere. I typically take an old test and make numerical and nomenclatural changes. Thus, the main body of the test remains the same; this is especially useful for preparing makeup exams.

There are several features to look for in a word processor. First, there must be provision for subscripts and superscripts. Without this ability, it is difficult to write formulas or exponents; however, it may be inconvenient to use these features because special printer codes are required. My word processor uses the ESC key for upper case, and control keys for subscripting and superscripting. Writing the formula for sulfuric acid uses the following key sequence:

ESC H CTL B ESC 4 CTL B ESC ESC S CTL B i 2 CTL B ESC 5 ESC S ESC 0 CTL B ESC 4 CTL B ESC ESC H CTL B i 4 CTL B ESC 5

It is hardly worth the trouble.

Second, the screen display should indicate exactly how the document will appear on the printed page. One must know where the margins and the end of the page will be. When I write a question on a test, I leave space for the calculation and answer. Therefore, I must know exactly how it is formatted and where it will be on the page.

Next, it is very helpful if one can see an entire line of text. Since my computer has only a 40 column display, and the printer 80 columns, this could he a disadvantage. There is hardware available that will give an 80 column display but this is often expensive. My solution has been to purchase a word processor which uses the computer's hi-res graphics to show 70 columns and lower case. I have been using the Magic Window II word processor by Artsci and have been extremely pleased. My only complaint is that it is protected software; it is not possible to make a back-up copy of it. The company does offer a liberal warranty, but if for some reason I accidentally damage the disk, I will not be able to access any of my documents until a replacement disk arrives.

To print numerous copies of any one document it is necessary to make dittos because we do not have access to a photocopier. There is a problem, however. A dot matrix printer does not impact hard enough to make a ditto. Thermofax® dittos of the original can be made, but this does not always produce a clear copy. Therefore, to get around this problem I make a ditto using a Thermofax® master directly in the printer. In order to obtain best results I use both the double strike and emphasized printing modes. In addition, I remove the printer ribbon so that the pins strike directly on the Thermofax master.

One final problem is that my printer is tractor feed only, and Thermofax® dittos will not pass through. One solution is to tape the ditto to the paper. A better solution is the purchase of a Paper Porter.⁵ This is a plastic sleeve carrier that will allow regular paper or dittos to go through the printer.

VISICALC®

The VISICALC® program is an electronic spread sheet. It can be used to make forecasts or projections as well as store data. We have used the program to perform calculations with large amounts of data. A number of teachers use this program for their gradebooks. Recently, we have used Visicalc® for contract negotiations. The current salary schedules were placed in the program; then, using the projection feature of the program, our school system could see how the values would change if certain percent pay increases were granted. The administration may want to use Visicalc® to make projections of student counts, costs of utilities, etc. Visicalc® is probably one of the most important programs ever written for the computer.

I have described a few ways in which the microcomputer can be helpful to the classroom teacher. I would never want to be without one again.

⁴ Softalk, 44 (March 1983).

⁵ Beeline Services, 57 18 Ponderosa, Stevensville, MI 49127.

The Basic Elements of Writing a Scientific Paper: The Art of Scientific Style

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Winston Churchill is reported to have said of literary critics who insisted that sentences never end in a preposition (1), "This is the type of arrant pedantry up with which I shall not put." This historic example of what is and what is not considered proper in good writing applies to technical scientific writing as well as other, more literary forms of communication. For those who do not write regularly, the experience can be intimidating. Knowing what is important and reviewing some common pitfalls of science writing at the outset is always helpful.

Scientific writing is a form of writing called expository. Its primary goal is to explain. Implicit in any expository writing is another goal: to persuade. The two go hand in hand, for it is hard to explain a scientific fact without taking a position on it. The goal, then, is both to have your readers understand you and to convince them that your interpretation of your data

is the only correct one.

Correct and Concise Usage: Less Is More

Good writing begins with a profound respect for words, their precise denotations, and their connotations. Do not use three or four words when one will suffice. Every word of every sentence should work for maximum efficiency to achieve clarity and brevity. What looks like a natural gift to write is really great persistence, compulsiveness, and discipline.

Along with brevity and clarity, accuracy is the third element of good scientific writing. The words "scientific" and "data" themselves suggest knowledgeable, documented, and organized information. Any manuscript should be written with the goal of its becoming a permanent and accurate record in the scientific literature.

Organization and Continuity

Good scientific writing, then, is direct and definite. It demonstrates confidence and inspires confidence in your readers. Weak writing, on the other hand, reveals uncertainty. One serious fault that weakens the reporting of careful scientific work is the lack of organization. Results reported in a disorganized manner take more time to interpret than readers are willing to spend. Without a well-organized presentation of the data, years of work and money may be wasted.

For good organization, effort is required. For any subject, interrelationships should be addressed and then recapitulated as they relate to other elements. Transitional aentences, which bridge thoughts, are often missing in poorly written pieces.

Inherent in good organization is continuity. Every sentence should connect the one preceding it to the one following it. Often neglected are explicit connectors that signal to the reader that the direction of the argument is changing, being paralleled, or being contrasted to an earlier one. The signposts to use in these cases are conjunctive adverbs or brief transitional phrases that signal the thought coming next. The following list offers a variety of choices for creating continuity and greater precision. Use them often.

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above all accordingly and so again also besides consequently finally first for example for instance furthermore hence however in addition in conclusion indeed in fact

in particular instead in summary likewise moreover more specifically nevertheless nonetheless on the other hand rather second similarly still then therefore though thus to sum up

Specific Parts of Scientific Papers

Science writing is a unique process because scientific papers consist of specific elements that include the title, introduction, methods, results, discussion, conclusions, summary, and bibliography. Do not underestimate the importance of the title. It is a clear statement of the paper's content and contains key words that will be indexed for information retrieval systems.

The introduction gives the necessary historical perspective and then states why the work was done. It should seize the attention of the readers and emphasize the area of interest. Often the introduction is more effective if it is written last.

Unfortunately, the structured methods and results are often written as rote copies of previous, similar works. This can result in incongruities between these two complementary sections. The important point is to give the reader enough accurate information to allow a good understanding of how the work was done and what the results were.

In the discussion and conclusion, it is necessary to return to the argument you planted earlier in the introduction. Your readers cannot be left seeing the trees but no forest. A comparison of your work with others' and explanations of similarities or discrepancies form the discussion, which moves to a logical justification and conclusion of your paper.

The writing of a summary follows easily. The summary is composed of highlights of each preceding section, and though it often appears first as the paper's abstract, it is best written

It is hoped that your readers will respond intellectually to your information. Disagreement with your conclusions is far better than disinterest in ideas that are not clearly enough stated to be understood. The goal of all writing is to get a message across. A well-written paper is a pleasure to read and a great satisfaction to the seeker of scientific information.

Common Pitfails

The hardest step for most writers is getting past the first draft. One must be able to say, "This wonderful creation of mine still needs work." Compulsiveness is a trait of good writers. When you think that you have a finished product, go back over it several times to check the specific points outlined

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below which identify some of the most common errors and weaknesses.

Read your manuscript through once, looking exclusively at your subjects and verbs. Are subjects and verbs matched for singular and plural forms? Check that verb tense and form denote conviction instead of doubt. Do not use constructions like "appeared to be" and "can be seen to" if verbs like "occurs" and "shows" would state the same ideas. The latter not only result in more decisive statements but also use fewer words.

Next read through your manuscript checking to see that each procedure described in the methods section was actually performed and reported on in the results section. At the same time, compare every figure and table to the statements attributed to them in the text. Make certain that the text fully describes these illustrations. In addition, captions for figures and tables should stand by themselves as brief explanations of such visual representatives of the data.

Recall that brevity and clarity are essential. Do not use three or four words where one will suffice. Why say "in the event that" instead of "if"; "on the order of" instead of "about"; "for the reason that" instead of "since"; or "one and the same" instead of "the same"?

Finally, check the cited references to insure that they actually contain the material attributed to them. Do not rely on references from similar papers. Typing errors are very common among the numbers used in bibliographical information.

Odds and Ends

What follows is a catch-all of various stylistic and procedural items that particularly plague science writing.

Punctuation

Semicolons. A semicolon replaces a connecting word like "and" and can be replaced by a period; it is not a substitute for a comma. It is often used to combine two or more related independent clauses. Another common use of the semicolon is to separate items in a series. This is not a violation of the rule that each part must be a complete sentence; the form may be viewed as elliptical, the missing words being understood. The writings of Mark Twain and G. B. Shaw abound with semicolons. An illustration of the use of semicolons in good scientific writing occurs in the paragraph below (2) in which the words "These hybrids have been used for" are understood as a common prelude to each phrase separated by semicolons:

In this paper I review newer experimental developments in our laboratory, which are based on development of auxotrophic and other mutants of mammalian cells and the construction of a series of hybrid Chinese hamster overy (CHO) cells containing single, or small numbers of, human chromosomes. These hybrids have been used for genetic, biochemical, and differentiation analysis of cell surface macromolecules; regional mapping of particular genetic markers; an approach to biochemical understanding of the human aneuploid diseases; a new method for detection of environmental mutagens and carcinogens; and an amalgamation of somatic cell genetic techniques with those of recombinant DNA in order to devise a new method for mapping the human genes, which promises wide application and high resolving power (2).

Commas. Insert a comma where there is a light natural pause. Reading aloud your words is the best way to determine this. Conjunctive adverhs and signpost expressions like "moreover," "therefore," and "on the other hand," must be set off hy commas both before and after if they occur in the middle of a sentence. Never connect two independent clauses by a comma; use only a semicolon.

Colons. The colon, like the semicolon, joins related thoughts; however, it is used only when the first thought introduces the second. Any colon used properly can be replaced by "that is" or "namely."

Abbreviations

Abbreviations that have not become standardized must be

defined the first time they are used in your text. Some well-known abbreviations that are generally acceptable, but commonly misused, are given with their full meaning:

e.g., exempli gratias, for example—Use commas before and after and periods after each letter of the abbreviation.

et al., et alii, and others—Since "et" is a complete Latin word, do not use a period after it. The second word is abbreviated, and a period must follow it.

i.e., id est, that is—As with "e.g.", i.e. must be set off with commas before and after and periods after each letter.

viz., videlicet, namely—Also set this off with commas before and after.

Some Commonly Misused Words

Affect-effect. "Affect" is commonly used as a verb that means to influence and less commonly as a noun that means an artificiality. "Effect" is used commonly as a noun to mean the result or outcome and less commonly as a verb that means to cause or to bring about.

Consensus. It is redundant to use the phrase a "consensus of opinion" because consensus means a collective opinion.

Criterion-Criteria. Criterion is singular; criteria is plural. Other related words are medium-media, datum-data, and stratum-strata.

Different from-Different than. The preferred preposition after different is from; however, different than is acceptable if it avoids a wordy clause.

Factor. This word resonates with scientific overuse; its synonyms—element, ingredient, and component—are underused.

First-Firstly. "First" is a genuine adverb itself and should be used without the suffix "-ly." "Second," "third," etc., fall into this same category.

Imply-Infer. If an author implies something in his paper, something is hinted at; the reader infers or understands the hint.

Like-As. In formal usage "like" should be used only as a preposition. "As" is acceptable as both a preposition and a conjunction.

Only. Make sure "only" is placed immediately before the word it is intended to modify.

Principal-Principle. A rule or truth is a principle and it is used only as a noun. Its homonym, "principal," is a noun or adjective and means chief or leading.

Revert back. Simply use "revert"; "revert back" is redundant.

Reason is because, "Because" means "for that reason"; this is a common redundancy.

Thus-Thusly. "Thus" is an adverb by itself and needs no suffix.

Unique. There is only one of a kind of a unique thing. "Most unique," "very unique," or "rather unique" events do not exist. Use "unusual" or "rare" in place of these incorrect terms.

Everyone can develop skill in the use of language that conveys scientific information in a meaningful, persuasive, and understandable manner. It is an accomplishment that is learned and that grows by paying attention to good writing to see how these skills are used to their fullest. None of these learned skills are intended to conflict with an individual's writing style, which is a unique portrayal of the author's personality. A natural writing style is the best and most pleasurable to read; such a style comes only with practice and a desire to improve your writing. Two quotes, one from a scientist and the other from a well-known literary figure, sum up these ideas appropriately.

When we encounter a natural style, we are astonished and delighted; for we expected to see an author, and we find a man.

Pascal (3)

Interviewer: How much rewriting do you do?

Hemingway: It depends. I rewrote the last page of Forewell to Arms thirty-nine times before I was satisfied. Interviewer: Was there some technical problem there? What was it that stumped you?

Hemingway: Getting the words right.

Ernest Hemingway interviewed by George Plimpton (4)

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Scenarios in Science

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Many students who are nonscience majors are enrolling in science courses today at both the high school and college levels. These students are interested in learning more than science history and fact. They want to know how science and technology are affecting them now and how it will affect them in the future. A technique that we have employed while teaching nonscience majors at our school involves the use of scenarios as introductions to the topics under discussion. These scenarios are sometimes biased and may take either a positive or negative view of the subject matter. Most important, the scenario gets the student involved in the topic and sets the stage for an in-depth discussion once a particular chapter in the course has been covered.

Here is our suggested method of operation. A scenario is presented to the student in hand-out form at the time that a new topic is introduced. The majority of students have not yet begun to read the assigned chapter. A short discussion of the subject matter follows and students are allowed to ask questions pertaining to the topic. On many occasions it becomes apparent that the students are not familiar with the subject matter and are not able to discuss the issues raised by the scenario. The students clearly see the need to read the text assignment, as well as any supplementary material available, and attend the lectures so that they will be able to participate in an in-depth discussion of the scenario upon conclusion of the topic.

What follows are examples of three scenarios that we use in our nonscience majors chemistry course. The first scenario is entitled "New Bodies for Old." It is used as an introduction to the course when discussing the impact of chemical science and chemical technology in today's world. The second scenario is called "The Day We Lost New Jersey." It presents a somewhat biased view of nuclear energy and serves as an introduction to the topic of nuclear energy and nuclear power. We must point out, lest we offend the proponents of nuclear power, that although this particular scenario appears somewhat one-sided, it is quite successful in getting the students involved in the subject matter. A well-balanced view of nuclear energy is presented in class. When students have read the assigned material and attended lectures, they have sufficient information to allow them to make their own decisions regarding nuclear power.

The third scenario entitled "Starting Off Right" is used to introduce the subject of food chemistry. The scenario deals with the topic of infant formula versus breast milk. As you read these short scenarios, keep in mind their main purpose which is to whet the student's interest and foster involvement in the subject matter.

Scenario: New Bodies for Old

The year is 2050. During the first fifty years of the 21st century science and technology were used by the governments of the earth to improve the quality of life on this planet for all people. It was the year 2000 when the major powers on this planet agreed to stop spending billions of dollars in weapons of war and destruction and decided instead to pool their knowledge and wealth to improve the human condition. Many of the problems that plagued human society in the late 1900's were brought under control by 2025. Programs to stabilize population growth and produce adequate food for those living on the planet were becoming effective. Medical science, as well as the natural sciences such as biology, chemistry, and physics reached new frontiers.

However, it was the discovery in this year of 2050 that was to bring startling news to the scientific community. Scientists and engineers had transplanted the brain of an individual into an artificial body. The new body had the appearance of a human being and functioned in a completely humanlike manner. The transplant had been a success. The ramifications of this event were awesome. This new body would not age and would last 200 years!

Scenario: The Day We Lost New Jersey

It is a bright, sunny day in New Jersey on April 5, 1990. New Jersey has grown through the years to become a major industrial state in the northeast; a state that consumes a tremendous amount of industrial power. Almost 80% of this power is supplied by ten nuclear power plants located either in the state or surrounding it. Two of these power plants are off the coast of Atlantic City, built on manmade islands in the Atlantic Ocean. New Jersey is not a state that is prone to many natural hazards. Tornados, hurricanes, and earthquakes are infrequent. That is why it came as such a complete suprise when on this day a major earthquake hit the state, sending shock waves from Boston to Virginia Beach. The quake was as strong as the one that devastated the city of San Francisco in the early 1900's. However, in New Jersey the results were more devastating. The earthquake demolished numerous buildings and tore up many roads. The quake was centered on the central Jersey coast, not a highly populated region. Large numbers of people were not killed by the initial devastation. The problems arose with the four nuclear power plants located just off the coast and with those located on the coast of the Jersey shore.

Although these plants were supposed to be earthquakeproof, they were not strong enough to withstand the power of this quake. Sections of these power plants broke away. Cooling systems were lost and the atomic cores heated to meltdown. Radioactive clouds of steam were dispersed into the atmosphere. Offshore breezes hlew the clouds across the state. Tens-of-thousands of New Jersey residents died of the effects of this radiation and tens-of-thousands more were to die of radiation-linked diseases.

Scenario: Starting Off Right

It is the year 2010; a step into the 21st century. A baby has just been born and has been given to her mother to be fed. The baby is being hreast-fed and a natural process is taking place once again. The mother is relaxed and comfortable and the baby is being well nourished.

Toward the end of the 20th century, during the last few decades, a trend toward artificial feeding of infants was seen. In the industrialized countries of the world substitutes for breast milk became easily available. Millions of mothers gave their infants formulas made from pasteurized cow's milk. These babies showed a fine pattern of growth and weight gain. But experts learned that breast milk was better. It provides the infant with some forms of immunity to disease. It is more easily digested and it rarely causes an allergic reaction. Breast milk also contains a natural laxative.

Problems arose with artificial feeding in many of the Middle Eastern and African countries and in South and Central America, as well. Largely as a result of commercial advertising. urban women of these countries abandoned breast-feeding and swtiched to milk formulas. In the absence of absolutely safe drinking water, good sanitary conditions, and refrigeration, baby formulas sometimes hecame carriers of common infections. This caused several diseases which were once seen mainly in older children to be seen in infants. Re-education of the population as to the values of breast-feeding reversed this trend. Even an undernourished mother is able to produce 400 to 600 ml of milk daily for her child. In the year 2010, this is the more advisable method of feeding infants throughout the world.

Using the Scenarios

After reading these introductory scenarios, the student realizes that in order to understand and discuss a sciencerelated issue, the scientific concepts behind the issue must be studied. At this point the instructor begins the lecture material. The six basic questions-who, what, where, when, how, and why-will be answered in the lecture and lead to an understanding of the topic. The instructor must be careful to point out to the students that their opinions must not necessarily agree with the view presented in the scenario. The

scenarios are in many cases one-sided, and designed specifically to promote discussion. After studying nuclear power it might be a good idea to plan a nuclear power plant discussion session. Students can choose or be assigned pro-nuclear or anti-nuclear sides. They then present their views in a debate or planned discussion session. Students will see that the group armed with the greatest amount of research material and facts will be able to argue a stronger case. Students might also try to write their own scenarios to demonstrate another point of view on some of the other topics.

There are several uses for this teaching tool in science education. It can be the basis of a one-semester course at the high school level called "Decision Making in our Technological Age." Here students would be presented with the various issues facing us today and learn how to evaluate these issues. Another use at the high school level is the application of this technique to add relevance to the topics studied in science class. After scientific principles are learned, the instructor can point out the applications of these scientific principles and discuss the issues which have developed as a result of these technological advancements. Finally, we use this technique in our college level nonscience majors course to introduce and motivate students in chemistry and teach about the decision-making process.

As we progress in the area of science education it is clear that science courses for nonscience majors and high school students which present only science fact are not sufficient. While understanding concepts is central to learning and uncovering new information, the effect of science on humanity is of significance. The students of today who will be the leaders of the future must have a clear picture of how scientific discoveries can affect us both positively as well as negatively. Only in this manner will they be able to make logical decisions based primarily on fact and not on emotional persuasion.

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thumbnail sketches

is Sugar from Sugar Beets the Same as Sugar from Sugar Cane?

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At the beginning of this century when the beet sugar industry in this country was relatively young, there were those who insisted that cane sugar was different from and superior to beet sugar. Chemists took no stock in the arguments because to them it was obvious that a pure compound was the same regardless of the source. Nevertheless, it actually is possible to tell whether a given sample of sugar came from cane or from heets by means of a mass spectrometer, an instrument now in common use in most laboratories, since the ratio of isotopes of carbon ¹³C to ¹²C is different in the two kinds of sugar.

These two stable isotopes of carbon normally exist in the ratio 1.104 to 98.892. (For present purposes we can forget about the minute amounts of 14C whose weak radioactivity makes carbon dating possible.) In the products of photosynthesis the ratio of ¹³C to ¹²C is slightly less than their ratio in the CO₂ of the atmosphere. Such isotopic selectivity is known for many reactions. However, the conversion of CO2 to carhohydrates in plants takes place by two routes: the familiar

Brief descriptions of phenomena, topics, and facts which chemical educators have found to be of interest in their teaching, are presented in a "note type" format throughout the Journal.

path involving the three-carbon intermediate phosphoglycerate (1), and a more recently established path involving a four-carbon dicarboxvlic acid intermediate (2). Plants are divided rather sharply into two classes, designated C3 and C4 according to the number of carbon atoms present in the photosynthetic intermediate. The selective rejection of ¹³C is greater by the C_3 pathway than by the C_4 pathway (3). If δ^{13} C equals the difference of the ratio of 13 C to 12 C, times 1000, in a sample and the ratio in a reference standard marine carbonate, then δ^{13} for atmospheric carbon dioxide is -7, the average for C₃ plants is -26.5, and for C₄ plants, -12.5. Now, sugar beets are C_3 plants and sugar cane a C_4 plant. So a mass spectroscopic examination of the products of combustion will indicate the source of the sugar.

Since bees gather honey from C₃ plants and corn syrup comes from C₄ plants, a measurement of the ¹³C/¹²C ratio of. a sample will show whether it is pure honey or one diluted with low-cost, high-fructose corn syrup (4). Similarly, knowledge of the ratio will indicate whether a glass of orange juice is the real thing, which has a large negative shift in 13C/12C, or a synthetic one made from orange pulp, artificial flavoring, and high-fructose corn syrup, with a smaller negative shift in $^{13}\mathrm{C}/^{12}\mathrm{C}$ (5). Archaeologists are even using δ^{13} values of bone collagen to reconstruct the diets of ancient man (3, 6).

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Peroxides Can Be Treacherous

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Peroxides are unstable, shock-, thermal-, and frictionsensitive compounds whose sensitivity increases with concentration. Organic peroxides are all highly flammable. High school teachers need to be aware of the possibility of peroxide formation in aging organic solvents and stored alkali metals. "A peroxide present as a contaminant in a reagent or solvent can change the course of a planned reaction" (1). That change can be a violent explosion.

In normal oxides each oxygen atom has a -2 oxidation state. In peroxides two oxygens form a nonpolar covalent bond with a net -2 oxidation state (2). The oxygen linkage (-0-0-) of the peroxy group in some organic compounds is actually useful when properly handled. The (-0-0-) bond splits, producing free radicals which can initiate polymerization. This instability makes them useful in polymer industries (3). But industrial settings are far removed from first year chemistry courses. Some peroxides are so sensitive they have no commercial value.

Different peroxides vary in their degrees of hazard, depending on the structure of the compound and the concentration of the active oxygens. Dangerously reactive peroxides can build up in old solvents such as diethyl ether and isopropyl ether. Half-empty containers of ether can form treacherous peroxides from autooxidation. Peroxides of this type are more shock sensitive than TNT. Any purchase of ethers for use in a high school has to be questioned. Where the high school needs to be especially concerned is in the accumulation of unwisely purchased solvents such as ethers, or alkali metals such as potassium, in which dangerous peroxides could be accumulating.

Even hydrogen peroxide should be handled with extreme care, particularly the 30% solution commonly found in high school labs. Besides being a very strong oxidant, contamination of the $\rm H_2O_2$ from metals and metal ions can cause violent decomposition reactions as large quantities of oxygen gas are generated. Dilute hydrogen peroxide mixed with dilute acetic acid forms explosive peracetic acid when heated to $110^{\circ}\rm C$. Hydrogen peroxide mixed with organic matter under some circumstances has the same explosive power as an equivalent weight of TNT (4).

One high school chemistry teacher inherited a bottle of cyclohexene that had been in the stockroom for at least a decade. The teacher, new to the school, noticed crystals in the bottle and suspected peroxide formation. The problem was reported to school authorities. After some persuasive conversation, they took the problem seriously. A phone call to the state police was made to have the bottle removed. The police checked with chemical safety experts and were convinced of the hazard. When school was not in session, the police removed the bottle with the same care as a suspected bomb (5).

"Safety Tips" presents safety information and practical suggestions to meet the special needs of high school chemistry teachers. It is also a forum in which teachers can share their experiences and seek solutions to safety related problems.

On the question of possible unstable, unwanted peroxide contamination of a reagent, one is wise to err on the side of safety. There are tests that will detect the presence of peroxides. However (6).

Any suspect material will be in some kind of container. If there is a deposit of sensitive peroxide in and around the cap of that container, the act of removing the cap—in order to obtain a sample to test for the presence of peroxide—may initiate the detonation of the peroxide. This test, though reliably positive for the presence of peroxide, yields undesirable results. Therefore, a first principal policy statement:

If I think I ought to make a test for the presence of peroxide then I have already kept it too long; instead of testing I should assume as certain that unstable peroxides are present and dispose of the material in a suitable manner.

Life would be much easier if there were a list of peroxide formers and reliable information on how to store them safely. Unfortunately, the problem is too complex for the simple solutions. CHAS Notes (7) offers some suggestions on potential peroxide formers. One such list includes organic compounds with these structural components (examples are illustrative, not definitive):

Other compounds and elements:

alkali metals potassium alkali metal alkoxides and amides sodamide organometellics Grignard reagents

Regarding the problem of storage, as noted above, high school teachers should carefully weigh the merits of getting involved with peroxidizable reagents before ordering supplies. Does the benefit justify the risk? It is hard to imagine any situation where a safer experiment, a good film, or even a challenging problem for the computer would not suffice to

teach the principles involved at the high school level. If chemicals prone to peroxide formation must be purchased, limit the order to the minimum amounts required. Then, "store peroxide formers out of heat and light in closed vessels, perferably in the container furnished by the supplier . . . [and] keep no peroxide formers on hand longer than two months' (7).

If a high school teacher has to handle peroxides or potential peroxide formers, a few cautions for handling them should be followed (8):

- 1) Unused peroxides should never be returned to the container.
- 2) Clean up organic peroxide spills immediately with vermiculite; dilute the waste to a concentration of 2% or less, then transfer to a polyethylene screw-top container containing an aqueous solution of a reducing agent such as ferrous sulfata.
- Never concentrate by evaporation or distillation.
- Do not use metal spatulas; instead, use ceramic or wooden spatulas. This caution is particularly important for those using alkali metals.

- 5) Avoid all potential for friction or impact hazards. No grinding!
- 6) Do not use glass containers with screw caps or glass stoppers for storage. Use polyethylene bottles with screw caps.

In a high school lab, where the naiveté of students can make any experiment risky, peroxide problems are best avoided by avoiding the chemicals that can produce them.

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tested demonstrations

Diffusion of Gases—Kinetic Molecular Theory of Gases

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The pressure inside a container with a porous surface can he changed due to the rate of diffusion of low molecular weight gases.

Materials

Plastic wash bottle (250-ml or 500-ml) Porous cup (such as Coors #60495 or 70001 or Sargent-Welch #S-437550A) Rubber stoppers and glass tubing Cylinder of H₂ or He 600-ml beaker

Procedure

Hook up the wash bottle and porous cup with the stoppers and glass tubing as indicated in the figure. Fill the wash bottle with water, but not so full that siphon action would begin. A dye such as methylene blue may be added to improve visibility from a distance. Fill an inverted beaker with hydrogen or helium gas. Place the inverted beaker over the porous cup. Water should "magically" 1 begin to squirt from the wash bottle. Lift the beaker, and it stops. Repeat the procedure. Empty the beaker of the gas by turning it right side up (you



may wish to discuss gas densities at this point) and try it again. This time the wash bottle does not squirt since the beaker has air in it.

Problems

The porous cup *must* be dry. A wet surface slows the diffusion sufficiently to prevent the bottle from squirting. If the porous cup gets wet, oven dry it for several hours. Also, if the water level in the wash bottle gets too low, the demonstration does not work well.

Hazards

Hydrogen is flammable. Helium is much safer.

Discussion

Low molecular weight gases diffuse or effuse more rapidly than do heavy gases. (Kinetic Molecular Theory of Gases says two gases at the same temperature have the same average kinetic energy, $\overline{KE} = \frac{1}{2}mv^2$, so light gases must have higher average velocities and hence diffuse faster.)2 Thus, when the beaker is held over the porous cup, H2 or He goes into the cup faster than the other heavier gases (air) can leave, thereby creating a positive pressure. Measurements made on this system with a manometer indicate that the pressure inside the porous cup can increase by almost 0.25 atm within 10-15 s. The process described here occurs due to the difference in concentration of H₂ or He on the two sides of the porous surface. The pressure difference between the two sides of the porous surface should drop to zero after the concentration of H_2 or He is the same on both sides. Again manometer measurements verify that the pressure drops slowly to atmospheric pressure. Within 1-2 min, 90% of the peak pressure is lost. If the H2- or He-filled beaker is removed after it has been over the porous surface for more than a minute, the pressure difference is immediately reversed as H2 or He diffuses out of the cup, creating a negative pressure. Air bubbles are observed entering the wash bottle through the spigot. Of course, in a short time equilibrium will again be established and no pressure difference will exist.

³ A digression on the difference between "magic" and a scientific demonstration: In magic one tries to deceive the audience by sleight of hand, but in scientific demonstrations, one uses laws and theories to explain observations. It would be very easy to perform this demonstration as a magic trick if the gas cylinder and its tubing were con-

² Boikess, R. S., and Edelson, E., "Chemical Principles," 2nd ed., Harper & Row, New York, 1981, pp. 113-116.

Chemical Storage of Solar Energy Using an Old Color Change Demonstration

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One of the major problems associated with the utilization of solar energy as a primary energy source for heating and cooling is the lack of a practical, efficient means of storing large amounts of energy after it has been collected (1). Below we describe the results of a student research project that could be used as a class or group experiment at the high school or first-year college level to illustrate the potential of hydrated salts for solar energy storage. It involves a demonstration often used to illustrate the ease with which some transition metal ions can change their coordination numbers (2). The demonstration requires a solution, containing approximately 10 g CoCl₂-6H₂O per 100 mL of isopropyl alcohol, that has been made distinctly pink by the dropwise addition of water.

At room temperature, the pink color of the solution is due to the octahedral complex, $Co(H_2O)_6^{2+}$. On heating in a hot water bath, the solution changes to a deep blue color due to the formation of the tetrahedral complex, $CoCl_4^{2-}$. This system can be described by the equation

$$Co(H_2O)_6^{2+} + 4Cl^- + heat \rightleftharpoons CoCl_4^{2-} + 6H_2O$$

Since this reaction is endothermic, it provides a potential means of storing solar energy via the unhydrated CoCl₄²⁻ ion. On cooling (the reverse reaction), energy would be released based on the heat of hydration and the specific heat of solution

To determine the potential capacity of this system for solar energy storage it is necessary to know the following: (1) the solubility of CoCl₂ in isopropyl alcohol at different temperatures, (2) the heat of hydration for CoCl₄²⁻, (3) the specific heat of the solutions, and (4) the effects of H₂O and Cl⁻ on the equilibrium system. Based on these data and published data on solar energy systems and energy use, calculations can be made to determine the amount of CoCl₂-6H₂O/isopropyl alcohol solution that would be needed to store the necessary energy required for a average residence in the United States. The same procedures may also be applied to other hydrated salt systems in anhydrous solvents.

The different sets of data needed to complete this project may be assigned to different students or groups. The only items of equipment needed to obtain the data are a balance, constant temperature bath, drying oven, and a visible-range spectrophotometer. Expanded polystyrene cup calorimeters can be used for determining the heat of hydration and the specific heat. The needed solar energy and energy use data can be obtained from a number of publications (3).

Experimental Procedures

Determination of Calibration Plots

In order to measure the amounts of $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$ present in the test solutions, Beer's Law plots must be determined since it is necessary to use the Beer's Law ex-

Part of this paper was presented at the Sixth International Conference on Chemical Education, University of Maryland at College Park, August, 1991.

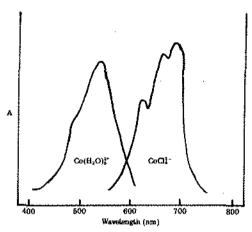


Figure 1. The visible spectra of Co(H₂O)₆²⁺ and CoCl₄²⁺.

pressions for a system with two absorbing species (4). A spectrophotometric scan of both the pink and blue solutions indicated a maximum absorbance of the pink complex at 513 nm and a maximum absorbance of the blue complex at 655 nm (see Fig. 1). Calibration plots of absorbance versus molarity were made for $CoCl_d^{2-}$ at 513 and 655 nm and for $Co(H_2O)_6^{2+}$ at 513 and 655 nm, using a cell pathlength of 1.0 cm, and the following molar absorptivity values determined (P = pink complex and B = blue complex)

plex and B = blue complex)
$$a(L/\text{mole-cm})$$
513 nm
$$a_{B'} = 18.0 \qquad a_{P'} = 5.46$$
655 nm
$$a_{B''} = 491 \qquad a_{P''} = 0.60$$

Since the molar absorptivity constant a_P'' is very small compared to a_B'' , it can be approximated that at 655 nm

$$c_{\rm B} = \frac{A_{655}}{a_{\rm B}''b_{\rm B}''}$$

However at 513 nm the relatively large value for $a_{B^{'}}$ requires that

$$c_{\rm P} = \frac{{\rm A}_{513} - a_{\rm B}' b_{\rm B}' c_{\rm B}}{a_{\rm P}' b_{\rm P}'}$$

Thus, it is necessary to determine $c_{\rm B}$ before calculating the value for $c_{\rm P}$.

Solubility Determinations

The amount of cobalt chloride which can be dissolved in isopropyl alcohol solutions would be important to the efficiency of a solar energy storage system; the more that can be dissolved, the greater the energy storage capacity. For these determinations twelve solutions were prepared using three different concentrations of water and heated at four different temperatures. Large amounts of CoCl₂-6H₂O were placed in each solution to insure saturation. After one hour, the values for $c_{\rm B}$ and $c_{\rm P}$ were determined from absorbance measure-

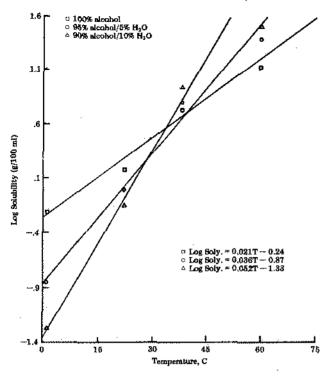


Figure 2. Logarithmic plots of the solubility of CoCl_{2*}(H₂O)₆ in isopropyl alcohol/H₂O solutions at different temperatures.

ments, and then added to obtain the total concentration of dissolved cobalt chloride. The results of these measurements are shown in Figure 2.

Determination of Product/ Reactant Ratios

For the reaction in this study the equilibrium constant expression can be written as

$$K_{\rm eq} = \frac{[{\rm CoCl_4^{2-}}][{\rm H_2O}]^6}{[{\rm Co(H_2O)_6^{2+}}][{\rm Cl^-}]^4}$$

Due to the difficulty in measuring values for the free water concentration in this system, values for the ratio $[CoCI_4^{2-}]/[Co(H_2O)_6^{2+}]$ were used instead of K_{ac} .

[Co(H₂O)₆²⁺] were used instead of K_{eq}.

Effects of H₂O on the CoCl₄²⁻/Co(H₂O)₆²⁺ ratio. Fifteen solutions were prepared with five different concentrations of added water and heated at one of three different temperatures. After one hour of heating, the product/reactant ratios were determined and plotted as a function of temperature (Fig. 3). This data is important since it shows the sensitivity of the system to the water content of the solvent.

Another set of measurements was made at room temperature to further illustrate the sensitivity of this equilibrium system to water. For this experiment seven solutions of varying water concentration and a constant total concentration of cobalt chloride were prepared and their $\text{CoCl}_4^{2-}/\text{Co}(\text{H}_2\text{O})_6^{2+}$ ratios determined after one hour. The sample with the highest water concentration was selected as a reference and a plot of the per cent increase in the $\text{CoCl}_4^{2-}/\text{Co}(\text{H}_2\text{O})_6^{2+}$ ratio versus the per cent decrease in water concentration was made using the other six sets of data (see Fig. 4).

Effects of Cl^- on the $CoCl_4^{2-}/Co(H_2O)_8^{2+}$ ratio. For this experiment five solutions of varying chloride concentration and a constant total concentration of cohalt chloride were prepared and their product/reactant ratios measured after one hour at room temperature. The sample with the lowest chloride concentration was selected as a reference and a plot of the percent increase in the $CoCl_4^{2-}/Co(H_2O)_6^{2+}$ ratio versus the percent increase in Cl^- concentration was made (see Fig. 5).

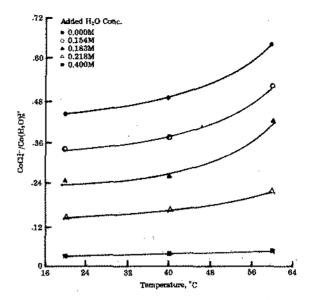


Figure 3. Effect of temperature and $\rm H_2O$ on the $\rm CoCl_4^{2--}/Co(H_2O)_8^{2+}$ ratio.

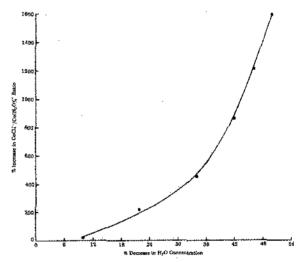


Figure 4. Effect of H₂O on the CoCl₄2⁻⁻/Co(H₂O)₆2⁺ ratio.

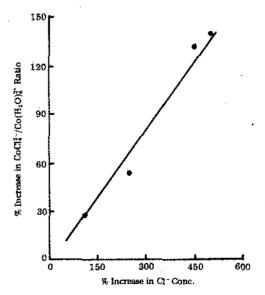


Figure 5, Effect of CIT on the CoCl₄2-/Co(H₂O)₆2+ ratio.

Determination of Specific Heat

The specific heat describes the amount of heat a particular solution can absorb. A solution of 0.1 M cobalt chloride in isopropyl alcohol was selected as representative for this study, and a double-walled expanded polystyrene, student-type calorimeter used for the measurements (5). A value of 3.37 J/g/°C was determined.

Determination of the Heat of Hydration of CoCl-

The major reason for considering a hydrated salt system for energy storage is that the heat of hydration associated with the salt can store and release larger amounts of energy than just the specific heat associated with the heating and cooling of a liquid such as water. Using a modified Nalgene® Dewar flask with cover for a calorimeter and a previously reported method for determining the heats of hydration (6), a value of 92.7 kJ/mole was obtained for the heat of hydration of CoCl₂. This value is higher than a reported literature value of 76.8 kJ/mole for the heat of solution of CoCl₂ (7), and a value of 89.4 kJ/mole calculated based on the heats of solution for CoCl₂ and CoCl₂·6H₂O (8).

Energy Calculations

Some basic properties of a solar heating system using cobalt chloride as a heat storage medium were calculated based upon data collected in this study and from various published documents.

Daily Heat Energy Requirement for the Average U.S. Residence

Assuming that the average U.S. residence of 1500 ft² requires 1000 therms of heat per year (3), the daily heat requirement is

 $(1000 \text{ therms/yr}) \times (1.055 \times 10^8 \text{ J/therm})$

 $\times (1 \text{ yz/365 days}) = 2.89 \times 10^8 \text{ J/day}$

Concentration of Cobalt Chloride

The solar collector was assumed to concentrate incoming heat at a 4:1 ratio, and to operate at a mean temperature of 60°C. Using Figure 2, the concentration of cobalt chloride in a saturated solution of 100% alcohol was determined to be 10.47 M at 60°C.

Heat Content of Solution

The heat content of the solution is due to both the heat of hydration and the specific heat. In Figure 3, it is seen that for 100% alcohol at 60° C, the $CoCl_4^{2-}/Co(H_2O)_6^{2+}$ ratio is 0.64 and at 20°C it decreases to 0.44. From these values it can be determined that at 60°C, 39% is unhydrated, and at 20°C, 30.6% is unhydrated. Thus on cooling from 60°C to 20°C, 8.4% of the CoCl₄²⁻ undergoes hydration.

 $(92.7 \text{ kJ/mole}) \times (10.47 \text{ moles/L}) \times (0.084) = 81.5 \text{ kJ/L}$

The specific heat of 1.0 L of a 10.47 M solution is approximately

 $(3.37 \text{ J/g/}^{\circ}\text{C}) \times (0.793 \text{ g/mL}) \times (1000 \text{ mL/L}) = 2.67 \text{ kJ/}^{\circ}\text{C/L}$

Volume of Energy Storage Solution Needed

For these calculations it is assumed that the energy storage solution is circulated only once in a 24-h period and that the temperature of the cooled solution is 20°C and that of the heated solution is 60°C. The heat absorbed per liter of the solution is

$$81.5 \text{ kJ/L} + 2.67 \text{ kJ/°C/L} \times 40^{\circ}\text{C} = 188 \text{ kJ/L}$$

Since the amount of heat needed per day is 2.89×10^8 J/day. the required volume of solution needed per day is

$$(2.89 \times 10^5 \text{ kJ/day}) \times (1 \text{ L/188 kJ}) = 1537 \text{ L/day}$$

= 1.067 L/min.

Volume of Storage Tank Required

The volume of the heat storage tank required to store a one-day supply of heat using the above conditions is thus 1537 L or 1.537 m³. If a 50% efficiency factor for heat storage is assumed, a 7.9-m3 tank could store a three-day supply of energy. If only water were to be used for energy storage under these conditions, a volume of 10.4 m³ would be required. Obviously, if the solution were circulated faster than 1.067 L/min, more energy would be available and thus a smaller storage volume would be required. Circulation rates of 10-40 L/min are commonly used for aqueous systems.

Solar Heat Collector Surface Area Required

Assuming that the solar collector is exposed to 2.05×10^4 kJ of heat per square meter of surface area per day, an accepted figure for the southern United States (3), the available solar energy per square meter per minute would be 14.2 kJ. Earlier we found that 2.89×10^5 kJ/day, or 200 kJ/min, of heat are needed for the average residence. Assuming a 100% collector efficiency, the area of collector surface needed is

$$(200 \text{ kJ/min}) \times (1 \text{ m}^2 \text{ min}/14.2 \text{ kJ}) = 14.1 \text{ m}^2$$

Assuming a more realistic figure of 50% efficiency for the collector, 28.2 m² of collector surface area would be required. Using a 4:1 heat concentration ratio and a 1:6 collector tubing area to collector surface area ratio, 42.3 m2 of collector area would be needed for the solar heat collector.

Possible Oil Dollars Saved by Using a Solar Heating System

Assuming that the residential heating requirements for the above residence are obtained only from imported oil, the oil dollars saved by using only solar energy would be

 $(1.066 \times 10^{11} \text{ J/yr}) \times (1 \text{ barrel/} 3.06 \times 10^{9} \text{ J})$

× (\$34/barrel) = \$1,184

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filtrates & residues

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Spectrophotometry: Mechanics and Measurement

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Purpose

This experiment is designed to be an introduction to spectrophotometry and to general spectral analysis techniques. Students will become acquainted with the basic components of a spectrophotometer and their functions, will use a spectrophotometer in an open-ended experiment, and will use Beer's Law in several different ways. In addition, they may compare the detectability (tolerance) of the spectrophotometer with visual detection limits as an optional activity.

The concepts involved in these experiments are not new. The arrangement and method of presentation is, however, thought to be unique at the secondary level.

Equipment

Spectruphotometer
Pipets (1-ml through 25-ml, in 5-ml graduations)
Volumetric flasks (100-ml)
100-200 ml of stock solution for each unknown (see special notes)

Procedure

Because of the open-ended nature of these experiments, students do not necessarily need a detailed, step-by-step procedure. They may only be given a general procedure and an "unknown" solution. Both the general procedure and one abbreviated step-by-step procedure are given in the following sections.

Spectrophotometric Determination of the Concentration of an Unknown Solution

General Procedure

Students first determine the wavelength of maximum absorbance of a colored "unknown" solution by scanning. They prepare a series of solutions of this "unknown" of varying concentrations (0.01–2.0 M). These solutions are from this point referred to as standards. Then, at the optimum wavelength (identified earlier), students determine the absorbance of each of the standards. Subsequently, the calibration curve is prepared by graphing the results of absorbance versus concentration. Using this graph, the students apply Beer's Law to identify the concentration of the original "unknown" solution.

Abbreviated Procedure: The Absorption Spectrum

1) Prepare the spectrophotometer for use, as directed.

 Fill one cell with distilled water and the other cell with your colored "unknown" solution.

- Adjust the wavelength selector knob to 350 nm; determine the percentage transmittance of your unknown solution at this wavelength.
- Record the wavelength and corresponding percentage transmittance obtained.

New lectures and laboratory experiments and directions in Leaching chemistry through the use of the laboratory are provided in this feature. Experiments will be fully detailed and will be field tested before they are published. Contributions should be sent to the feature aditor.

- Repeat the above process, in increments of 50 nm, until a wavelength of 800 nm is reached. Record the data obtained.
- 6) By looking over the data, determine the wavelength regions where a peak of absorbance (minimum %T) occurred. In these regions, scan (repeat steps 3-5) the solution in increments of 10 nm.
- 7) Again, where a peak of absorbance occurs (minimum %T), scan the solution again; first in increments of 5 nm, and then in increments of 2 nm, to determine the exact wavelength of minimum transmittance. It should be noted that the regions scanned in these smaller increments should only be less than 50 nm. This entire procedure is called scanning a spectrum.

8) Calculate the absorbance from the percentage transmittance data and graph the results (absorbance versus wavelength). This graph is known as an absorption spectrum.

Abbreviated Procedure: Calibration Curve/ Beer's Law

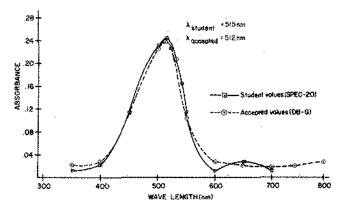
- 1) Using volumetric flasks, pipets, and distilled water, prepare a series of solutions of your "unknown" from a stock solution identified by your instructor. (Instructor's Note: Usually 1 M stock solutions are used.) At least four solutions of varying concentrations should be prepared; for example, 0.1 M, 0.25 M, 0.50 M, and 1.0 M solutions might be considered a series of standards. Be sure to record solution preparation methods in your notebook.
- 2) Prepare the spectrophotometer for use, as directed.
- 3) Adjust the wavelength selector knob to the maximum absorption peak determined in the Absorption Spectrum Procedure, which will be called the optimum wavelength. If two strong absorption peaks occur, choose the wavelengths nearest 500 nm, that is, choose the wavelength nearest the center of the visible spectrum, rather than at one end.
- 4) At this optimum wavelength, determine the percentage transmittance for each prepared solution as well as for your unknown. Record the data. (The reference solution should be distilled water.)
- 5) Calculate the absorbance from your percentage transmittance data. Graph the results, absorbance varsus concentration for all the standards prepared. This graph is known as a calibration curve or a Beer's Law plot.
- From the linear relationship graphed, read the concentration of your unknown. Record this concentration and report it to your instructor.

Limits of Detectability (Optional) General Procedure

Students prepare several solutions (10-20) of varying concentrations of their "unknown" ranging from very dilute to very concentrated and determine the absorbances at the optimum wavelength. To determine the limits of detection, the students continue to vary the concentration of the solutions until a concentration is reached which exceeds 85% transmittance (lowest limit) or transmits less than 20% (upper limit). These two concentrations, then, are identified as the limits of detectability for the unknown substance.

Abbreviated Procedure: The Limits of Detectability

- Prepare 1 M, 0.10 M, and 0.01 M solutions of the chemical compound you studied previously. Record preparation methods in your notebook.
- Prepare the spectrophotometer for use as directed. Adjust the wevelength to the optimum wavelength determined in the Absorption Spectrum princedure.
- At this optimum wavelength, determine and record the percentage transmittance for each prepared solution. The reference solution should be distilled water.
- If needed, prepare more dilute solutions and repeat the measurement procedure (step 3) until a solution concentration is



Graph of absorbance versus wavelength for determining the optimum wavelength for $Co(NO_3)_2 \cdot 6H_2Q$.

reached, that, when tested, transmits 80-85% of the light. This solution represents the lower limit of detection concentra-

- 5) If needed, prepare more concentration solutions and repeat the measurement procedure (step 3) until a solution concentration is reached, that, when tested, transmits only 15-20% of the light. This solution represents the upper limit of detection concentration. Be sure to record all data, including the solution preparation method.
- 6) In order to make a comparison between the instrumental detection limits and the visual detection limits, note the color and shade of each solution tested.
- Calculate the absorbance from the percentage transmittance data for each solution tested, and put in tabular form with the corresponding concentrations (in molarity).
- (optional) Plot the data (absorbance versus concentration) to determine whether Beer's Law is obeyed over the entire range of concentrations tested.

Special Notes

- This experiment offers the students the opportunity to explore spectrophotometry while gaining the experience, practice, and confidence necessary for independent research. Although students are not usually given a detailed, refined procedure, they are given the general instructions presented here, along with a list of background articles (1-9). Therefore, this experiment would be especially useful in an AP or second-year chemistry class. Other references appropriate for the instructor and/or student are listed below (10-20).
- 2) The preparation for this experiment is extensive the first time, since all accepted values must be determined experimentally.

On a modern spectrophotometer (like the Beckman DB-G), where manual and automatic scanning can be done interchangeably, the absorption spectrum of several colored solutions can be obtained. For each of these solutions, the concentration is adjusted so that no percentage transmittance (300-800 nm) falls below 10%, and so that the major peaks of absorption (400-700 nm) are clearly indicated, preferably with at least a minimum transmittance of 25%. These solutions, then, become the student "unknowns." For student use, they should be labeled with their chemical name but without a concentration.

It is usually convenient, at this time, to prepare 100-200 ml of 1 M stock solution for each compound used. In this way, solutions are available for many of the standards and weighing can be kept to a minimum. All solutions should be stored in amber bottles. Alternatively, students may prepare their own stock

The following compounds seem to work best as student "unknowns": nickel(H) choride hydrate, nickel(H) nitrate hydrate, cobalt(II) chloride hydrate, cobalt(II) nitrate hydrate, copper(II) nitrate hydrate, copper(II) sulfate hydrate, chromium(III) nitrate hydrate, iron(III) chloride hydrate, iron(III) nitrate hydrate, potassium permanganate and potassium chromate. The yellow solutions (iron chloride, iron nitrate, and potassium chromate) are more difficult to work with because the color remains intense even at lower concentrations. Neither manganese(II) sulfate nor potassium dichromate are recommended. Sample studeut data and a graph of absorbance versus wavelength for determining the optimum wavelength are given in the table and figure for Co(NO₃)₂-6H₂O.

Limits of Detectability (Student Data) for Co(NO₃)₂ · 6H₂O

wavelength ≈ λ ≈ 512 nm				elit = 0.05 mm		
dilution preparation from 1 M solution	mòlarity	ovc	% T	absorbance (calc)	cólár	
5 ml-10 ml	0.5 M	×	0.38	2.42	dk. red	
3 ml-10 mi	0.3 M	×	3.39	1.47	red	
2 ml10 ml	0.2 M	x	8.12	1.09	red	
17 ml- 100 ml	0.17 M*	×	15.8	0.801	It. red	
15 ml-100 ml	0.15 M	×	23.5	0.629	ft. réd	
12 ml 100 ml	0.12 M	x	22.0	0.658	lt. red	
10 ml~100 ml	0.10 M	x	31.2	0.505	lt. red	
5 ml~100 mt	0.05 M	x	61.2	0,213	pink	
3 ml-100 ml	0.03 M	×	74.7	0.127	pìnk	
2 ml-100 ml	0.02 M*	х	86.9	0.061	ft. plnik	
1 ml⊷100 ml	0.01 M	x	96.3	0.018	pale pin	

O = opaque V = visibly detectable C = clear (not visibly detectable)

= detectable fimite (spectrophotometric)

This instructor scanned the solutions listed on a Beckman DB-G. The data obtained, with the corresponding absorbances, was available for comparison as a set of "theoretically-accepted" values. Therefore, errors were quickly identifiable. The most common student errors are: (1) dilution errors in either calculation or volumetric equipment usage and (2) the choice of a minor absorption peak (on one end of the visible spectrum) as the optimum wavelength. Students find it helpful to develop a computer program to calculate absorbance and print out the data calculation.

The only disadvantage of the experiment is the extensive solution preparation required. The fact that it is an introductory experiment does mean that students may do more retrials than is usual for an experiment. However, in spite of this, all students seem to find the experiment interesting and a bit of a challenge, and are able to complete it well within eight hours of laboratory time.1

Editor's Note: To obtain further information on student handout materials, laboratory procedures, and DB-G ("accepted values") data, contact the author directly.

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A New Method of Separating ²¹⁰Pb from Ra-DEF for a Radioactive Equilibrium Experiment

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The decay of ²¹⁰Pb to ²¹⁰Bi provides a good system to illustrate secular equilibrium between a long-lived parent and a short-lived daughter.

210Pb
$$\xrightarrow{\beta=0.061 \text{MeV}}$$
 210Bi $\xrightarrow{\beta=1.17 \text{MeV}}$ 210Po $\xrightarrow{\alpha 5.3 \text{MeV}}$ 206Pb (stable)

A general procedure of separating ²¹⁰Pb from ²¹⁰Bi for this experiment is by means of a precipitation technique (1). Carrier solutions made of bismuth nitrate and lead nitrate are generally used for the precipitation of either radioactive isotope. Incomplete separation of ²¹⁰Pb and ²¹⁰Bi may result if pH of solution is not carefully controlled in the precipitation procedure. Another difficulty involved is to handle small quantities of precipitate and to make it into a uniform and thin-layer sample for counting. We have recently developed a new method of separating 210Pb from 210Bi and 210Po by means of solvent extraction of their diethyldithiocarbamate (C₂H₅)₂CS₂⁻ complexes. This method involves a simple extraction procedure which allows complete separation of ²¹⁰Pb from Ra-DEF within several minutes. Since the radioisotopes are separated in different solutions, they can be easily transferred and made into uniform thin samples by evaporation. The experimental procedure and the basis of this separation method are described in this article.

Experimental

Reagents

The proposed extraction procedure requires a diethyldithiocarbamate (DDC) complex, Bi(DDC)3, which can be easily synthesized in the laboratory. The starting materials for synthesizing Bi(DDC)3 are sodium diethyldithiocarbamate and a bismuth salt such as bismuth nitrate. The former can be obtained from Baker or other major chemical companies. The synthetic procedure involves the reaction of Bi³⁺ ion with DDC in aqueous solution followed by extraction of the metal complex with chloroform. After discarding the aqueous phase, ethanol was added to the solution and the mixture was heated to 70°C to drive off chloroform. To avoid inhalation of chloroform vapor, the whole experiment should be carried out in a hood. After evaporation, Bi(DDC)3 which is insoluble in ethanol, is recovered by filtration. The metal complex can be stored in a bottle for a prolonged period of time. Radioactive Ra-DEF solution used in the experiment cen be obtained from Amersham or New England Nuclear.

Separation of 210 Pb from Ra-DEF

About 0.1 to 1 μ Ci of Ra-DEF is sufficient for a typical radioactive equilibrium experiment. ²¹⁰Pb is separated from a solution of Ra-DEF by extracting ²¹⁰Bi and ²¹⁰Po into a chloroform solution containing Bi(DDC)₃. The extraction can be performed in a 5-ml polyethylene liquid-scintillation vial with a plastic cap. The Ra-DEF solution is introduced into 1 ml of a 2.4% HNO₃ solution placed in a plastic vial. An equal volume of CHCl₃ solution containing about 1.5 \times 10⁻³ M Bi(DDC)₃ is then added to the radioactive solution. The acid solution is used to prevent adsorption of radioactivities to the

container walls and to control the forms of the ionic species in solution. After shaking the mixture for about a minute, the system is allowed to stand still for the separation of two phases. If a centrifuge is used, phase separation can be achieved within a minute. The aqueous phase which contains pure ²¹⁰Pb is ready for the secular equilibrium experiment. The time when two phases are separated is taken as the zero time for the experiment.

To prepare a pure ^{210}Pb source, an aliquot of the aqueous solution is taken from the vial and placed in a planchet. Depending on the activities of the Ra-DEF solution used, the aliquot size can vary from $20~\mu\text{l}$ to $200~\mu\text{l}$. The radioactive solution is evaporated to dryness either at room temperature or under a lamp.

Results and Discussion

Theoretical Basis of the Separation Method

The proposed method of separating ²¹⁰Pb from ²¹⁰Bi and ²¹⁰Po is based on the difference in their complex formation constants with diethyldithiocarbamate. The extraction constants of some metal-DDC complexes are given in the table.

The extraction constant of Pb(DDC)₂ is much smaller than that of Bi(DDC)₃ or Po(DDC)₄. Therefore, Pb²⁺ can be separated from Bi³⁺ and Po⁴⁺ in aqueous phase using a metal-DDC complex which has an extraction constant between those of Pb(DDC)₂ and Bi(DDC)₃.

In this experiment, we chose to use $Bi(DDC)_3$ to extract ^{210}Bi and ^{210}Po from the Ra-DEF solution. The concentration of $Bi(DDC)_3$ used in this experiment (about $10^{-3}\,M$) is much greater than that of ^{210}Bi present in the aqueous phase (about $4\times 10^{-11}\,M$). Because of the large extraction constant for $Bi(DDC)_3$, virtually all ^{210}Bi present in the aqueous phase should be extracted into the organic phase by isotope exchange with nonradioactive Bi in Bi(DDC). The extraction constant for $Po(DDC)_4$ has been determined to be greater than that of $Bi(DDC)_3$ (4). Therefore, in the extraction process, ^{230}Po will replace Bi^{3+} to form $Po(DDC)_4$ leaving essentially pure ^{210}Pb behind in the aqueous phase.

Growth of 210Bi from 210Pb

In general, the growth of a radioactive daughter product from a pure parent can be expressed by the following equation (5):

$$A_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} A_1 \left(1 - e^{-(\lambda_2 - \lambda_1)t} \right) \tag{1}$$

Extraction Constants of Some Metal-Diethyldithiocarbamate Complexes

Metal ion	Complex	Extraction constant *	Reference
₽b ²⁺	Pb(DDC) ₂	9.48	(2)
Cu ²⁺	Cu(DDC) ₂	13.4	(2)
Ði ³⁺	Bi(DDC) _a	13.8	(3)
Po ⁴⁺	Po(DDC) ₄	14.1	(4)

*Extraction constant = $1/m \log K_{MODO)_m}$, where $K_{MODO)_m} \log \text{defined as } \{M(DDC)_m\}_{org} / \{M^m\} \} \{DDC^-\}^m \text{ and } m \text{ is the charge of the metal ions.}$

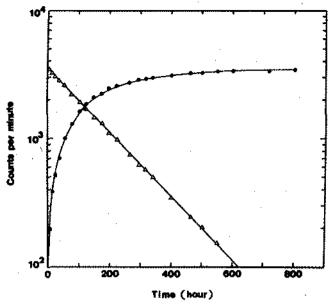


Figure 1. Growth of Bi from a pure 210pb sample ● and the decay of a pure 210Bi sample A.

where A and λ represent activity and decay constant and subscript 1 and 2 are for the parent and the daughter, respectively. If λ_2 is much greater than λ_1 as in the case of a long-lived parent and a short-lived daughter, eqn. (1) can be simplified as

$$A_2 = A_1(1 - e^{-\lambda_2 t}) \tag{2}$$

The beta activities from the decay of 210Bi can be measured by a Geiger-Müller counter. A thin aluminum absorber (about 10 mg/cm²) should be placed between the sample and the G-M tube to remove weak beta emitted from 210Pb and to absorb the Po alpha particles. The growth of 210Bi from a pure 210Pb source obtained by this method is shown in Figure 1. The decay of a pure 210Bi source obtained from the same experiment is also shown in Figure 1.

Since at equilibrium $A_1 = A_2$, eqn. (2) can also be expressed as

$$A_2 = A_2^{eq} (1 - e^{-\lambda_2 t}) \tag{3}$$

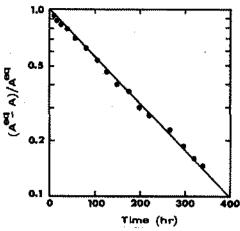


Figure 2. Plot of $(A_{\alpha} = A)/A_{\alpha}$ for the growth of ²¹⁰Bi,

If ^{210}Pb and ^{210}Bi are in equilibrium in the Ra-DEF solution to start with, the activity of 210Bi found in the organic phase after $Bi(DDC)_3$ extraction should represent A_2^{eq} . Another graphical illustration of the secular equilibrium is by plotting $\ln(A_2^{\text{eq}} - A_2)/A_2^{\text{eq}})$ versus t as shown in Figure 2. The slope of the line should be $-\lambda_2$.

This new method of separating Ra-DEF provides a simple and fast procedure for studying the secular equilibrium between ²¹⁰Pb and ²¹⁰Bi. It illustrates several important concepts such as solvent extraction, complex formation, and isotope exchange which are relevant to undergraduate laboratory experiments in radiochemistry and in analytical chemistry. The mathematical aspects of this experiment are important for understanding the relations between parent and daughter in a radioactive decay series.

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A Simple Method for Cleaning Mercury

The usual method for the purification of mercury involves initial filtration, treatment with dilute nitric acid, and then distillation under reduced pressure. The facilities required are not always available in school laboratories and in many instances such highly purified mercury is not essential. Often, all that is required is a shiny mercury that does not stick to glass, and is suitable for filling manometers, etc. The following procedure is extremely simple, requires nothing more than a bottle and some sugar, and converts all those dirty old mercury samples into a bright, shiny, free-flowing liquid again.

Procedure. Place the sample of mercury to be purified (say 1-10 ml) in a glass (or plastic) jar with a tight-fitting lid, add an equal volume of white sugar crystals (ordinary sucrose), and shake vigorously for several minutes. Pour the resulting mercury/sugar mixture into a large beaker or jar containing water, stir gently until the sugar has dissolved, decant the sugar solution and wash the mercury several times with water. The mercury can be dried either by rinsing several times with acetone, or by air-drying after removing the last droplets of water with a little absorbent paper (filter paper).

We have been unable to find any reference to this method in the more common inorganic chemistry texts, but a similar procedure was reported late in the last century. No explanation was offered as to why the method works, but presumably the major impurities (metal oxides, dust) are adsorbed onto the surface of the sucrose and in this finely dispersed form are easily floated off by the water upon dissolution of the sucrose.

CAUTION; Carry out in a well ventilated area and carefully recover any spilt mercury droplets, Mercury vapor is highly poisonous and the effect is cumulative.

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³ 1874--1959.

Growth and Decay

An Experiment Demonstrating Radioactivity Relationships and Chelate Solvent Extraction Separations

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Many important techniques discussed in lecture material frequently are not covered by laboratory experiments due to limitations in available laboratory time. Thus, experiments which demonstrate more than one concept are often more beneficial to the student than those which cover only one topic. We have attempted to include in the undergraduate radiochemistry laboratory course at West Virginia University experiments which teach both important radiochemistry concepts and analytical chemistry techniques that are not covered in our formal analytical laboratory courses. These experiments include the determination of solubility product and solvent extraction partition coefficients, quantitative paper and thin-layer chromatography, metal separations by ion exchange and solvent extraction, X-ray fluorescence and activation analysis.

One of the experiments, the separation of lead and bismuth by chelate solvent extraction, is of interest because of the simplicity which the use of radiotracers allows in its demonstration. Chelate solvent extraction metal separations are usually discussed in the introductory analytical course but are seldom demonstrated by experiment. Yet the separation of lead and bismuth may be conveniently followed with ²¹²Pb and ²¹²Bi which are readily obtained from natural thorium. Furthermore, the parent-daughter relationship and the relatively short half-lives of the tracers make possible the teaching of the laws of radioactivity in the same experiment.

Theory

Metal ions may be extracted very effectively from aqueous solutions by the formation of chelates with weak acids which are soluble in organic solvents. The general chelate extraction process may be represented by

$$M^{n+} + n(HR)_0 \approx (MR_n)_0 + nH^+$$
 (1)

for a metal ion, M^{n+} , and chelate, HR, with the subscript "o" denoting the organic phase and no subscript denoting the aqueous phase. A nonthermodynamic equilibrium constant may be used to describe the process. That is

$$K_{\rm ex} = \frac{[MR_n]_0 [H^+]^n}{[M^n]_0 [HR]_0 n}$$
 (2)

Quantitative separation of metal M' from metal M'' is defined as

$$\frac{[\mathbf{M}'\mathbf{R}_n]_o}{[\mathbf{M}''\mathbf{R}_n]_o} > 100 \tag{3}$$

for the organic phase, and

$$\frac{[M']}{[M'']} < 0.01$$
 (4)

for the aqueous phase. The separation factor, α , is defined as

$$\alpha = \frac{[\mathbf{M}'\mathbf{R}_n]_o[\mathbf{M}'']}{[\mathbf{M}''\mathbf{R}_n]_o[\mathbf{M}']}$$
 (5)

and must be greater than 10^4 for quantitative separation. It may be seen from eqn. (2) that α is simply $K'_{\rm ex}/K''_{\rm ex}$ for two equally charged metal ions. For the separation of metal ions which differ by one unit in charge value, α is dependent on the

aqueous hydrogen ion concentration and the equilibrium chelate concentration in the organic layer, i.e.,

$$x = \frac{K'_{\text{ex}}[HR]_{\text{o}}}{K''_{\text{ex}}[H^+]}$$
 (6)

Where K'_{ex} is the extraction constant for the metal ion of larger charge value.

It is useful to express eqn. (2) in logarithmic form:

$$\log K_{\rm ex} = \log [MR_n]_0 + n \log [H^+] - \log [M^{n+}] - n \log [HA]$$
 (7)

Rearrangement gives

$$pH = \frac{1}{n} \log \{MR_n\}_o - \frac{1}{n} \log [M^{n+}] - \log [HA]_o - \frac{1}{n} \log K_{ex}$$
 (8)

Equation (8) may be used to calculate the threshold pH value which is the lowest value for complete extraction of the metal. It may be seen that the threshold pH is dependent on the concentrations of extracted metal chelate, residual (unextracted) metal ion, and unreacted chelating reagent in the organic layer. Thus, a threshold pH is calculated for a particular metal extraction based on the anticipated concentrations; then a pH value higher than the threshold pH is selected and used in the extraction to allow for variable conditions.

The separation of $\rm Bi^{3+}$ from $\rm Pb^{2+}$ with dithizone (diphenylthiocarbazone) is a classic example of a chelate solvent extraction separation (1). The published $\log K_{\rm ex}$ values for these metals are 9.98 and 0.44, respectively (2) and these values allow the calculation of threshold pH values by eqn. (8) for the separation conditions presented in the experiment below. If a final aqueous metal concentration of $1\times 10^{-8}\,M$ is the criterion for complete extraction ($\sim 100\%$ extracted) from a solution of initial metal concentration $2\times 10^{-5}\,\rm with$ an initial organic phase of initial chelate concentration $8\times 10^{-5}\,M$, then the threshold pH values are 2.46 for $\rm Bi^{3+}$ and $\rm 5.83$ for $\rm Pb^{2+}$. Other values for the extraction of $\rm Bi^{3+}$ and $\rm Pb^{2+}$ have been calculated from eqn. (8) and are plotted in terms of the percentage of metal extracted versus pH in Figure 1. These curves

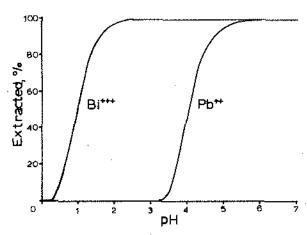
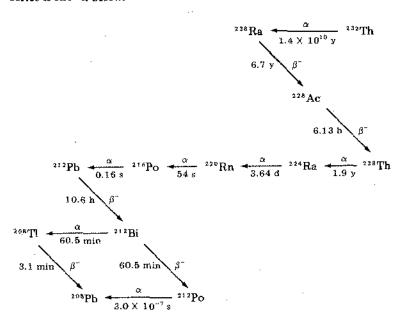


Figure 1. Effect of pH on the extraction of Bl $^{3+}$ and Pb $^{2+}$ with diffusione in carbon tetrachloride (initial concentrations: $C_M=2\times 10^{-5}~M$, $C_D=8\times 10^{-5}~M$).

are developed on the assumption that the dithizone concentration is negligible in the aqueous phase and there are no secondary complexing reagents present. Experimentally, it is found that optimum extraction for ${\rm Bi}^{3+}$ occurs at pH 3.2–3.4 and for ${\rm Pb}^{2+}$ at pH 8.6–9.2 (3). At pH 3.2, the α value for the ${\rm Bi}^{3+}/{\rm Pb}^{2+}$ separation calculated from eqn. (6) is well in excess of 10^4 and quantitative separation should be obtained.

Several natural radioactive series were discovered early in the history of nuclear science. One of these series has its origin in ²³²Th, which is 100% of natural thorium. The transformation of the radioactive ²³²Th to stable ²⁰³Pb proceeds through a variety of intermediate radioactive daughters by means of six alpha and four beta decays. This group of radionuclides is called the "4n" series since all the mass numbers are evenly divisible by four. The overall decay scheme of the thorium (4n) series is shown below.



It may be seen that ²²⁰Rn is an intermediate product of the decay series. The radon is released as a gas from the solid parent material and provides a ready source of the short-lived daughter products that follow its decay. To collect these daughter products a platinum wire electrode at high negative potential may be suspended over a solid thorium compound and the ²²⁰Rn, which is positively charged due to the loss of electrons in the decay of its parent, migrates to the electrode where it deposits its daughters as it decays. Such an apparatus for collecting the short-lived daughters may be built with common laboratory equipment and is known as a "thorium cow" because it may be "milked" at 2–3-day intervals (4). Other procedures for collecting the short-lived daughters have also been suggested (5, 6).

Washing the wire electrode with nitric acid provides a tracer solution consisting of ^{212}Pb ($t_{1/2}=10.6$ h), ^{212}Bi ($t_{1/2}=60.5$ min) and ^{208}Tl ($t_{1/2}=3.1$ min) in radioactive equilibrium. These tracers are very convenient for use in the monitoring of the Bi/Pb separation discussed above. Furthermore they exhibit properties which make them useful for studying the laws of radioactivity. The ^{212}Bi may be separated from the ^{212}Pb by the dithizone extraction procedure. The separated ^{212}Bi may then be monitored with a Geiger-Müller detector to determine its half-life. More ^{212}Bi will begin to form in the separated ^{212}Pb as it decays and this activity may be monitored to demonstrate the growth of daughter products in a radioactive parent.

The 212 Pb emits up to 0.4 MeV β^- in its decay whereas 212 Bi emits up to 2.2 MeV β^- particles. If an aluminum absorber of 80–100 mg/cm² thickness is placed between the separated 212 Pb and the G-M tube, the detector will initially record no

counts above background. However, the ²¹²Bi will "grow" with time in the parent ²¹²Pb according to the equation

$$\frac{dN_{Bi}}{dt} = \lambda_{Pb} N_{Pb} - \lambda_{Di} N_{Bi}$$
 (9)

where the λ values are the decay constants (0.693/ $t_{1/2}$) and N represents the number of atoms at a specific time after preparation of the radiochemically pure ²¹²Pb. Solution of eqn. (9) for the number of ²¹²Bi atoms at any decay time gives

$$N_{\rm Bi} = \frac{\lambda_{\rm Pb}}{\lambda_{\rm Bi} - \lambda_{\rm Pb}} N^{\circ}_{\rm Pb} \left(\exp(-\lambda_{\rm Pb} t) - \exp(-\lambda_{\rm Bi} t) \right) \tag{10}$$

when there is no initial 212 Bi present and N^{o}_{Pb} is the initial number of 212 Pb atoms. Figure 2 illustrates the growth and decay of the radioactive materials. It may be seen that a

maximum activity of the daughter is attained after 2.7 h and that radioactive equilibrium is attained after 3.8 h. After 3.8 h the ²¹²Bi decays at the same rate as it is produced and the activity of the mixture decreases with the characteristic half-life of the parent ²¹²Ph.

Experimental

Materials

A thorium cow should be prepared in the manner suggested by Morimoto and Kahn (4). Enough Th(OH)₄ should be present to give 500 counts/s by G-M counting on the wire to provide sufficient activity for good counting statistics. The apparatus may be set up in a fume hood and left as a permanent source of the short-lived daughters.

Two Geiger-Müller counters, each consisting of a G-M tube in a shielded lead castle and scaler/timer with aluminum absorbers (80 mg/cm²), and a NaI(Tl) Scintillation Detector with signal led into a Multichannel Analyzer (MCA) should be available for β - particle counting and

γ spectra collection. A standard pH meter with glass electrode and reference electrode is used for pH adjustment.

Chemicals. Electrode calibration buffers (pH 4.0, 7.0, and 10.0); 2 M nitric acid; 1/10 nitric acid; concentrated aqueous ammonia; 1/10 aqueous ammonia; ammonia/ammonium chloride huffer; Pb²⁺ carrier (0.1 mg/mL); Bi²⁺ carrier (0.1 mg/mL); dithizone (20.0 mg/L) in carbon tetrachloride.

Other materials. Test tube, Bunsen burner, separatory funnel, calibrated pipets, volumetric pipets, 10-mL volumetric

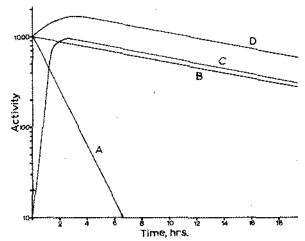


Figure 2. Activity variations with time. (A) decay of 212 Bi; (B) decay of 212 Pb; (C) growth and decay of 212 Bi in initially pure 212 Pb; (D) total activity of the mixture (B) + (C).

flasks, counting planchets, heat lamp, and disposable gloves.

Procedure

Warning: The student should be cautioned of the hazards of radioactive materials and volatile solvents. All work except counting should be carried out in fume hoods and students should wear safety glasses, lab aprons, and disposable gloves at all times. Film badges, pocket dosimeters, and/or survey meters should be used, and appropriate containers for radioactive waste disposal must be provided. The student should be aware of the particular hazard of accidentally ingesting alpha-emitting radioisotopes and therefore pipetting by mouth must not be done. Radon gas is released upon opening the thorium cow, and it must be kept in a properly vented fume hood to prevent inhalation.

Transfer the wire electrode from the thorium cow to the small test tube, add 2 mL of 2 M nitric acid, 0.5 mL of each carrier solution, and heat to dissolve the radioactive daughter products. Carefully transfer the cooled solution to a small beaker, immerse the calibrated pH electrode and add several drops of concentrated ammonia to neutralize the acid. Carefully adjust the pH to 3.0 using 1/10 ammonia and/or 1/10 nitric acid. Transfer the solution to a 10-mL volumetric flask and dilute to volume with distilled water. Pipet exactly 1.0 mL of this solution into a counting planchet (planchet "A") (Note 2) and evaporate to dryness with an infrared lamp. Planchet "A" serves a reference as it contains both 212Bi and 212Pb. Count the planchet in the G-M castle with the aluminum absorber in place and determine the original counts per minute (cpm) due to ²¹²Bi (Note 3). Meanwhile, quantitatively transfer the remainder of the aqueous solution to a separatory funnel with as small a volume of distilled water as possible (Note 1) and extract twice with 4-mL portions of the dithizone solution (Note 4). Quantitatively transfer the extract to a second 10-mL volumetric flask and dilute to volume with CCl4. Pipet 1 mL of this solution into a planchet (Planchet "B") and evaporate to dryness. Transfer planchet "A" to the NaI(T)) detector and record the cpm for the 0.24 MeV peak of 212Pb. Meanwhile count planchet "B" in the G-M castle under the same conditions as planchet "A" and record the 212Bi cpm. When the beta counts of 212Bi are recorded, transfer planchet "B" to the NaI(Tl) and record the gamma spectrum. Adjust the pH of the residual aqueous layer in the separatory funnel to 8.8-9.2 with a few drops of ammonia/ ammonium chloride buffer. Extract twice with 4-ml portions of the dithizone solution. Quantitatively transfer the extract to a third 10-mL volumetric flask and dilute to volume with

CCl4. Pipet 1 mL of this solution into a planchet (Planchet "C") and evaporate to dryness. Allow a 10-min decay of planchet "C" to reduce the activity of any coextracted 208 Tl $(t_{1/2} = 3.1 \text{ min})$ and count in the GM castle and NaI(Tl) detector as for planchets "A" and "B". The half-life of 212Bi may be determined graphically from the data recorded by counting planchet "B" in successive 10-min intervals for up to 2 h. The growth of 212 Bi in 212 Pb may be observed by counting planchet "C" for successive 10-min intervals in the second G-M castle with an aluminum absorber in place.

Results

Planchet "B" should contain 212Bi free from 212Pb contamination. Comparison of the beta activity cpm as determined by the G-M counting of planchets "A" and "B" will indicate the completeness of extraction and may be used to indicate the students' laboratory technique. The students may be asked to comment on the "error" in the beta counts of planchet "A" due to the gamma activity of 212Pb. The radiochemical purity of the extracted 212Bi will be evident from the lack of a 0.24 MeV 212Pb peak in its gamma spectrum. The completeness of the 212Pb extraction will be indicated by the comparison of the 0.24 MeV peak counts for planchets ' and "C". Any residual 212Bi that is coextracted with the 212Pb will be evident in the G-M count for planchet "C". The halflife of 212Bi may be determined from a plot of log activity (cpm) versus decay time. The growth of ²¹²Bi in ²¹²Pb may be demonstrated on the same graph by plotting the log beta activity of planchet "C" versus time.

Notes

- 1) The dilution should not significantly change the solution pH.
- The extraction of Bi3+ proceeds slowly. Shake the separatory fuunel for 4-6 min per extraction.
- The aluminum absorbers prevent the weak beta particles of ²¹²Pb from reaching the detector.
- 4) The student should calculate the net full energy peak counts as explained by Bauer et al. (7).

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Double Balloons—Long Term Protection for Sensitive Materials

In this laboratory we have been protecting basic solutions from carbon dioxide with an inert, dry nitrogen atmosphere. Nurmally one could use an ascarite tube (sodium hydroxide on asbestos) and change it periodically.

We have discovered an excellent way to protect a solution with an inert atmosphere with a very inexpensive apparatus: one balloon positioned inside a second balloon. One balloon is forced inside of a second balloon with a pencil and the inner balloon is inflated with nitrogen. These "double balloons" are attached to the solution through a glass tube which protects the solution with a positive nitrogen atmosphere.

These "double balloons" will last for several weeks and when they do break the outer balloon will always break first and leave the inner balloon still inflated. When one notices the breakage of the outer balloon, the double balloons should be replaced.

The beauty of this system is that if one is gone for a weekend, the outer balloon may break but not the inner balloon. We have not checked the duration of the second balloon but we do know it has gone for several days without breaking

> Robert C. Duty Illinois State University Normal, IL 61761

Phosphorus Determination by Derivative Activation Analysis: A Multifaceted Radiochemical Application

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Traditional neutron activation analysis (NAA) is a sensitive technique which is applicable to about two-thirds of the elements. The remaining third, whose nuclear properties make them difficult if not impossible to determine, include some biologically essential and environmentally important elements; conventional methods for many of these are both complex and fraught with interferences. Hence the development of derivative activation analysis (DAA), a method which extends the applicability of NAA to some of these elements, is particularly significant.

The determination of phosphorus is important in biology, physiology, and environmental science; however, the traditional gravimetric and colorimetric methods are cumbersome and lack the requisite sensitivity (1). We have adapted the DAA determination of phosphorus (2) for use in a radiochemistry laboratory course, although this experiment would be apropos in many other settings. The DAA method itself is useful in teaching not only the principles of NAA, but also problem-solving through the combination of several techniques. In this case, chemical, radiochemical, and instrumental methods are combined to accomplish what could not readily be achieved by any one of them alone.

Theory

In thermal NAA (3, 4), a stable nuclide captures a neutron to form a heavier isotope, which typically decays by the emission of a beta particle and one or more gamma rays. Since the gamma-ray energy is characteristic of the particular radionuclide, and the number of gamma rays emitted is directly proportional to the number of atoms of this radionuclide (and element), hoth qualitative and quantitative determinations are possible.

The success with which any particular element can be determined depends on its nuclear properties. The activable isotope should have a high isotopic abundance and a large thermal neutron capture cross section.³ The product nuclide must be radioactive, with an appropriate half-life. Moreover, the emission of one or more gamma rays by the product nuclide is essential to instrumental isolation of the element.

Vanadium exemplifies elements amenable to NAA:

$$^{51}\text{V} + \text{n} \rightarrow ^{52}\text{V} \rightarrow ^{52}\text{Cr} + \beta^{-} + \overline{\nu} + \gamma (1.43 \text{ MeV})$$

The isotopic abundance of ⁵¹V is 99.75% and its thermal neutron capture cross section is 4.91 harns. The product nuclide, ⁵²V, has a beta-decay half-life of 3.76 min and emits a 1.43-MeV gamma ray (5).

Neutron capture by phosphorus (100% ³¹P), on the other hand, produces ³²P, a pure negatron emitter (5).

$$^{31}P + n \rightarrow ^{32}P \rightarrow ^{32}S + \beta^{-} + \overline{\nu}$$

The absence of gamma-ray emission in the decay of 32P ren-

ders its determination by NAA in the presence of other beta emitters impracticable without extensive chemical separations.

Through the derivative activation technique, the desirable traits of an element such as vanadium can be employed to determine phosphorus. If phosphorus and vanadium are chemically combined with a definite stoichiometry, determination of the indicator element (vanadium) will give an indirect measure of the amount of phosphorus present. Of course, the chemical complex must be relatively stable and easily separable from any excess of the indicator element.

While phosphorus has been determined through activation of tungsten in tungstophosphoric acid (6), the more sensitive technique we have appropriated involves the formation of a stable phosphovanadomolybdate complex. This entity has a phosphorus-vanadium ratio of 1:2 under our experimental conditions and can be quantitatively extracted into methyl isobutyl ketone (MIBK) (2).

Once the complex has been formed and isolated, the procedure duplicates the NAA determination of vanadium. Following irradiation of the sample, the 1.43-MeV gamma rays from the decay of ⁵²V are instrumentally segregated and counted.

If absolute activity (A) can be ascertained, the amount of vanadium present can be determined from the activation analysis equation (3).

$$A = nf\sigma(1 - e^{-\lambda t_i})e^{-\lambda t_d}$$

where n= number of $^{51}{\rm V}$ atoms, f= flux density in neutrons cm $^{-2}$ s $^{-1}$, $\sigma=^{51}{\rm V}$ capture cross section, $\lambda=^{52}{\rm V}$ decay constant, $t_i=$ irradiation time, and $t_d=$ delay time between irradiation and counting. A more practical procedure is to treat the sample and a suitable standard identically. Then a direct comparison of gamma-ray count rate to quantity of vanadium (and hence phosphorus) present can be made.

Experiment

In this experiment, phosphorus is determined in a commercial plant food preparation (Ortho House Plant Food 5-10-5), nominally containing 10% phosphoric anhydride (P_2O_5). The student carries out the analysis logically from beginning to end, starting with sample preparation. However, in order to expedite matters and avoid cluttering the procedure with needless details, a minimal amount of groundwork is done by the instructor prior to the laboratory period.

Reagents. Stock solutions of ammonium meta-vanadate (0.01 M) and ammonium molybdate 4-hydrate (0.1 M) are prepared beforehand. The molybdate is particularly slow to dissolve and may precipitate upon standing. Nevertheless, since the concentration of these solutions is not crucial, filtration through coarse paper will make the molybdate solution utile. Concentrated nitric acid, MIBK, commercial plant food, and solid potassium dihydrogen orthophosphate (KH₂PO₄) for use as a standard are provided at the laboratory station.

Present address: Arkansas Eastman, Batesville, AR 72501.
 Present address: Rockwell International, Rocky Flats Plant, P.O.

464, Golden, CO 80401.

Paper presented at the Southeastern Regional Meeting of the American Chemical Society, Lexington, KY, November 1981.

³ Nuclear reaction cross sections are a measure of the probability of reaction occurring and are given units of barns, 1 barn = 1×10^{-24} cm².

⁴ This value represents a "minimum guarantee."

 $^{^5}$ At the time of our measurements the 1.25-mg (April 1971) $^{252}\mathrm{Cf}$ source had decayed approximately four half-lives, so that the flux quoted is about $V_{16}\mathrm{th}$ the initial value.

			Specific Activity				
Student	Count Rate (cpm)			Standard	Samples	Results	
Group	Standard	Samples	Background	(cpm/mg P)	(cpm/mg PF)	(%P)	
2	527 ± 8ª	519 ± 8	368 ± 7	238 ± 19	13.1 ± 0.9	4:63 ± 0.44	
		495 ± 8			14.0 ± 0.9	3.89 ± 0.41	
		507 ± 8			12.0 ± 0.9	4.24 ± 0.43	
4	199 ± 5	205 ± 5	119 ± 5	138 ± 12	6.85 ± 0.55	4.82 ± 0.56	
		207 ± 5			6.80 ± 0.55	4.93 ± 0.58	
		211 ± 5			7.11 ± 0.55	5.15 ± 0.60	

Statistical uncertainties only are presented.

Equipment. The chemical procedures are carried out with readily available laboratory accounterments. Volumetric glassware, separatory funnels, irradiation vials, and an analytical balance are accessible for general use.

Neutron source. The irradiation vials are lowered into ports 4 cm from a 252 Cf source⁵ where the flux density is about 2×10^6 neutrons cm⁻² s⁻¹.

Instrumentation. Figure 1 shows a block diagram of the instrumentation used. The irradiation vials fit snugly into the well of the 3.8 cm \times 3.8 cm Nal(Ti) crystal. The single channel analyzer is set by leaving the window wide open and raising the discriminator until no appreciable count rate is observed with a 137 Cs source ($E_{\gamma} = 0.662$ MeV) (6) near the crystal.

Procedure. Standard (KH₂PO₄) and sample (plant food) solutions are accurately prepared with distilled, deionized water to be about 20 ppm phosphorus. Analysis is performed on 25-mL aliquots of standard and sample.

The phosphovanadomolybdate complex is formed directly in separatory funnels, as follows: To each aliquot of phosphorus solution, 5 mL of concentrated nitric acid, 5 mL of vanadate solution, and 10 mL of molybdate solution are added. Pipets are used to measure all volumes. Each separatory funnel is shaken well and allowed to equilibrate for 5 min. The appearance of a bright yellow color in solution indicates the formation of the complex.

A 10-mL aliquot of MIBK is pipeted into each funnel. The organic and aqueous layers are intimately mixed by shaking at 30-s intervals for 5 min. The layers are then allowed to separate undisturbed for 30 min. Half of each organic layer (5 mL) is transferred to a labelled polyethylene irradiation vial. The vials are sealed with epoxy or "heat sealed."

Each specimen is irradiated for 10 min in the ²⁵²Cf source and counted for 8 min in the NaI(Tl) well crystal. A 1-min waiting period is allocated between irradiation and counting to allow for transfer of the vial from the neutron facility to the gamma-ray detector.

Results

Representative data are presented in the table. The signal-to-background ratio is limited both by the efficiency of the relatively small well crystal and by the amount of complex soluble in 5 mL of MIBK. The great variation in counting rate originates from the use of various counting conditions and shielding arrangements around the detector.

The calculations, although straightforward, involve several steps. There are many ways to obtain the results from the data; presumably the most instructive is to carry out the calculations in the same logical order in which the experiment was performed (Fig. 2). This method serves to reinforce the logic and purpose of the experimental procedure.

Results calculated from student data are presented in Figure 3. All students worked in groups of two or three and analyzed the same plant food. Each result is a weighted average of three sample determinations. The error quoted is obtained through propagation of a one-sigma statistical uncertainty, associated with the counting of decay events.

Discussion

In any experiment involving radioactivity, the question of safety invariably will arise. Derivative activation analysis is particularly appropriate for a teaching laboratory in this regard. All chemical procedures are carried out before any radioactivity is induced. When activity is handled, it is in a sealed vial, and the short half-life of ⁵²V and relatively small amount of vanadium present keep the total activity quite low. In addition, no radioactive waste is generated; within a half-hour of removal from the neutron source, less than 1% of the

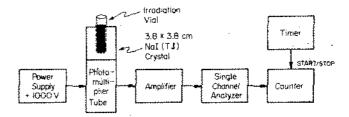


Figure 1. Block diagram of gamma-ray detector and electronics.

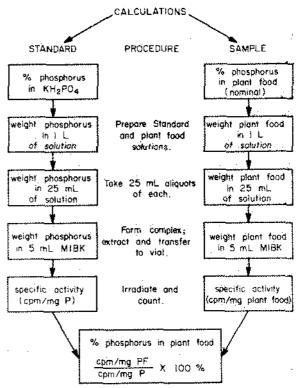


Figure 2. Logical sequence of calculational steps for determining %P.

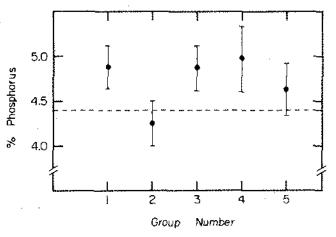


Figure 3. Student results for %P in Ortho House Plant Food 5-10-5. The dashed line depicts 10 % P2O5 (4.4 % P), as quoted on the plant food label and presumably represents a lower limit.

initial activity is present and the organic solutions may be disposed of through normal procedures.

This experiment has two features which particularly recommend it as a teaching tool. First, it can be completed in one laboratory period. All students performing the experiment carried out their laboratory work comfortably in 3-4 h. Second, this determination yields good results without undue meticulousness. Student data attest the fact that the method

While activation analysis with a nuclear reactor as the source of neutrons has been widely exploited (7), this experiment is viable with more available neutron facilities. For example, plutonium-beryllium sources provide up to 1.4×10^7 neutrons s^{-1} Ci⁻¹ (3), which is more than ample for this experiment; and small 252Cf sources are becoming increasingly more commonplace. Less potent sources could be used in conjunction with more concentrated samples and a larger volume of MIBK in order to yield the requisite level of ac-

In nitric acid medium, there are virtually no ionic interferences to the determination of phosphorus. Samples of water, coal, biological tissue, and rock and mineral matter have been assayed successfully by DAA (2). Solid samples must first be dissolved, and all samples must be preconcentrated or diluted, if the phosphorus concentration is not between 1 ng/mL and $\sim 30 \,\mu\text{g/mL}$. The upper limit is determined by the solubility of the phosphovanadomolybdate complex in MIBK, and the lower limit by the available neutron flux density (1 \times 10¹³ n cm⁻² s⁻¹ for 1 ng/mL) (2).

With its wide options for sample type, neutron source, and counting instrumentation, DAA of phosphorus emerges as a versatile analytical method in addition to being a very useful teaching tool.

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HPLC Analysis of Chlorophyll a, Chlorophyll b, and β -Carotene in Collard Greens

A Project for a Problem-Oriented Laboratory Course

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The theory and application of high performance liquid chromatography should be an integral part of college chemistry curricula since many students will be utilizing this technique in their profession. A popular experiment (1,2) in undergraduate organic laboratories is the separation of a carotenoid, such as β -carotene, from the chlorophylls in vegetables (e.g., collard greens, spinach, etc.) using column or thin layer chromatography (TLC). We have expanded this traditional experiment by utilizing high performance liquid chromatography (HPLC) to separate and quantitate β -carotene, chlorophyll a, and chlorophyll b originating from collard greens. This experiment clearly illustrates to the student the versatility of HPLC as a powerful analytical technique. A project undertaken by SUNY Oswego students who have previously (3-5) heen involved in project-oriented laboratories, is described.

Presented in part at the American Chemical Society, 11th Northeast

Regional Meeting, October 18–21, 1981, Rochester, NY.

¹ Information about Ominsolv™ glass-distilled solvents may be obtained from MCB Manufacturing Chemists, Inc., 2909 Highland Ave., Cincinnati, OH 45212.

Experimental

Instrumentation

The instrument used was a Varian 5020 liquid chromatograph equipped with a Model UV-10 variable wavelength detector and a Model 9171-02 dual-pen, strip-chart recorder. The 4-mm × 30-cm prepacked analytical column for this separation was a MicroPak Si-5(Silica). A 4-mm × 30-cm bonded reverse-phase column (monomeric octadecylsilane) MicroPak MCH-10 also was used. For a comprehensive discussion of reverse-phase chromatography, see reference (6). Each of these analytical columns was preceded by its appropriate 4.6-mm × 3-cm pre-column. The mobile phase was a nonlinear, step-and-hold gradient of isooctane:isopropanol (99:1 V/V) to a final composition of 85:15(V/V) (isooctane: isopropanol). All solvents used were Omnisolv™ glass-distilled.1

The solvent flow rate was 1 ml/min. The detector was fixed at 0.8 nm and 0.005 AUFS. The sample size was 10 μ l (10⁻⁶l) and was introduced by a Valco Model AH-CV-6-UHPa-N60 air-activated sample injector. The chart speed was 1 cm/ min.

Sample Preparation

Separatory Funnel Extraction Method, Crush approximately 15 g of fresh or frozen collard greens in 50 ml methanol with a mortar and pestle. This is to remove as much water from the plant cells as possible. Decant and discard the methanol solution and press the vegetable as free of solvent as possible. Regrind the collard greens with 15 ml methanol and 25 ml isooctane. Filter the mixture through a glass funnel plugged with absorbent cotton into a 125-ml separatory funnel. Again, regrind the vegetable with 15 ml methanol and 25 ml isooctane. Filter as previously and place in the separatory funnel.

Discard the lower methanol phase and add 30 ml water to the separatory funnel and shake gently. If an emulsion appears, add sodium chloride. Repeat as previously with another 30 ml water.

Place the isooctane solution into a 125-ml Erlenmeyer flask, and dry by adding 1-2 g anhydrous sodium sulfate. Decant the liquid into a sample bottle with a screw top. Fill to the top with additional isooctane as needed. This minimizes contact of the sample with oxygen. Strong light and oxygen hasten the decomposition of components. To exclude light, the sample bottle is wrapped tightly with aluminum foil. Save the sample for HPLC analysis.

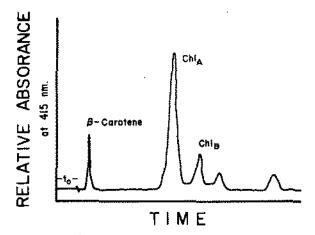
SEP-PAK ** 2 Extraction Procedure (7). Add 10 ml 2-propanol to 5-10 g of collard greens and stir with a mortar and pestle for 1 min. The 2-propanol serves to eliminate the water from the disrupted cells (i.e., same as methanol). Press the vegetable as free of solvent as possible and decant the mixture.

Extract the pigments by adding 5-10 ml isooctane and stirring. Decant the green colored mixture. Evaporate the liquid almost to dryness using a steam bath. Add 2-5 ml isooctane through the silica SEP-PAK™ with a Luer-type syringe. Immediately dissolve the extracted residue in 3 ml isooctane and pump it onto the premoistened silica SEP-PAK cartridge with the Luer-type syringe. Flush 3 ml isooctane through the cartridge and discard the cluate. With 5 ml 2-propanol elute the yellow and green bands, collecting only the colored bands. Place this in a screw-top sample bottle, fill to the top with 2-propanol and cover the vial with aluminum foil.

Results and Discussion

A typical chromatogram obtained by students showing the separation of β -carotene from chlorophyll a and chlorophyll b is shown in the figure. The entire HPLC analysis can be accomplished in about 25 min. Interestingly, both the silica and the octadecysilane column gave comparable class results, with the more polar compounds being eluted last. Therefore, in the octadecylsilane run, one is actually observing a form of "reverse-reverse phase" (i.e., normal) chromatography. The HPLC class results from either the longer separatory funnel extraction method or the shorter SEP-PAK™ preparative procedure also gave comparable HPLC results.

² Information on SEP-PAK™ cartridges may be obtained from Waters Associates, 34 Maple Street, Milford, MA 01757.



Chromatograph of β -carolene, chlorophyll a (Chl_A), and chlorophyll b (Chl_B) from collard greens by the SEP-PAK™ method.

Average HPLC Student Results of β -Carolene, Chlorophyll a, and Chlorophyll b from Collard Greens

Pigment	Occurrence ^e
β-Carotene	4.7 × 10 ^{−6} g
Chiorophyll a	1.6 × 10 ⁶ g
Chiorophyil b	1.2 × 10 ^{−6} g

a Values are expressed as per gram fresh weight of collard greens, Standards were purchased from Sigma Chemical Company, P.O. Box 14508, St. Louis, MO 63178.

The selectivity (α) class value for chlorophyll a and b was 1.4, and the resolution was 1.1; this indicates that if one wished to collect the samples, one would obtain approximately 99.2% of each component. The average HPLC student results, expressed as per gram fresh weight of collard greens for β -carotene, chlorophyll a, and chlorophyll b are summarized in the table. The other, unidentified compounds appearing in the chromatogram are typically pheophytins (chlorophyll which has lost its magnesium), chlorophyllides (chlorophyll which has lost its long-chain alcohol, either phytol or farnesol), pheophorbides (chlorophyllides which have lost their magnesium), or pheophytins which have lost their phytol moiety.

The literature is replete with time-consuming separations utilizing column or thin layer chromatography (8-11). Evans et al. (12) have separated two chlorophyll derivatives with high-pressure liquid chromatography and Eskins et al. (13) have described a preparative HPLC procedure too lengthy for routine analysis. Shoaf (14) has separated chlorophyll a and b from aquatic algae utilizing dimethyl sulfoxide as the extracting solvent and water-methanol as the HPLC mobile phase and Braumann and Grimme (15) have done a singlestep separation of photosynthetic pigments with HPLC. The chromatographic separation of β -carotene, chlorophyll a, and chlorophyll b by TLC and open-column methods is timeconsuming and causes pigment decomposition by exposing these labile compounds to oxygen, light, solvents, and adsorbents for relatively long periods of time.

The project we have described demonstrates to the student that high performance liquid chromatography is useful for rapid quantitative identification and analysis of such compounds as plant pigments. Because the separation is rapid and requires only a few, inexpensive standards, it can be integrated easily into existing laboratory curricula.

Acknowledgment

A. Silveira, Jr. gratefully acknowledges the National Science Foundation for support in the purchase of the Varian HPLC 5020 High Performance Liquid Chromatograph and the State University of New York Research Foundation for Improvement of Undergraduate Instruction for its continued support of project-oriented laboratories.

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Southeast

edited by NANCY LEMASTER D. W. Daniel High School Centrel, SC 29630

ADVANCED PLACEMENT SEMINARS

April 3, 1984

University of Kentucky, Student Center Annex, Lexington, KY 40508.

For further information, contact: Timothy R. Burcham (606) 257-1606. April 10, 1984

Tennessee Technological University, University Center, Cookesville, TN 38501.

For further information, contact: James C. Perry, (615) 528-3868. For the State of Florida, the list of AP seminars may be obtained. For further information, see the February 1984 issue of this Journal...

May 10-12, 1984

37TH ACS FLORIDA SECTION ANNUAL MEETING at Florida Southern College, Lakeland, FL.

For further information, see the February 1984 issue of THIS JOURNAL.

Northeast

edited by WALLACE J. GLEEKMAN-Brookline High School Brookline, MA 02146

March 28-28, 1984

NEW YORK ACADEMY OF SCIENCES CONFERENCE ON MACRO-MOLECULES AS DRUGS AND AS CARRIERS FOR BIOLOGICALLY ACTIVE MATERIALS to be held at the Roosevett Hotel, New York, NY.

For further information, see the February 1984 issue of THIS JOURNAL.

April 5-8, 1984

32ND ANNUAL CONVENTION OF THE NATIONAL SCIENCE TEACHERS ASSOCIATION (NSTA) will be held at the Sheraton-Boston and the John B. Hynes Auditorium in Boston, MA.

For further information, see the February 1984 issue of THIS JOURNAL.

April 5, 1984

ALL DAY CONFERENCE ON ACID RAIN sponored by Northeastern Section, American Chemical Society to be held at the Sheraton-Lexington Hotel, Lexington, MA.

Keynote speaker: Dr. Michael Oppenheimer, Environmental Defense Fund, New York, NY.

For further information, contact: Marion Ryan, Polaroid Corporation, 750 Main Street----1R, Cambridge, MA 02139, (617) 577-3585.

April 7, 1984

AVERY A. ASHDOWN HIGH SCHOOL CHEMISTRY EXAMINATION CONTEST sponsored by the Northeastern Section, American Chemical Society to be held at Simmons College, 300 The Fenway, Boston, MA.

For further information, contact: Ivan VanderWorkeen, Chemistry Dept., Westwood High School, Westwood, MA 02090, (617) 328-7500.

May 21-23, 1984

18TH MIDDLE ATLANTIC REGIONAL MEETING, New Jersey Institute of Technology and Rutgers University, Newark, NJ.

For further information, contact: G. E. Heinze, Jansen Pharmaceutica inc., 501 George St., New Brunswick, NJ 08903, (201) 524-9575.

May 31-June 2, 1984

11TH CONFERENCE OF COLLEGE CHEMISTRY CANADA to be held at John Abbott College, Montreal, Quebec.

Theme: Life in Chemistry

Chemistry in Life
For further information contact: Shahld Jalil, John Abbott College, P.O.
Box 2000, Ste. Anne de Bellevue, P. Q. H9X 3L9.

June 10-14, 1984

14TH NORTHEAST REGIONAL MEETING, Fairfield University, Fairfield, CT.

For further information, contact: D. t., Swanson, American Cyanamki Co., Chemical Research Division, 1937 West Main Street, Stanford, CT 06904, (203) 348-7331.

Northcentral

edited by ROBERT SUITS D. H. Hickman High School Columbia, MO 65201

April 6-7, 1984

The 83RO 2YC₃ CONFERENCE at the St. Louis Community College at Florissant Valley, 3400 Parshall Road, St. Louis, MO 63135, in conjunction with the 187th ACS National Meeting April 8-13, 1984.

For further information, see the February 1984 issue of THIS JOURNAL.

April 8-13, 1984

187TH ACS NATIONAL MEETING, St. Louis, MO.

For further information, see the February 1984 issue of THIS JOURNAL.

April 9, 1984

"High School DAY" at the ACS National Meeting, St. Louis, MO.
For further information, see the February 1984 issue of THIS JOURNAL.

May 23-25, 1984

JOINT GREAT LAKES CENTRAL REGIONAL MEETING, Kelamezoo, Mi

For further information, contact: L. E. Hines, Upjohn Co., 301 Henrietta Street, Kalamazoo, MJ 49001, (618) 385-7818,

Northwest

edited by Doug MANDT Sumner High School Sumner, WA 98390

June 13-15, 1984

39th NORTHWEST REGIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY at the University of Idaho, Moscow, ID.

For further information, contact: Dr. Stave Brown Washington State University, Pullman, WA 99184.

edited by ERIC STREITBERGER University of California-Fullerton Fullerton, CA 96231

TEACHER WORKSHOPS sponsored by the Colorado ACS Section, Regis College, Room 312 Science Bidg., Denver, CO 80221, 8:00 a.m.-5:00 p.m.

April 7, 1984 Descriptive Chemistry of Metals May 5, 1984 Descriptive Chemistry of Non-Metals

For further information, contact: Evelyn Bank Chairman of the Colorado ACS Section, Westminster, CO 80030, (303) 428-9541 Ext. 243 or (303) 424-3162.

WEDNESDAY AFTERNOON LECTURES being held at California Institute of Technology, 3rd floor, Baxter Hall, Pasadena, CA.

These lectures begin at 3:30 p.m. and are free for secondary school students and teachers. They are as follows:

April 4, 1984

The Crack: the Most Expensive "Nothing"

Speaker: Dr. W. T. Knauss, Professor of Aeronautics & Applied Mechanics

May 2, 1964

The Atomic Nucleus: Quantum Physics on a Grand Scale

Speaker: Dr. S. C. Koonin, Professor of Theoretical Physics.

For further information on the above lectures, contact Lee F. Browne, or Phyllis Brewster, California institute of Technology, Pasadena, CA 91125, (213) 356-6624.

LETTERS

The Error in in x To the Editor:

I found Leonard Nash's article on the "Ice Point and Triple Point" in the December 1981 issue quite interesting, particularly his pointing out that a four digit logarithm can yield a six digit antilogarithm.

Although his demonstration was most convincing, I should like to suggest an alternative derivation of his result. If we use the notation of calculus for *finite* changes (errors), then we may write than an error in x, d(x), causes, in the logarithm of x, $\ln x$, an error $d(\ln x)$ given by

$$d(\ln x) = \frac{1}{2}d(x)$$

Thus $d(x) = x d(\ln x)$, the error in x is x itself multiplied by the error in the logarithm.

In one of Nash's cases, where $\ln x = -8.230 \times 10^{-4} = -0.0008230$, if we assume an error of ± 1 in the last digit quoted, then $d(\ln x) = 2 \times 10^{-7}$. Now x itself is manifestly near 1 (i.e., 0.9991...), thus

$$d(x) \approx (1)(2 \times 10^{-7})$$

or the resulting x is determined to within 2 in the seventh figure.

Note that the above relationship indicates that the error increases with increasing x and that the inverse process of obtaining $\ln x$, given x, can lead to quite large errors if x is very small.

Oliver G. Ludwig

Villanova University Villanova, PA 19085

More on Chemical Stereoviews

To the Editor:

Since writing the note on the construction of a resource file for chemical stereoviews, I have come across a number of additional references dealing with the history of chemical stereoviews as well as several new sources of potentially useful stereoviews, both of which may be of interest to the readers of THIS JOURNAL. Dr. Ivan Bernal has called my attention to an extremely interesting collection of stereoscopic drawings, edited by von Laue and Mises, and published as two separate volumes by Springer Verlag in 1926 and 1936. These volumes contain a total of 48 hand-drawn stereoviews illustrating the 14 Bravais lattices and the structures of 34 elements and simple inorganic compounds, ranging from NaCl to perovskite. The 1921 crystallography text by Groth³ also contains a collection of stereoviews, though these are stereophotographs of actual physical models rather than line drawings.

The back cover of the April, 1929 issue of the JOURNAL OF CHEMICAL EDUCATION carries an advertisement for Fisher Scientific, complete with a photograph, of a "Camerascope" for "visual instruction in X-ray crystallography." This device sold for the then rather expensive price of \$18.00 and consisted of a small folding stereoscope and 37 stereoviews.⁴ From the description it is apparent that it was essentially an American version of the Bragg set mentioned in my original note.

As for sources of stereoviews, the first volume of the series "Molecular Structures and Dimensions," published by the International Union of Crystallography,⁵ contains close to 920 computer-drawn stereoviews of organic compounds, organometallic π -complexes, charge-transfer complexes, clathrates, carboranes, and traditional metal complexes of organic ligands. Regrettably, a similar source of stereoviews for non-molecular solids is apparently still lacking.

William B. Jensen

University of Wisconsin Medison, WI 53706

lographie," Oldenbourg, Berlin, 1921.

The Supporting, Rather than Initiating, Role of Science in Technology

To the Editor:

In his editorial in the May, 1982 issue of THIS JOURNAL ("The Public Attitude Toward Science"), J. J. Lagowski correctly laments the priorities of the American public for the support of science and technology with tax revenues, as indicated by the most recent annual report of the National Science Board, Science Indicators 1980. He comments that "It should be more than slightly disturbing to the scientific community that the general public perceives the acquisition of new knowledge-the fundamental basis of modern technology—to be so lacking in merit as to place it among the lowest on the list of areas to be supported." While the public's lack of appreciation for the benefits to modern society of fundamental research is indeed cause for concern, Lagowski's justification for the acquisition of new knowledge as "the fundamental basis of modern technology" is ill-suited to his purpose. Historians of science and technology have in recent years devoted much effort towards the elucidation of the in-

¹ Jensen, W. B., J. CHEM. EDUC., **59,** 385 (1982).

² von Laue, M., and Mises, R. (*Editors*), "Stereoscopic Drawings of Crystal Structures," Vols. 1 and 2, Springer, Berlin, 1926 and 1936. ³ Groth, P., "Elemente der Physikalischen und Chemischen Kristal-

⁴ J. CHEM. EDUC., **6**, 4 (1929).

⁵ Kennard, O., et al. (*Editors*), "Molecular Structures and Dimensions," Vol. A1, International Union of Crystallography, **1972**,

teraction between science and technology, and a consensus has emerged that technological innovation most often evolves from prior technology, and that when pure science does play a role, its relation to the technological developments are seldom those of cause and effect. In a careful study, for example, of 84 successful British technological innovations of 1966/67, F. R. Jevons found the role of science to be a supporting, rather than an initiating, one and that in no single case was an innovation induced by a scientific discovery.¹

If we choose, as many of us do, to justify the pursuit of knowledge primarily by consequent technological innovations, then the importance of pure research will be diminished if, as seems likely, the justification is rendered invalid. It is important for modern scientists, of whom chemists form a large percentage, to seek societal support for the pursuit of new knowledge as an integral part of the cultural attainments of mankind, a part moreover which encourages us to appreciate, utilize, and live in harmony with, the world around us.

Melvyn C. Usselman

University of Western Ontario London, Ontario Canada N6A 5B7

Liability Insurance

To the Editor:

A contribution to the Safety Column last November by N. T. and Marilyn C. Kurnath¹ has pointed out the increasing numbers of law suits charging negligence on the part of laboratory teachers. This has raised questions about liability insurance for the financial protection of teachers and prompts us to call special attention to the ACS Professional Liability Insurance Plan, just in case our readers failed to note the paid advertisement on page A344 of that same issue.

Reductions in rates have made this coverage a genuine bargain in the opinion of your Column Editor. For peace of mind and the protection of your solvency we recommend writing for full information. Address inquiries to the American Professional Agency, Inc., 95 Broadway, Amityville, NY 11701. (The plan also includes coverage for industrial chemists, and an alternative plan is available for consultants.)

Malcolm M. Renfew

University of Idaho Moscow, ID 83843

Crib Cards for Tests

To the Editor:

I would like to note that Whitmer's suggested use of a 3 × 5 "crib card" on tests [J. CHEM. EDUC., 60, 85 (1983)] is not limited to physical chemistry. I have successfully used the same idea for several years in my sophomore organic chemistry course and I concur with Whitmer's comment that preparing the card is an excellent focus for study. I have had students complain that by the time they have figured out what they are going to put on the card they no longer need the card. I recommend its use by instructors interested in testing the use of facts without testing the memorization of those facts.

John Henderson

Jackson Community College Jackson, Mt 49201

Soiled Chemistry

To the Editor:

There are significant agronomic errors in the experiment entitled, "Soil Analysis for High School Chemistry Students," by Mary A. Eisenmann, published in J. CHEM. EDUC., 57, 897 (1980). The Discussion section has several significant errors: 1) The fertilizer analysis 15-5-10 means 15% N, 5% P_2O_5 , and 10% K_2O , not 5% P and 10% K as stated in the article. The state fertilizer registration laws are 20-30 years behind the times. 2) In soil that is too alkaline (basic) (pH \geq 8), the micronutrients zinc, copper, iron, and manganese are tied up as insoluble phosphates and the phosphate ions (HPO₄2-) are unavailable because of the formation of insoluble calcium and magnesium phosphates. 3) In acidic soils (pH \leq 5) the micronutrients (trace elements) manganese and iron become too available and may reach toxic levels. Aluminum becomes a significant problem also. The ideal soil pH is 6.5, the pH of maximum major and secondary nutrient availability and proper micronutrient availability.

A professional soil testing laboratory tests for the primary and secondary plant nutrients—N as NO₃⁻ by specific ion electrode, P colorimetrically as the blue phosphomolybdate complex, and K, Ca, and Mg by atomic absorption-emission spectroscopy. The micronutrients are also determined by AA. A soil lab does not test for HCO₃⁻. pH is measured with a pH meter. Na-Churs Plant Food Company analyzes approximately 130,000 soil sample a year for its fertilizer customers.

I will be happy to answer any questions about soil testing, agronomic recommendations, fertilizer manufacture, etc.

Walter C. Crouse

Director, Product Research Ne-Churs Plant Food Company 421 Leader St. Marlon, OH 43302

An Alternative Proof

To The Editor:

Carl W. David's article, "Why is an LCAO-MO Not Necessarily an Eigenfunction," which appeared in the April 1982 JOURNAL provided one demonstration that $\psi_{\text{trial}} = 1s_a + 1s_b$ is not an eigenfunction of the one-electron Hamiltonian H. I would like to suggest a much simpler and perhaps more interesting proof.

Consider

$$H\psi_{\text{trial}} = [-(\hbar^2/2m)\nabla^2 - Ze^2/r_B - Ze^2/r_b](1s_a + 1s_b)$$

But $1s_a$ is an eigenfunction of the first two terms in H, and $1s_b$ is an eigenfunction of the first plus the last term in H. In each case, the eigenvalue is simply the hydrogen-like atom ground state energy $E_{\rm HL} = -(13.6~{\rm eV})Z^2$. Therefore

$$H1s_a = (E_{HL} - Ze^2/r_b)1s_a$$

 $H1s_b = (E_{HL} - Ze^2/r_a)1s_b$

and

$$H\psi_{\text{trial}} = E_{\text{HL}}(1s_a + 1s_b) - (Ze^2/r_b)1s_a - (Ze^2/r_a)1s_b$$
$$= E_{\text{HL}}\psi_{\text{trial}} - (Ze^2/r_b)1s_a - (Ze^2/r_a)1s_b$$

It is impossible to factor the last two terms to yield simply ψ_{trial} multiplied by a constant. Therefore, ψ_{trial} is not an eigenfunction of H.

This proof exploits essential properties of the Hamiltonian H as well as of the AO's $1s_a$ and $1s_b$, and offsets any need to consider specific functional details.

Frank O. Elilson

University of Pittsburgh Pittsburgh, PA 15260

¹ Jevons, F. R., Technology & Culture, 17, 729 (1976).

¹ Kurnath, N. T. and Kurnath, Marilyn C., J. Снем. EDUc., **58**, A329 (1981).

BOOK REVIEWS

General Chemistry Principles and Structure, Third Edition, SI Version

James E. Brady and Gererd E. Humiston, John Wiley & Sons, Somerset, NJ, 1983. xix + 826 pp. Figs. and tables. 22 × 26 cm. \$30.95.

The appearance of an SI version of this respected textbook [see my review in this Journal, 60, A103 (1983)] is a sign of a healthy sales picture, which for the admirable text under review is altogether deserved. Unfortunately, however, the need for two alternative versions of first-year textbooks reflects a deplorable lack of agreement among chemists over the basic grammar and spelling of our science. At this time no consensus has yet been reached on the names that should be given to the well-defined physical quantities and the symbols for those names, the names given to well-defined units and the symbols for those names, and the rules for the expression of relations involving numerical values between such physical quantities and such units. Thus, students of chemistry at all levels are currently taught an incredible mishmash of names and symbols, depending on the whim of the particular instructor. In this situation we look to editors and textbook authors for the leadership which will lead us to a more logical and rational future. Against this is the conservatism of the professoriate who, after all, can control at least the textbook market by exercising the power not to adopt.

Even in this version of the excellent text under review, Professor Heikkinen, a well-practiced chemical educator, has retained the standard atmosphere (atm) as a convenient synonym for 101,325 N m⁻² (101.325 kPa), even though the N m⁻² (pascal) is used as the SI-derived unit of pressure throughout the taxt.

This popular and serious textbook is highly recommended.

J. J. Zuckerman University of Oklahoma Norman, OK 73019

Introduction to Chemistry, Fourth Edition

T. R. Dickson, John Wiley & Sons, Somerset, NJ, 1983, xvii + 540 pp. Figs. and tables, 19 × 24 cm. \$25.95.

This textbook, intended for a one-term course in chemistry, is supposed to fulfill the needs of two different groups of students—those who need a foundation for additional courses in chemistry and those who wish to have only an introductory course. It is a challenge to teach both groups, and it is a significant challenge to find an appropriate textbook.

The author recognizes the need to provide students with an appropriate background in systems of measurement and problem solving. This is handled well through the factorlabel method in the first chapter and through the use of three appendices.

Chapter two covers the chemical elements (nature of matter, atomic theory, nuclear atom, isotopes, and atomic weights), chapter three covers compounds and formulas, and chapter four looks at atomic structure and the periodic table, including electronic configurations.

Subsequent chapters cover chemical bonds, chemical nomenclature, chemical reactions and equations, chemical stoichiometry, gases, water and solutions, solution dynamics and chemical equilibrium, acids, and bases, oxidation and reduction, liquids and solids, nuclear energy, organic chemistry, and biochemistry.

In short, most significant topics of general chemistry are considered (though, obviously, in limited detail). At first glance, then it might seem that the book is written for the second student group. Actually, the author has faced the dilemma of what to include and has responded by providing all students with an honest view of chemistry as the basic, exciting, relevant central science that it is.

There is a lot of material here, but it is well presented, and the instructor can alter the

order of chapters after the first four without penalty.

A final point: this book does not have that fourth edition the-author-listened-to-every-advisor-around look. It is a polished, well-written, attractively designed textbook. It is recommended for those who are faced with the challenge of teaching the course for which it is written.

Dean F. Martin University of South Florida Tampa, FL 33620

Practice of Thin Layer Chromatography, Second Edition

Joseph C. Touchstone and Murrell F. Dobbins, John Wiley & Sons, Somerset, NJ, 1983. iii + 405 pp. Figs. and tables, 16 X 23.5 cm. \$40.00,

The authors present a follow-up volume of their successful first edition which was published in 1978. The book consists of 16 chapters and is intended primarily for practicing chromatographers. It contains much "how to" information and is full of practical advice,

Comparing the second to the first edition, one finds that the majority of the chapters was left essentially untouched. In many cases the chapters are identical, including the lists of references. The only significant changes were made in Chapter 4 dealing with sample preparation and application, and Chapter 10 which has been relabelled from "Radioactive Procedures" to "Procedures fur Radioactivity." The anthors have, however, paid tribute to 2 new developments, revise phase tech-

(Continued on page A114)

Reviewed in this Issue-

James E. Brady and Gerard E. Humiston, General Chemistry Principles and Structure, Third Edition, SI Version

T. R. Discon, Introduction to Chemistry, Fourth Edition

Joseph C. Touchstone and Murrell F. Dobbins, Practice of Thin Layer Chromatography, Second Edition

Titles of Interest

Continuing Series

Reviewer

J. J. Zuckerman

A113

Deaл F. Martin

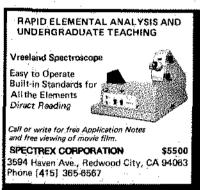
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Wolfgang Bertsch

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DOK REVIEWS

niques, and high performance thin layer chromatography (HPTLC). These two topics are introduced in Chapters 13 and 14.

Reversed phase methods are not expected to play a similar role in TLC as they do in liquid column chromatography. Nevertheless, they are a useful addition to the repertoire of TLC. Most papers referenced in Chapter 13 are less than 10 years old which is a clear indication of the relatively recent introduction of RP methods. The chapter is short but well written and informative. HPTLC, also a relative newcomer, does not fare as well. Although the battle is still raging whether HPTLC deserves the prefix HP or is merely a refinement of existing technology. the fact remains that it is rapidly expanding. Two symposia dedicated to the subject have been held in Europe with several hundred scientists and practitioners in attendance.

The 16 papers from the first and 28 from the second symposium proceedings book are not mentioned in the text and obviously have been overlooked by the authors. This is somewhat surprising since the proceedings from the first conference were published in regular book form in 1980.

Practicing chromatographers, especially organic chemists and applications oriented users who are not interested in thin layer chromatography as a science but only as a tool to accomplish a specific task will find the book of considerable value. The reader is not introduced to any theory and is exposed only to a minimum of instrumentation. The improvements offered by the second over the first edition are amall. Readers who already have access to the carlier edition ahoold stick to the older version. Newcomers to the field will find an above average text at a reasonable price.

Wolfgang Bertsch

The University of Alabama University, AL 35486

NEW JOURNAL ANNOUNCEMENT

Drying Technology and International Journal, Volume 1, Number 1

Carl W. Hall (Editor), Marcel Dekker, Inc., New York, NY, 1983, 163 pp. Figs. and tabies. 15 × 23 cm. Two issues per volume: institutional rate, \$95.00; individual rate,

TITLES OF INTEREST

History of Clinical Chemistry

J. Buttner, (Editor) Walter de Gruyter and Co., Berlin, Germany, 1983, 91 pp. Figs. and tables, 18,5 × 26,5 cm, \$44,50,

This volume is a collection of eight (8) papers on the history of Clinical Chemistry that originally appeared in the Journal of Clinical Chemistry and Clinical Biochemistry in 1981. and 1982.

TITLES OF INTEREST Symposium

Analytical Chemistry Symposia Series. Volume 15, Computer Applications in Chemistry

S. R. Heller and R. Potenzone, (Editors), Elsevier Science Publishers, New York, NY, 1983, xii + 394 pp. Figs. and tables. 17 X 24.5 cm.

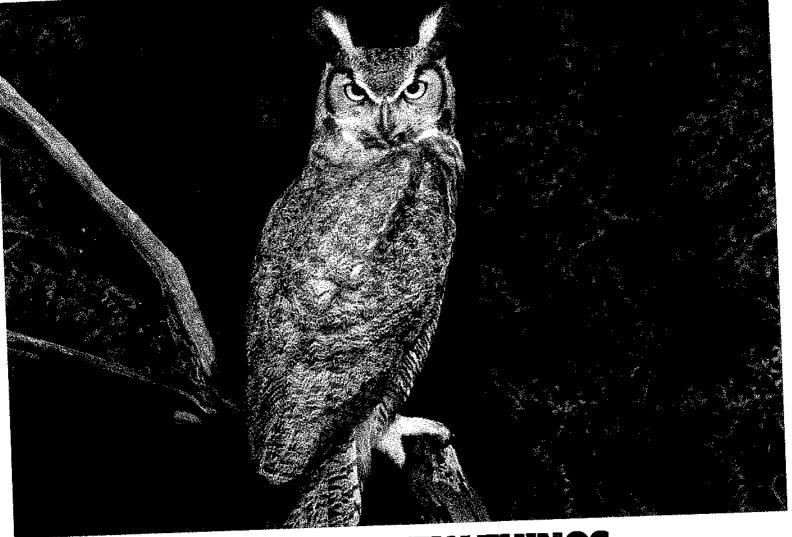
Topics Covered: The Neglected Ingredient in Chemical Computer Systems; Directions in Macromolecular Structure Representation and Display; Some Aspects of the Application of Pattern Recognition Methods in Chemistry; Knowledge-Base Enhancement via Training Sequence: The Education of SYNCHEM2: Chemical Information Systems; A Centralized Computer System with Distributed Satellites for the Acquisition and Interpretation of Analytical Data; Teaching with a Microcomputer; Local Area Networks, Fourth Generation Languages and Microelectronics in the Research Laboratory; Computer Networks for Scientific Applications: A Status Report; Computerized Standard Reference Data; The Random Graph-Like State of Matter; The Federal Role in the Support of U.S. Science and Technology: A View from Congress; Computer-Assisted Structure Elucidation System-Functions that "CHEMICS" System Can Perform; Computers in Chemical Research at the Novosibirsk Scientific Centre/Tha Chemistry in Future Moleculer Computers; Comparison of Logical Three-Dimensional Molecular Structures by Means of an Auto-Correlation Procedure; Computer-Assisted Drug Design.

This volume contains papers printed at the 6th international Conference on Computers in Chemical Research and Education in Washington, D.C., on July 11-16,

CONTINUING SERIES

Stereoelectronic Effects in Organic Chemistry, Volume 1

Pierre Deslongchamps, Pergamon Press, inc., Eimsford, NY, 1983. xì + 375 pp. Figs. and tables. 15×23 cm. \$27.50.



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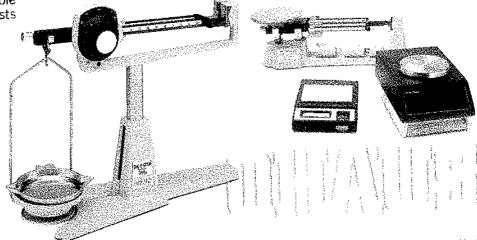
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