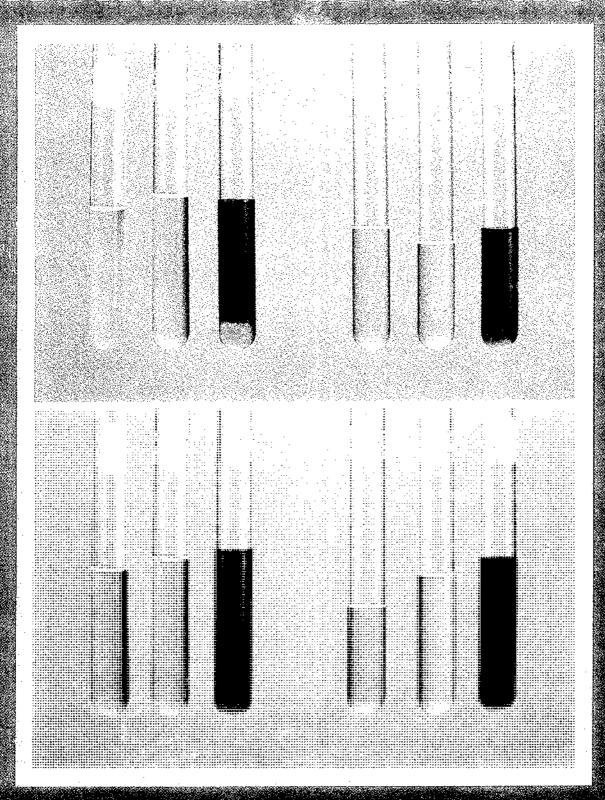
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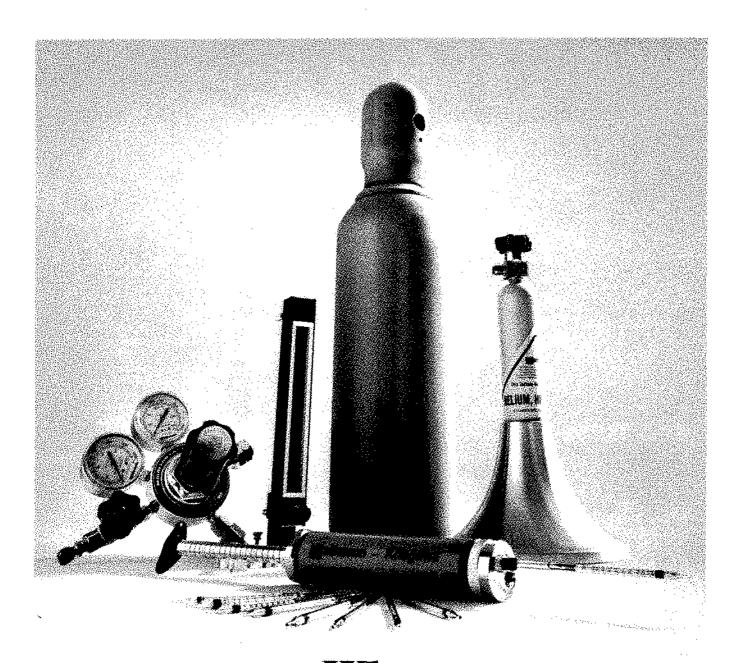
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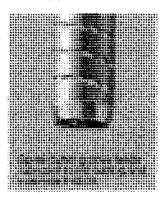
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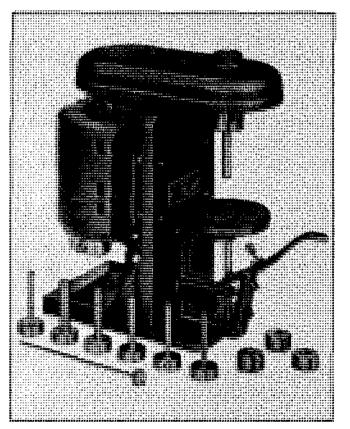


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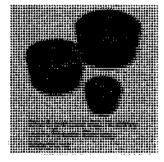
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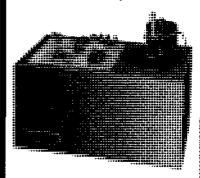
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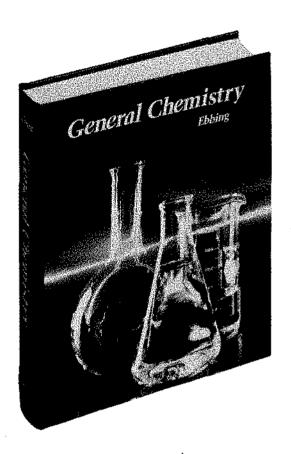
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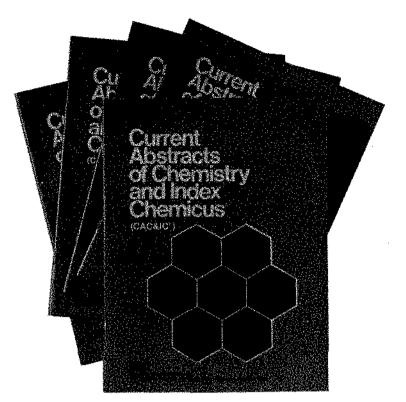
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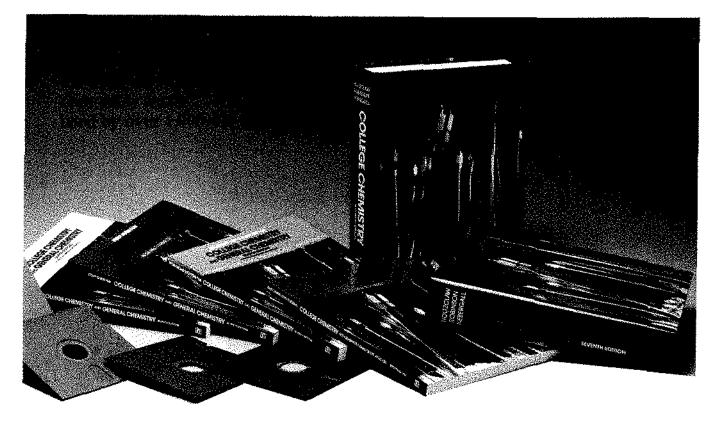
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Ronald A. DeLorenzo, Middle Georgia College 1981 Paper 482 pages

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safety in the chemical laboratory

edited by MALCOLM M. RENFREW University of Idaho Moscow, Idaho 83843

Chemical Management

A Method for Waste Reduction

Stanley H. Pine

California State University, Los Angeles, CA 90032

Chemicals! A word to which the public reacts with emotion, usually negative. For the laboratory instructor and researcher, chemicals are the basis for their operations. Yet these scientists are faced with an increasing array uf regulatory and social problems because their work with chemicals can produce chemical wastes. Considerable effort and expense is being expended to properly dispose of those wastes. A large industry of waste disposers and regulatory advisors has developed to face the many problems which have arisen.

For those of us who are involved with academic or small industrial laboratories, the necessity to handle and dispose of chemicals properly has become a rather burdensome obligation. An approach to the problem which has been relatively neglected, particularly in academic laboratories, is the management of chemicals so as to minimize the generation of waste. In fact, the management of chemicals can have a broader impact than just waste reduction. The use of valuable resources (chemical compounds) will be reduced, costs to the institution can be minimized, and the general efficiency of laboratory operations will be improved.

Let us consider the beginning of the acquisition process for a chemical—purchasing.

Stanley Pine is Professor of Chemistry at California State University, Los Angeles. He earned a PhD at UCLA and spent a post-doctoral year at Harvard before joining the Cal State faculty in 1964. He has spent research sabbaticafs at CalTech and at the University of Strasbourg, France where he was a Fuibright Visiting Professor. Pine is the University Chemical Safety Officer at Cal State, Los Angeles, and is a 1983 recipient of the Governor's Safety Award. He is a member of the American Chemical Society Committee on Chemical Safety and is the chairman of the ACS Task Force on RCRA.

The economics of buying chemicals (or almost any other commodity) is: more is cheaper. We can usually buy a 1-kg quantity at five or six times the cost of a 100-g quantity. That is reasonable since packaging and handling of ten containers costs considerably more than similar handling of one container.

However, from the viewpoint of overall economics and efficiency, is buying large actually cheaper? We should ask whether that large, 1-kg quantity is needed? Will it be consumed in some reasonable amount of time? How will the large container be stored? Large bottles take up considerable space and they never seem to fit on the storeroom shelves! And finally, if it is not used up, how and at what cost will the excess be disposed of?

The last question has become the economic thorn for many of us. The costs of safely and legally disposing of partially filled and even extra unopened containers of chemicals is straining the budgets of many laboratory operations.

How foolish it is to pay to waste valuable resources!

Purchase and inventory control is one way to get a handle on the chemicals used by our institutions. We should buy only what we will need over a reasonable period of time. (The major chemical auppliers tell us that packaging size largely depends on consumer demand.)

We should know where chemicals are located. From an emergency preparedness view we must know what chemicals are located in a specific laboratory or storeroom. As a model remember that we have clearly identified the location of radioactive materials for many, many years.

Inventory control provides the basis for another important aspect of chemical management—sharing chemicals. All of us, unfortunately, have been indoctrinated with the idea that opened bottles of chemicals are not to be trusted. In most cases that is not reasonable. We readily borrow chemicals from a neighboriog laboratory when they are not

available in the central storeroom. If purity is in question, a rapid spectral analysis can be obtained.

Partially used bottles of chemicals no longer needed by one laboratory can be made available to other labs of the institution. This requires some coordination, but nothing beyond the inventory control systems that most of us use; i.e., some kind of card file system. And as we move into the computer age this inventory process can be made more and more efficient. At least one industrial facility now uses a computer-linked system at each laboratory door to record when chemical containers enter and leave. I would guess that most chemical labels will soon include a universal bar code for rapid scan identification.

We must be careful not to let the sharing of chemicals generate a safety problem. Date the chemical containers when they initially enter the facility. It might be helpful to have secondary dating as a chemical travels from lab to lah. And a record of who has previously used the chemical could be helpful if quality is in question or if problems arise.

Repackaging of bulk chemicals is another consideration in the economics of chemical management. Here the bulk buying approach is employed. Most institutions already repackage bulk solvents.

There are however, costs associated with repackaging. The practice requires a suitable work area as well as proper containers and labeling. Safety is a critical consideration. I would guess that the safety practices in most instances of solvent repackaging are rather marginal.

On-site purification and redistribution of solvents has been common in most European laboratories. That, in part, is a consequence of the very high price (compared to the U.S.) of these materials. Though safety considerations for a distillation facility are quite rigorous, the economics of solvent disposal could make recovery practical.

(Continued on page A46)

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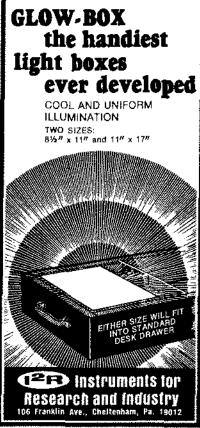
Many commercial concerns will now purchase drums of used solvents for recycling. There are also various methods for recycling surplus (unwanted) but useful chemicals, though this is usually directed toward large industrial quantities. California, for example, has a state-coordinated waste exchange program. One hopes that procedures for exchanging bottles of chemicals between different laboratory facilities will become general. Returning unopened bottles of reagents to the original manufacturer is a concept that is being discussed.

One last idea for academic institutions relates to the instructional laboratories. Economics and safety suggest that we minimize the quantities of chemicals used for experiments-within the limits of good education. An extension of these ideas is jucluded in the laboratory book "Zero Effluent Laboratory" by Corwin, Roth, and Morton, and first introduced a few years ago at Brown University. The approach uses products as starting materials for subsequent work and even recovers solvents. It seems reasonable that the laboratory experience of students should include the understanding that it is possible to handle chemicals safely and with the total environment in mind.

Once all possibilities have been exhausted for the use of surplus chemicals, then the end of the management sequence becomes disposal. But don't panic! Some chemicals can be safely and legally disposed of on-site, Many materials, when properly neutralized and diluted, can be added to the sanitary sewer effluent. (Check your municipality fur local regulations.) Careful evaporation of small amounts of some solvents is another method for on-site disposal. The new National Research Council book "Prudent Practices for Disposal of Chemicals in Laboratories" provides a broad spectum of ideas in this regard.

Finally, those little bits of real waste remaining must be disposed of in a safe environmentally sound manner. Retaining a waste disposal contractor is the best approach for most of us. But be sure that you know your contractor. Remember that the generator ultimately shares the legal and financial responsibility if its wastes are not disposed of properly.

Management of chemicals should become a way of life for all of us. The thoughtful approach to chemical handling and disposal will, I believe, show long term economic advantages and can go a long way in changing the rather negative public image of chemicals and chemists. Innovative approaches to complex problems have always been the scientists mode of operation.

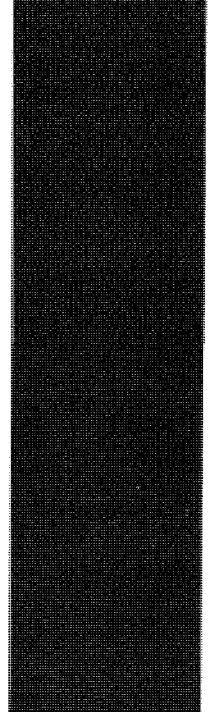


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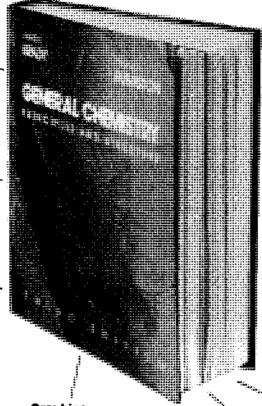
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Choosing the Right Instrument: The Modular Approach

Part I

Howard A. Strobel
Duke University, Durham, NC 27706

In recent years two major developments have occurred in chemical instrumentation: first, the design and construction of instruments have become more complex; second, control and data-processing capabilities have been revolutionized by the introduction of microprocessora. As a further complication in the choice of an instrument, manufacturers have now begun to emphasize the control and data processing aspect to the exclusion of any adequate description of the basic design. Undisputedly, instruments are used more intelligently when this use is based on an understanding of their design and operation. Such an understanding is greatly enhanced through a modular or systems approach, which is basically a conceptual approach. It may be defined as the understanding of an instrument as a system, each module of which performs a needed function, such as detecting the signal from a sample, and not basically as a collection of integrated circuits, switches, optical slits, and other parts. It may appear to those unfamiliar with the modular way of viewing instruments that such an approach might be impossibly mathematical and abstract. A homely example will dispel the notion. We grow up familiar with a modular approach to our gasoline-operated automubiles: we understand the automotive system to be a carburetor module through which a gasoline-air mixture is introduced to an internal combustion engine module whose crankshaft connects through a gear reduction module and drive shaft to a differential gear

Howard Strobel is a professor of chemistry at Duke University. He is a graduate of Washington State University and has worked on the Manhattan Project and at Brown University where he earned his PhD. His book, "Chemical Instrumentation," (Addison-Wesley) is slated to appear soon in a third edition. His research interests include nonaqueous ion exchange and study of solvent structure in mixed solvents.

and moving wheels that propel the vehicle.

A conceptual understanding seems especially important for instrument users, teachers of future instrument users, and for those writing instrument brochures, who also have a teaching role. This paper intends basically to present the modular approach in fashion that will help the user raise questions that will lead to the choice of the most effective instruments for particular applications and then apply them more effectively. Such applications may involve characterizing chemical or biological systems, identifying substances, measuring concentrations, or determining microphysical or chemical structure.¹

The Modular Approach

Taking a modular view means, as suggested, that we consider instruments as systems. Incidentally, the widespread use of block diagrams reminde us that such devices have long been conceived and explained in terms of modules (2-5). To muve toward this view it is useful to consider how a measurement on a sample is made. In the classical sense it involves completing the following sequential steps: (1) generation of an energy flow ("signal"), (2) impinging the energy flow on the sample, (3) detecting the signal arising from interaction of the flow with the sample, (4) amplification of the aignal as necessary, (5) processsing of the signal, (6) computation of analytical information about the sample, and (7) display or read-out of the result(s). It is a modular approach that seems best to mesh this description of measurement with actual

Appropriate measurement techniques must, of course, also be identified by the user. In selecting methods it is valuable to have access to an analysis of the potentialities of such methods. A fine example of such an evaluation is the brochure developed by research persunnel of the Dow Chemical Company and published as "Modern Meth-

ods of Research and Analysis" (1).

instruments.

In this context a module is considered to be the group of components that performs a particular function, e.g., detection or amplification. If we open an instrument case, we will always see a myriad of resistors, wires, integrated circuits, slits, mirrors, filters, phototubes, transformers, and other components. By moving conceptually to a higher level, however, we can in effect ignore them. If we keep the function of a module in mind, it should be possible to identify its principal components. Only if we must calibrate or test a module and do not have access to test points or circuits set up by the manufacturer are we likely to have to identify many parts. In the case of electronic modules our task is fortunately eased since many of them appear on individual circuit boards.

Is the implication that most instruments are made from a standard collection of modules correct? Is it also true that only a fairly small set of modules is important enough to study extensively? If the answer to both queries is affirmative, an important question remains. Can one successfully trace instrument specifications to like specifications for individual modules? All these questions can be answered "yes." It is even true that often one module sets a specification.

Furthermore, nearly all modules are types that will appear in new instruments into the indefinite future. Improvements in design will enhance their operation but the modules will continue to perform the same function. In many cases both the original and improved version continue in use. A good example is the upgrading of the phototube to a photomultiplier tube; each type of detector has found

(Continued on page A54)

This paper is based on a report, "An Overview of Instrument Modules and Chemical Instrumentation," developed for NSF Project SIINC (Scientific Instrumentation Information Network and Curricula), Frank A. Settle, Jr., Director, Virginia Military Institute, Lexington, VA 24450.

its own area of application.

Modeling the Module: General Properties

What surt of a sub-system is a module? In Figure 1, a common single-channel spectrophotometer is pictured as a train of modules. The names of the modules identify the functions they perform and show how the measurement steps described earlier can be implemented practically in a given case. Double and single arrows indicate the movement of optical and electrical "signal," respectively, from one module to the next. Not shown, since it is not part of the signal train, is the power supply which supplies do electrical energy to several of the modules. Some comments are in order.

The modules listed differ to a striking degree in complexity. For example, if a spectrophotometer is to operate in the visible and near IR regione the continuous source of Figure 1 may be a tungsten-filament incandescent bulb. We are generally familiar with the emission pattern of such bulbs. By contrast, the monochromator will be much more complex. It will consist of at least an entrance and exit slit, a dispersing device, such as a (diffraction) grating, several baffles, and a precision mechanism to vary the orientation

| Module | Function | Input | Output | (Usual name for) Sensitivity of Module |
|----------------------------|-------------------------------|--------------------------------------|-----------------------------|---|
| Tungsten-fliament lamp | Light emission (source) | DC current | Light | Efficiency |
| X-ray tube | X-ray emission (source) | | | Efficiency |
| Monochromator | Isolation of narrow λ band | Polychrometic radiation | Monochromatic redistion | Efficiency |
| Photomultiplier tube | Detection | Light | Current | Efficiency |
| Thermocouple | Detection | Temperature | Voltage | Response |
| ion-selective electrode | Detection | fon activity (concen- tration) | Voltage | Response |
| Amplifier | Amplification | Voltage or current | Voltage or current | Gain |
| Counter | Counting (processing) | Voltage pulses | Binary or decimal sum | |
| Light-emitting diode (LED) | Emission (readout) | DC current | Light | Efficiency |

input) is "transduced" linearly to current if it is within a given range of intensities. The lower limit or threshold is usually set by internal noise, i.e., random unavoidable fluctuations. The upper intensity limit is reached when a further increase produces no additional growth in output. The module is said to limit or reach saturation. Figure 2 shows a representative plot of output as a function of input for another detector-transducer module, a photographic emulsion. The bro-

Figure 1. Line modular diagram of a single-channel spectrophotometer.

of the dispersing device. In general, it will also have collimating and focusing optics.

Second, "signal" has been used in its general sense of a defined energy flow, e.g., a light beam or current. When that flow is encoded with information about a chemical sample, the quotation marks can be discarded. Some modules such as a chopper may also add a carrier frequency to a signal, many will add background energy (e.g., a monochromator adds stray light) and all will add noise. It is the function of good design and processing to minimize these additions. Third, it will be appropriate later to examine whether the modular approach is also applicable to double channel design, to instruments with microprocessor or minicomputer control, and to tandem or hyphenated instruments such as GC-MS systems.

What sort of a system is a module? Note again by reference to Figure 1 that for a module a "signal" appears at its input, is modified in some characteristic fashion, and then appears as its output. How can we think about the input, modification, and output aspects of modules in a consistent way so that we may easily characterize all modules, familiar and unfamiliar?

First, the type and intensity range of input a module can accept must be known. Examining the behavior of a photomultiplier tube as a detector will make the point clearer. UV and visible radiation reaching the photocathode of the multiplier phototube (its

ken lines in the plot correspond to threshold and saturation values. The range of useful input lies between these limits. From the discussion it is evident that everything centers on the transfer function.

We are mainly interested in modules because of their ability to mudify signals in a characteristic fashion. This property can be described in terms of a transfer function, f, which is defined by the expression $I_0 = f(I_j)$,

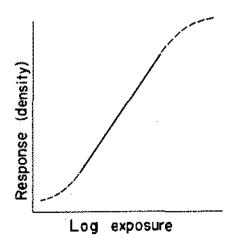


Figure 2, Representative response curve: image dansity versus the logarithm of exposure for a photographic amulsion.

where I_i is the input signal and I_o the nutput signal. If function f is linear in input intensity, as in the central portion of the response curve in Figure 2, the module will transform an input to an output without distortion.

In the table several types of modules are listed to illustrate the variety of ways in which modules interact with "signals." When modules also transduce inputs, i.e., alter them in form, they are often called input transducers if used as detectors and output transducers if used as sonrce or readout modules. Detectors must always have an electrical output since the modules that follow require an electric signal.

The rate of change of output signal with input signal is another important module characteristic. This property is termed its sensitivity S and is formulated as $S = dI_o/dI_i$. A module's response to input (given a time longer than its response time) thus is measured by its sensitivity. It was this property of a photographic emulsion that was plotted in Figure 2. It should be observed that sensitivity is defined here in its precise sense, which is magnitude of response for a given input.²

There are many synonyms for sensitivity S (see table). For an amplifier it is called gain, for a filter, attenuation factor, for an optical detector, response. Further, S is sometimes defined logarithmically (decibel notation). At other times it, or its reciprocal 1/S, is used and termed a scale factor. The latter notation is cummon for a module such as an operational amplifier where sensitivity may be changed by altering the resistance in the feedback circuit incrementally giving scale factors of $10\times$, $100\times$, etc.

(Continued on page A56)

² Sensitivity as applied to a whole instrument system does not by itself determine the smallest concentration of an analyte for which an instrument response occurs that may be differentiated from one caused by noise. This minimum concentration is properly termed the limit of detection. Clearly, the irreducible noise levels of each module "combine" to fix that minimum. The greater the slope of the response curve at very low levels of input signal, however, the lower the level yielding a discernable response.

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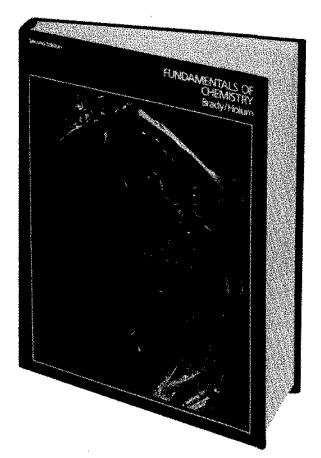
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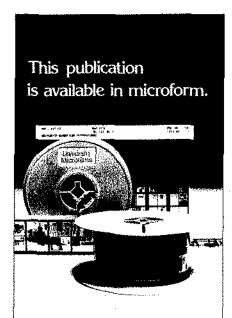
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instrumentation

Coupling of Modules

By examining the line-modular diagram of a spectrophotometer in Figure 1 once again, we observe that some attention must also be given to ways to couple modules. How much attention to give can be put in perspective by considering the following question. If an understanding of instruments can be developed at the modular level, why should manufacturers not sell modules and let users assemble instruments from them (except that manufacturers are in the business of serving users' convenience and saving them time)? We recall that spectrophotometers often come with attachments, and it is not difficult to connect them as needed.

In terms of the main modules of an instrument the problem of appropriateness of coupling can be severe. The flow of information and energy from module to module must be accomplished in particular ways to minimize noise, secure maximum throughput of energy, and insure reliable results. For example, in an optical instrument modules are usually housed in a way that excludes room light from the optical path. To do so requires that optical modules be brought under a common enclosure and that baffles be judiciously introduced. Or again, to couple an amplifier to an electric motor that it will drive, extra components ordinarily must be introduced to insure efficient transfer of energy. Without laboring the matter, these examples illustrate the point that good coupling is essential to an instrument system.

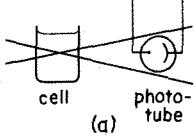
In the electrical domain, the term impedance is often used to describe coupling needs. The input impedance of a module, which is a dynamic factor, plays a main role in determining whether a signal is fully accepted at the input. Although the term is borrowed from the electrical domain it may be generalized easily.

poor coupling. In Figure 3b, however, a lens has been inserted to accommodate the finite optical aperture (input impedance) of the phototube. Alternatively, the detector might also be moved nearer the cell so that the beam would just illuminate its photocathode.

Before looking at instrument specifications there is a simplification in the modular approach that merits exploration. It proves useful to identify two general sequences of modules in instruments. The first will be called the characteristic cluster and comprises all modules in the signal channel from the source through the detector-transducer. It may be useful to refer to Figure 1 again in connection with this division. The second cluster of modules is simply the processing cluster. It completes the instrument and includes amplifier, processing modules, and readout. What is gained by the division is that the modules that relate to (a) the physical technique employed in the meausrement and (b) the sampling procedure are grouped. These modules will vary with the nature of the method and the mode of sample introduction. By contrast, modules in the processing cluster will be remarkably similar from instrument to instrument since data acquisition, data processing, and calculation of analytical quantities will require certain basic types of electronic and computational modules regardless of the kind of data. It is their data capacity and rates of processing that will mainly differ from instrument to instrument.

From this analysis there are useful conclusions. First, in coosidering different instruments, it will in general suffice to deal with their characteristic modules. Second, we can treat processing modules once and expect insights to be generally applicable to all in-

Part II, which is to appear next month, will examine the process of relating specifications for instruments to those for particular modules, the effect of microcomputers on the modular approach, and the extension of the modular approach to sophisticated devices such as "hyphenated" or tandem instruments.



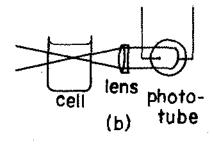


Figure 3. Coupling of sample cell and detector in an absorption spectrometer. (a) Poor coupling: allowing divergence of beam from sample cell causes much of signal to bypass phototube. (b) Better coupling: divergence arrested by insertion of iens before phototube.

Consider the example in Figure 3 based on coupling sample cell and phototube (detector) in a spectrophotometer. For good coupling all the optical beam (signal) from the cell must fall on the active area (photocathode) of the detector. Figure 3a thus illustrates

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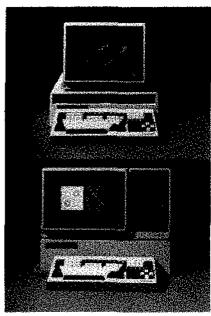
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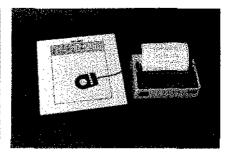


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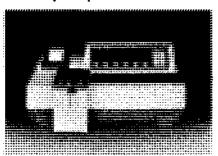
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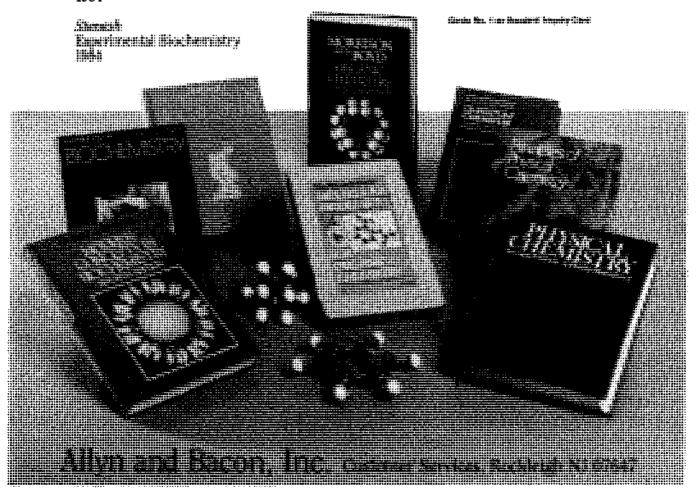
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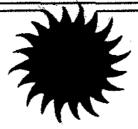
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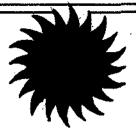
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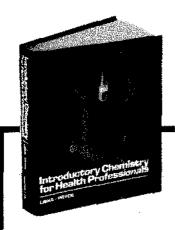
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editorially speaking

What is Good Science?

By the logic of some in federal government policy-making roles, good science must meet three criteria: excellence, pertinence, and appropriateness. Federal science policy does not appear to be aimed at the health of science and its institutions but rather at getting the best possible immediate return on an investment in science and technology. From this point of view, excellence, pertinence, and appropriateness take on potentially ominous implications regarding the identity of good science." It is easy to imagine good science being defined in terms of its relevance and importance to national objectives. This year the objective may be healthy economic growth, next year national defense, and the following year some other problem that is not perceived as such today. While we may all agree that current national objectives may be (momentarily) worthy, decisions based solely on these kinds of premises have the potential to initiate a sequence of events that will ultimately diminish our capacity to produce any kind of science. Changed perceptions of the nations' needs by policy-makers could impact heavily on science. What is considered "good science" and encouraged today could fall from favor tomorrow.

We are in serious trouble when our leaders believe that science can provide a solution to a technological problem in the time frame normally allocated to the accomplishment of "national objectives." We will have a crises of major proportions if those in charge of establishing such a relationship persist in believing that it will bear the desired fruit.

It is, perhaps, natural that man's interest in science and its technological consequences has evolved to the point where he sees it as a useful and necessary enterprise for keeping the modern world going. Unfortunately, however, the current mind-set in government circles confuses science with technology and research with development, Apparently many are eager and happy to encourage technology transfer, but few seem interested in trying to understand the relationship between science and technology and especially the critical need to support science for its own sake. Rather interestingly, the American public seems to be out of step with its elected leadership. A recent Harris survey indicated that 82% of those polled said that scientific research is an endeavor worth supporting even if it brings no immediate benefits. We may be witnessing the beginning of an era where "doing science" will require some specified level of clear relevance to be acceptable—probably first at a fiscal level followed shortly at the intellectual level. Our ability to do science for its own sake seems to be slipping away, partly because of the complexity of what we feel needs to be done and partly because of the way in which we think it should be done. Currently accepted requirements for "good science"-clear relevance and impor-

tance to national objectives-are obviously flawed if we are to be guided by history. Volta would not have gotten very far if he or any of his contemporaries had to argue that the study of twitching frog legs was critical to anything. Yet, in its own way, Volta's work laid the foundation for much of our electronically oriented society. History is replete with numerous such examples and similar situations are undoubtedly occurring today. For example, who can judge the importance-in the currently accepted sense of that word-of a study of the chemistry of sea squids? We know that there are those in positions of authority who tend to deride research which "sounds" funny to them; we also know that charlatans can be found throughout the current system which is designed to foster and support scientific research. Both of these groups would gain material advantages should the proposed criteria for identifying "good science" become firmly established. And the course of classical science will be severely impeded.

Experience has shown repeatedly that some discoveries which initially appear totally irrelevant to human affairs subsequently have great practical importance. In contrast, the practical importance of scientific work can easily be overestimated. Thus some historians believe that metallurgy was largely invented to facilitate the making of ornaments. The important point here is that the detailed usefulness of new knowledge cannot be predicted with any degree of assurance. To insist that the only science worth encouraging is that which has a clear relevance and importance to specific goals today is the height of folly. That policy will surely guarantee a future with an inadequate fundamental knowledge base. While encouraging relatively short-term solutions to important problems, such policies will also discourage doing science as an end in itself.

We cannot afford to continue to insist that the only science which is "good science" is that involved in meeting national objectives. While it might be true that other definitions of 'good science" are less precise and more difficult to apply, and perhaps less obviously important, vis-a-vis specific goals, we must be prepared to encourage some of our brightest minds to pursue "impractical" science without regard to its practicality. It is this "impractical knowledge" that is the ultimate underpinning of our current technology. The basic problem is that we cannot see the details of the important relationships, mainly because we cannot know-or agree upon-the character of the problems that will form the basis of future national objectives. There is one certainty however; we shall never have the fundamental knowledge-whatever it is-to form the basis of solutions to future problems if it is not permitted to be discovered. Good science is the means by which new knowledge is made known.

in this issue

G. N. Lewis

This issue contains the second installment of the proceedings of the G. N. Lewis Symposium which was given at the spring 1982 meeting of the American Chemical Society in Las-Vegas, Nevada. While the first set of papers gave us an overview of Lewis and his contributions to the development of the Department of Chemistry during his tenure at Berkeley, this group concentrates on the specific areas of physical chemistry on which he had profound influence. Seaborg (page 93) gives an eye-witness account of the development of the Lewis acid-base theory, and Brewer (page 101) relates his experiences with some surprising applications of that theory. Pitzer (page 104) focuses on the final period of Lewis' thermodynamic research before he and Randall published their classic hook on that topic, while Lewis' substantial accomplishments in isotope separation and isotope chemistry are summarized by Bigeleisen (page 108).

Lewis' diverse interests and omniverous curiosity led him to the answers to some of the most fundamental chemical questions being posed in the first half of this century. As a result, much of what we teach, even in introductory chemistry, is permeated with Lewis' ideas, particularly those on bonding and acid-base theory. This issue has a number of articles which involve one of these topics, either introducing interesting aspects of them or presenting ways of teaching them more effectively.

Bonding Theory

Lewis' octet theory and the shared electron pair are the foundation of modern bonding theory, and their use is so all-pervasive that it is difficult to imagine they were the center of controversy when Lewis first promulgated his ideas. Last month Calvin (page 14) related how the theory revolutionized the understanding of organic chemistry, and in next month's issue several authors will detail its effects elsewhere and the general response when it was introduced. In this issue, however, Saltzman (page 119), in a paper which was not part of the Lewis symposium, details the problems one of Lewis' contemporaries, W. A. Noyes, had in accepting the electron-pair concept of the chemical bond. This study gives an insight not only into the resolution of an important question in chemical theory but also into how personalities and local circumstances can influence the course of such a resolution.

Once the controversy was settled, however, the Lewis electron dot structure became an integral part of the introductory course, and teachers are still seeking new ways of helping their students to understand and apply this concept. Two articles in this issue (Clark, page 100, and Zandler and Talaty, page 124) present their authors' rules for a systematic approach to writing Lewis octet structures. Any teacher who has watched his or her students caught in the vicious cycle of repeatedly moving electron dots to satisfy the requirements of one atom only to find they have unbalanced an atom on the other end of the molecule will find one or the other of these approaches helpful.

Acids and Bases

The Lewis acid-base theory is almost as familiar to (and, unfortunately, often as misunderstood by) the introductory

chemistry student as the electron pair bond concept. Lewis turned to investigating the nature of acids and bases at least in part in an attempt to verify experimentally some of the general concepts put forth as part of his theory of bonding. Seaborg, who was his laboratory assistant at the time, relates the course of experiments which were used to demonstrate Lewis' generalized theory of acids and hases (page 93). This paper is remarkable not only because it has been possible to include many of the details of the experiments due to their simplicity but also because it shows the workings of two great scientific minds—Lewis at the peak of his reasoning and deductive powers and Seaborg as yet unaware of his full power but growing in sophistication and confidence through association with his mentor.

Since students need a thorough understanding of acid-base reactions, their teachers are often looking for new and interesting ways of presenting this chemistry. This month's Tested Demonstration, "The Rainbow Connection" by Hutton (page 172), uses a "magic" trick to illustrate the effect of pH on indicators and elicit a lively classroom discussion. For those introducing the concepts of the Bronsted-Lowry theory of acids and bases, Macomber (page 128) offers a readily understood analogy to use in explaining the leveling effect.

Two articles in this issue provide interesting information about acid-base chemistry. Poplin (page 117) points out that while it is well documented that neutral ions have an effect on acid-base balance in the body, the reasons are sometimes misunderstood. He then proceeds to give examples from the literature and explain the true relationships involved. The Chemical of the Month column features nitric acid; Pannu (page 174) outlines the history, preparation, and physical and chemical properties of this familiar acid.

The Periodic Table

The periodic table, another basic of the introductory course. is so familiar to us all that many may assume it is now engraved in stone, as immutable as the pyrimids or the Rocky Mountains. However, as Fernelius and Powell pointed out in the June 1982 issue (page 504), a serious ongoing problem with the use of the A and B subgroup terminology has finally come to a head in this past decade, and the American Chemical Society Committee on Nomenclature launched an urgent campaign to resolve the confusion as rationally as possible. After over a year of gathering comments and suggestions from all areas of the chemical community and carefully classifying and considering these, the Committee has issued a report (page 136) with a recommended format for the periodic table which both eliminates the A/B confusion and ties the subgroup designations more closely to their element's electronic configuration. Teachers of all areas of chemistry will want to examine these recommendations carefully and keep this new format in mind when selecting textbooks and purchasing new classroom wall charts.

One of the periodic properties used by Mendeleev in constructing the original periodic table was atomic volume. New data obtained by modern X-ray methods have been used by Singman (page 137) to refine our knowledge of the "Atomic Volume and Allotropy of the Elements." Feinstein (page 128) offers an interesting application of the diagonal relationships found in the periodic table that illustrates the usefulness of this concept.

The Research Style of Gilbert N. Lewis

Acids and Bases

Glenn T. Seaborg

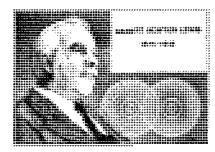
Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

I started my graduate work in the College of Chemistry at Berkeley in the fall of 1934. As an undergraduate at UCLA, I bad become acquainted with the 1923 book by Gilbert Newton Lewis "Valence and the Structure of Atoms and Molecules" and was fascinated by it. I wanted to meet and become acquainted with this remarkable man, but I could not then have envisioned that I would be working with him on a daily basis.

I was drawn to Berkeley by my admiration for Lewis and by the presence there of Ernest Orlando Lawrence and his cyclotron, for I was intrigued by the relatively new field of nuclear science. When I arrived and started my classes and research, I found the atmosphere and surroundings exciting to an extent that defies description. It was as if I were living in a sort of world of magic with continual stimulation. In addition to Lewis I met the authors of most of the chemistry textbooks I had used at UCLA-Joel Hildebrand, Wendell Latimer, William Bray, Walter Blasdale, Walter Porter. I took classes from Axel Olson, Gerald Branch, and William Giauque, and I opted to do my graduate research in the nuclear field under Ernest Gibson in a laboratory situated in Ernest Lawrence's nearby Radiation Laboratory. In my thermodynamics class with Olson I was introduced to the classic book "Thermodynamics and the Free Energy of Chemical Substances" hy G. N. Lewis and M. Randali, and this book was also used. although augmented by more recent material, in Giauque's more advanced thermodynamics course that I took during the second semester of my graduate work.

Nearly everyone who participated as a member of the College of Chemistry in the Lewis era recalls and comments on the Research Conference presided over by Lewis in his own mimitable style. This was held each Tuesday afternoon during the school year, starting at 4:10 p.m. and lasting until about 5:30 p.m. in Room 102 at the extreme south end on the first floor of Gilman Hall. Lewis' office was only a few doors away in Room 108, with its door usually open. His and the College of Chemistry's secretary, Mabel Kittredge (Mrs. Wilson), waa located next door to him in Room 110 (Fig. 1). At the Research Conference, Lewis always occupied the same place at the central table-the first chair on the right side facing the speaker and the blackboard. Members of the faculty sat at the table, and the others (graduate students, post docs, research fellows, etc.) sat in chairs set at two levels at the two sides and back of the room. Lewis always had one of his Alhambra Casino cigars in his hand or mouth and several more in his upper coat pocket (Fig. 2). The first of the two speakers, a graduate student giving a report from the literature, started when Lewis gave his inevitable signal: "Shall we begin!" The second speaker-a faculty member, research fellow, or advanced or finishing graduate student—then reported on research that had been conducted in the College. Although Lewis dominated the scene through sheer intellectual hrilliance, no matter what the topic, anyone was free to ask questions or speak his piece; in the latter instance, prudence suggested that the comment had best not be foolish or ill-informed. If Lewis had any weakness, it was that he did not suffer fools gladly-in fact. his tolerance level here was close to zero.

During my three years as a graduate student and the sub-



sequent years until the war, Lewis always attended the Nuclear Seminar held on Wednesday evenings in Room 102, Gilman Hall. This seminar was run by Willard Libby, together with Robert Fowler (until he left Berkeley in 1936), and was attended regularly by Wendell Latimer, William Bray and Ermon Eastman. Lewis also conducted some research with neutrons during 1936–1937. He was always highly supportive of my nuclear research, some of which was conducted in my spare time during the period that I served as his personal research assistant.

With this hackground in mind, let me now proceed to a description of my work with Lewis as a research associate. I'll never forget how this got started. I had completed my graduate research in the spring of 1937, my PhD degree had been awarded, and it was time for me to go and find a job someplace. Lewis didn't recommend me for a position anywhere, which I could have regarded as a bad sign. Actually, in this case, it was a good sign. That meant that I still had a chance to stay at Berkeley in some capacity—which, of course, was my objective. One day in July after the next academic year had actually started (so I was technically without any salary), Lewis called me into his office and asked me if I would like to be his research assistant. Lewis was unique in having a personal research assistant, whose salary at that time was \$1800 per year. Although I was fervently hoping to stay in some capacity, I was flabbergasted to find he thought me qualified for this role, and I expressed my doubts to him. He smiled and indicated that if he didn't think I could do the job he wouldn't have offered it to me. My acceptance of the position he offered was enthusiastic, and thus our two-year intimate association began.

Lewis had suffered some disappointment in his previous



Figure 1. Entrance door to Room 110, Gilman Hall, Mabel Kittredge's office and the official entrance to Lewis' office in Room 108.

research with neutrons. In fact, I had played a role in advising him frankly where he was going wrong, an act that took some courage on my part, and this may have influenced him in his decision to undertake the risk of having me as his research assistant. He told me that he had decided to forego research for a time, during which I would be free to continue the nuclear research that I had underway. As I have already indicated, I continued a rather substantial effort in the nuclear field, with his blessing, during the entire two-year period that I was associated with him.

In the late fall of 1937 Lewis resumed his research. He decided to try to separate the rare earths praseodymium and neodymium using a system involving repetitive exchange between the aqueous ions and their hydroxide precipitates. He employed a long, tubular, glass column extending from the third floor to the basement at the south end of Gilman Hall. The column was constructed with the help of Bill Cummings, the long-time glass blower in the College, and erected with the help of George Nelson, the irascible head of the machine shop. (He was irascible from the standpoint of graduate students,

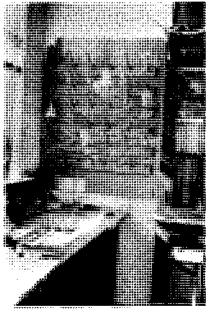


Figure 2, G. N. Lewis with his cigar as he was typically seen at the Tuesday afternoon Research Conference in Room, 102 of Glimen Hall.



Figure 3. (above) Entrance to Room 119, Gilman Hall, when Seaborg served from 1937~1939 as research associate with Gilbert N. Lewis.

Figure 4. Sink area in Room 119 where Seaborg serviced the experiments he performed with Lewis in between moonlighting as a nuclear chemist.



but very polite to Lewis and now to me in my prestigious role as the assistant to the "Chief.") The long column was serviced by a machine-driven system for agitation in order to keep the hydroxide precipitates suspended along the column's length. It was my duty to keep this operating, which I did with only limited success. Lewis, with no help from me, measured the degree of separation of the praseodymium from neodymium with the spectroscope in the darkroom off Room 301, Gilman Hall. For whatever reason, including possible shortcomings in my performance, no detectable separation of praseodymium from neodymium was achieved.

In the early spring of 1938, Lewis returned to his former interest in acids and bases—the theme of this essay. If I recall correctly (this was 44 years ago!) he was, at least in part, motivated by the need for an interesting topic, supported by feasible experimental demonstrations, for a talk that he was scheduled to give at the Franklin Institute in Philadelphia in May on the occasion of his receiving a Doctor of Science degree and Honorary Membership in the Franklin Institute in connection with the Dedication of the Benjamin Franklin Memorial (i.e., the large new building housing the Institute's activities, including the science museum). In any case, much of our first work in this area was concerned with such demonstration experiments.

Our experiments were directed toward his generalized concept of acids and bases. In his 1923 book "Valence and the Structure of Atoms and Molecules" Lewis had proposed a very general definition of acids and bases. According to that definition, a basic molecule is one that has an electron pair which may enter the valence shell of another atom to consummate the electron-pair bond, and an acid molecule is one which is capable of receiving such an electron pair into the shell of one of its atoms. Lewis wanted, with my help, to find a broad base of experimental evidence for this concept.

We worked in Room 119 (Fig. 3), at the north end of the first floor of Gilman Hall, a laboratory that Lewis had used for a number of years previously. It was here that he did his work with Ronald McDonald and others during 1933-35 on the isolation of deuterium by the electrolysis of water and the determination of a number of its properties. The apparatus used for this work was still there in the east side of the room, a part of the room that we didn't use at this time. We used the laboratory bench extending along the west side of the room. flanked in the back by a row of windows. The sink, at which I washed and cleaned our glassware each evening (Fig. 4), was at the extreme right (north) end of the bench and our writing desk adjoined the opposite end of the laboratory bench against the south wall. Our indicator experiments were performed on the laboratory bench top at the ambient room temperature in ordinary test tubes. For later, more sophisticated (but still basically simple) experiments, which I shall describe presently, we used a low temperature bath which consisted of a large, wide-mouthed Dewar filled with acetone which was cooled by the addition of chunks of dry ice. Our vacuum bench, used in later experiments, was in the center of the room, opposite and parallel to the laboratory bench.

I was immediately struck by the combination of simplicity and power in the Lewis research style and this impression grew during the entire period of my work with him. He disdained complex apparatus and measurements. He reveled in uncomplicated but highly meaningful experiments. And he had the capability to deduce a maximum of information, including equilibrium and heat of activation data, from our elementary experiments. I never ceased to marvel at his reasoning power and ability to plan the next logical step toward our goal. I learned from him habits of thought that were to aid continuously my subsequent scientific career. And, of course, working—and apparently holding my own—with him, boosted

¹ This aspect of Lewis' work is covered in the Symposium article by Bigeleisen on page 106 of this issue.

my self-confidence, which was not at a very high level at this stage of my life.

Starting at this time, I worked with Lewis on a daily basis, interspersed with intervals when he was otherwise occupied and during which I pursued my nuclear research. He would arrive each day between 10 and 11 a.m. in his green Dodge car, which he would park on the road (South Drive, Fig. 5) between the Chemistry buildings and the Men's Faculty Club. When I spotted his car, I knew that it was time to join him in Room 119. We then usually would work together until about noon or 1 p.m., when he went to the Faculty Club to play cards with his friends (he didn't eat any lunch) while I went to lunch. He usually returned to our laboratory at about 2 p.m. and we would work together until late afternoon. This gave me time to work on my other research projects before he came, during the noon break, and after he left. However, be often gave me assignments to assemble materials, prepare solutions, etc., over the noon hour, or overnight, or when he left town for a day or two. These assignments were usually unrealistically demanding for such a time scale, and I had to scramble to meet his demands. This was done not for the purpose of keeping me busy, but because he underestimated the size of the tasks. Sometimes we worked in the laboratory during the evening after dinner, often on Saturday morning, and occasionally on Sunday. We did most of the work on writing up our work for publication on Sunday afternoons.

I believe that the best way to capture the flavor of my experiments with Lewis on generalized acids and bases in preparation for his lecture at the Franklin Institute is to quote from my journal of that period.

Thursday, March 17, 1938

Today we performed exploratory indicator experiments to determine the color of a number of indicators (that is, colored organic molecules or dyes), dissolved in about 75 cc dioxane. Lewis plans to work with these indicators. They are:

- crystal violet
- 2. bromcresol green
- 3. methyl red
- 4. chlorphenol red
- 5. alizarin
- 6. bromthymol blue
- 7. cyanin orange
- thymol blue
- 9. phenoiphthalein

Friday, March 18, 1938

Professor Lewis and I continued the joint experiments that we began yesterday. We added 4-5 drops of SnCL, solution (10% in CCl₄) to approximately 1 cc of each of the nine indicators (in dioxane) prepared yesterday. In each case we observed the color change, or lack of change, as this generalized acid (SnCl₄) was added. In other experiments, we added 2-3 drops of pyridine solution (15% in dioxane) to approximately 1 cc each of the same indicators—there was very little color change (if any) in most cases.

Saturday, March 19, 1938

Continuing our experiments of yesterday and the day before, Lewis and I added 2-3 drops of triethylamine solution (approximately 10% in dioxane) to approximately 1 cc of each of the nine indicators (in dioxane) that we prepared on Thursday; this is for the purpose of observing the change in color (or lack of change in color) when this generalized base (trimethylamine) is added to the indicators. These are exploratory experiments to get the feel for the way generalized acids and base react to change the colors of indicators.

Monday, March 21, 1938

Today Lewis and I added 2-3 drops of BCl₈ solution (10 grams per 500 cc of CCl₄) to approximately 1 cc of each of the nine indicators (in dioxane) prepared last Thursday. The color changes produced by this generalized acid were observed in order to compare them with the color changes produced by the generalized acid SnCl₄ in our experiments last Friday. In general, the color changes, or lack of color changes, are strikingly similar for the two acids.

Thursday, March 24, 1938

I prepared indicators for Professor Lewis by dissolving a few tenths



Figure 5. Gilman Hall, Le Conte Hall, and Campanile, with South Drive in the foreground (~1941).

of a gram of each of the following in about 75 cc of acetone—brom-cresol purple, bromthymol blue, aurin, neutral red, phenol red, cyanin, tropaeolin 00, and thymol blue. We passed the acid SO_2 into small portions of each of these solutions and observed the color changes (or lack of color changes).

Friday, March 25, 1938

In our experiments today Professor Lewis and I added 3–4 drops of the base triethylamine (10% in dioxane) and in separate experiments again passed the acid SO₂ into portions of each of the indicator solutions prepared yesterday and observed in each case the color change. We then added the acid BCl₃ to portions of a number of these solutions and in separate experiments the acid SnCl₄ to some of these solutions (tropaelin 00 and thymol blue) and noted similarities in the color changes. The effects of the bases triethylamine and pyridine on tropaelin 00 and thymol blue were also noted.

Monday, March 28, 1938

Today Lewis and I set up and practiced a number of demonstration experiments on generalized acids and bases that he will use in his lecture at the Franklin Institute in May. We observed the color changes when bromcresol purple, bromthymol blue, neutral red, and thymol blue (all in acetone) were treated with the base triethylamine and after that with the acid SO₂. Similar experiments with the acid BCl₃ and the base pyridine with tropaelin 00 (in acetone) were also performed.

Wednesday, April 20, 1938

Today Lewis and I experimented with the indicator thymol blue (in acetone) to which a few drops of the acid $AgClO_4$ (in benzene) were added. The color change was observed, and theu 1-2 drops of the base pyridine (in dioxane) were added and the color change again noted. We found we could titrate back and forth successfully with this acid and this base. Similarly we found we could do this with the indicator tropaelin 00 (in acetone).

Thursday, May 5, 1938

Lewis and I experimented with the acid BCl₃ (in CCl₄) added to 2–3 cc methyl red (in dioxane). We found that the heavy precipitate which formed could be redissolved with the base pyridine (in dioxane).

Friday, May 13, 1938

Today I helped Professor Lewis pack his suitcase for his demonstration lecture at the Franklin Institute next Friday morning. He is travelling to Philadelphia by train. I was pleased to see him bring into our laboratory and place on the bench two suitcases, because I felt this would give me ample room to pack the material for his demonstration experiments. However, he told me that he would need much of this space for his cigar boxes. (He smokes "Alhambra Casino" cigars incessantly and will need a good supply to keep him going during his visit to Philadelphia.)

He filled one entire suitcase and part of the other with cigar boxes, which meant that I had to exercise some ingenuity in order to get the equipment, chemicals, etc., into the remaining space.

Lewis gave his talk at the Franklin Institute in Philadelphia on Friday morning, May 20, 1938, as scheduled. During his talk he performed the demonstration experiments that we had developed. So far as I know, his talk was well received. However, the main impact came from his publication, based on the talk, which appeared in the September issue of the Journal of the Franklin Institute [226, 293 (1938)]. In the preparation of this paper, which was written entirely by Lewis without my help, he used additional data that we developed in subsequent experiments. However, the main thrust of the paper was his beautiful exposition of his concept of generalized acids and bases, which had a worldwide impact and became the "bible" for workers in this field. His primary acids and bases are characterized by their instantaneous neutralization reactions, which occur without any heat of activation. He also introduced here his concept of secondary acids and hases, whose neutralization requires a heat of activation. I soon found that I was destined to work with him on a program of experimental verification of this idea.

Lewis and I resumed our experiments on generalized acids and bases during June and early July, 1938, after he returned from his trip to Philadelphia. We found many cases where, with one solvent and one indicator, the colors obtained seemed to be dependent only upon the acid or basic condition of the solution and not at all upon the particular acid or base. By means of the color changes the solutions could be titrated back and forth as in aqueous solution. For example, with thymol blue dissolved in acetone, the color was yellow with either pyridine or triethylamine, while the acids SnCl₄, BCl₃, SO₂, and AgClO₄ gave an apparently identical red color. With crystal violet in acetone, the color changes successively from violet to green to yellow upon the gradual addition of SnCl₄ or BCl₃, after which the original violet color could be restored upon the addition of an excess of triethylamine.

Because similar effects could also be obtained by HCl, and since we had been working in the open with reagents that had not been especially dried, we were afraid that some of the similarities in color produced by the different acids could be due to small impurities of H-acids in the reagents. We therefore conducted experiments with very dry solvents, given to us by Dr. C. H. Li, with indicators which themselves contain no labile hydrogen, such as butter yellow, cyanin, and crystal violet, and upon the vacuum bench to prevent the pick-up of water. These experiments gave the same results as those performed in the open with ordinary reagents. Again a couple of quotations from my journal can give the flavor of this work.

Thursday, June 9, 1938

Professor Lewis has returned from his trip to Philadelphia, and we recommenced our experiments on generalized acids and bases in Room 119. Today we did experiments in which we added the acid BCl_3 (in CCl_4) to crystal violet (in acetone) and observed a succession of color changes (blue, green, and yellow). We then added the acid SnCl4 to another, identical solution of crystal violet and observed the same succession of color changes. Lewis is writing his paper "Acids and Bases" for publication in the Journal of the Franklin Institute. This is based on his demonstration lecture at the Franklin Institute last month and will include information from additional experiments that we will now perform in order to round out his story.

Friday, June 17, 1938

Lewis and I continued our experiments on our new vacuum line. We observed the color change when the acid BCl_3 was added to a solution of crystal violet in ether which had been thoroughly dried by Dr. C. H. Li. We also added the acid BCl_3 to crystal violet in acetone (very thoroughly dried by Dr. C. H. Li) and again observed the successive color changes; then we added triethylamine (thoroughly dried) and noted the color change sequence back to the original color. Our titrations thus gave the same results when water was thoroughly excluded as our original work with ordinary reagents conducted openly on the laboratory bench.

Toward the end of June, Lewis gave me leave to go to San

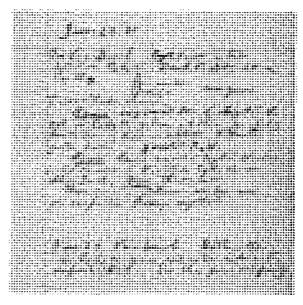


Figure θ. Entry in t.ewis' hand in Glenn Seaborg's laboratory notebook describing experiments on acid/base systems carried out in Seaborg's absence, 23 June 1938.

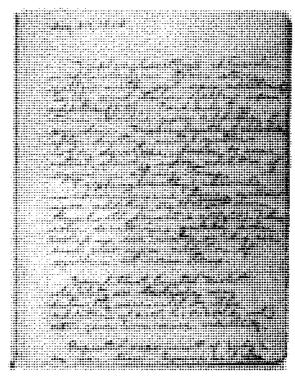


Figure 7. Sample page from Glenn Seaborg's laboratory notebook during his collaboration with Lewis, 23 August 1938.

Diego to give a talk on my nuclear work at a meeting of the American Physical Society. During my absence he conducted vacuum bench experiments to observe the color changes when SnCl₄ and triethylamine were added to a solution of crystal violet in thoroughly dried chlorobenzene, when SnCl₄ or HCl were added to a solution of butter yellow in chlorobenzene, etc. I reproduce in Figure 6 his notes covering one of these experiments as he recorded them in my notebook.

In addition to taking some vacation during the summer of 1938 with his family at their cottage in Inverness, he spent a good deal of time on his paper "Acids and Bases," which he was getting ready to send to the Journal of the Franklin Institute. The process of formulating his thoughts and setting them down on paper suggested to him many little confirma-

tory experiments which we then performed. I reproduce in Figure 7 a sample page from my journal (notebook) of this period.

In September Lewis turned to his next project—experiments related to his concept of secondary acids and bases—and from the latter part of September until Christmastime, I worked with him on a daily basis on much the schedule that I outlined earlier. We did some broadly based experiments which led to the publication of our background paper "Primary and Secondary Acids and Bases" [J. Amer. Chem. Soc., 61, 1886 (1939)], and a detailed investigation of a specific secondary and primary base, which was published as a companion paper entitled "Trinitrotriphenylmethide Ion as a Secondary and Primary Base" [J. Amer. Chem. Soc., 61, 1894 (1939)].

It was in the course of this detailed investigation of this secondary and primary base that I was to see firsthand a master researcher at work and to be privileged to be a participant. Here was a prime example of simple experiments leading to interesting and fascinating interpretations and in my description I shall do my best to capture the flavor of the process. As background for understanding these experiments, we should recall that Lewis had suggested that there is a large group of acids and bases, called primary, which require no energy of activation in their mutual neutralization, and there is another group, called secondary, which do not combine with each other (nor does a secondary base combine with a primary acid nor a secondary acid with a primary base) except when energy, and frequently a large energy, of activation, is provided.

Based on the results of some preliminary experiments and Lewis' intuition and analysis, we decided that the intensely blue 4,4',4"-trinitrotriphenylmethide ion should be a base that could exist in the primary and secondary forms and be a good material for experimentation to give support for and information on this concept. Our first experiments, performed in open test tubes, are described in my journal.

Wednesday, September 21, 1938

Lewis and I began test-tube experiments with 4,4',4"-trinitrotriphenyimethane which we believe can be used to test our ideas about primary and secondary bases. We titrated trinitrotriphenylmethanc in toluene at room temperature with sodium hydroxide (0.02 M in absolute alcohol) to form an instantaneous blue color and then with HCl (0.02 M in absolute alcohol) to form an instantaneous colorless solution. The blue color is due to trinitrotriphenylmethide ion while the colorless form is trinitrotriphenylmethane. When the experiment was repeated at ice temperature, we observed the same color changes except that it took 4-5 seconds for the blue solution to turn colorless upon the addition of HCl. At the temperature of liquid air (near the freezing point of the solution), there was very slow development of the blue color and of the colorless solution (order of minutes). Addition of more HCl to the blue basic solution gave a bright "orangeyellow" solution which slowly faded to colorless. When we repeated the experiment at ice temperature, the "orange-yellow" color formed upon the addition of the excess HCl. We also experimented with a solvent of three parts ethyl alcohol and one part toluene and found that we could titrate back and forth between the blue (with NaOH) and orange (with HCl) colors at low temperatures.

Thursday, September 22, 1938

Today Lewis and I did test-tube experiments with trinitrotriphenylmethane in a solvent containing three parts ethyl alcohol and une part toluene. We titrated with NaOH and acetic acid HAc (in absolute alcohol). We found that, with the acid HAc at liquid air temperature (freezing point of toluene), the "orange yellow" color did not appear. We also found that this is true when we used toluene with no alcohol. The fading of the blue color to colorless was quite fast upon the addition of HAc at ice temperature but slow at the lower temperature. Apparently HAc has a different effect than HCl. We measured the solubility of crystal violet chloride in various concentrations of phenol in toluene. We plan to use this blue solution as a comparison standard in our experiments to measure the rate of fading of the blue color of trinitrotriphenylmethide ion; this ion apparently acts as a secondary base, and we wish to investigate the kinetics of its trans-

formation to the colorless form which seems to be the primary base. A set of standard color comparison solutions will be prepared by diluting the crystal violet solutions successively by factors of two.

Lewis soon deduced that the action of the HCl was not our main concern and our first interest should be in the secondary base (B_s^-) in the blue form that requires a heat of activation to be converted to the primary form (B_p^-) in which it reacts instantaneously with the HAc. Thus he deduced that the two forms would have these formulae

We launched into a series of kinetic experiments to measure the rate of fading of the blue B_s^- upon the addition of acetic acid or other acids which combined instantaneously with the small proportion of B_p^- that was present. This mechanism, for any acid HY, can be summarized as follows

$$B_s^- \rightleftarrows B_n^- \tag{1}$$

$$B_p^- + HY \to BHY^- \tag{2}$$

$$\rightarrow$$
 HB + Y⁻⁻ (3)

He suggested that reaction (2) is the rate determining step, and that the concentration of B_p^- depends upon the concentration of B_s^- , the temperature, and the difference in energy between B_p^- and B_s^- . On this basis, the reaction should be bimolecular and the measured heat of activation should be the same with all acids (HY) of sufficient strength.

To test this we measured the rates of reactions (rate of fading of the blue color) over a range of temperatures in order to determine the heat of activation. The experimental method was simplicity itself. The first experiments were performed in open test tubes, but it was found that trinitrotriphenyimethane was sensitive to oxygen under the conditions used, and, therefore, the reaction vessels were evacuated. Our solvent was 85% ethyl alcohol and 15% toluene, and our first series of experiments were with acetic acid. The reaction vessel, in the form of an inverted Y, with the alkaline blue methide ion solution in one limb and the acid in the other, was placed in the low temperature bath (of acetone cooled with dry ice). When temperature equilibrium was attained, the vessel was tipped rapidly back and forth until the contents were thoroughly mixed. The reaction (rate of fading of the blue color) was then followed by comparing the color with a set of standard color tubes. (The set of standard color tubes consisted of solutions of crystal violet, which had blue colors nearly identical to those of the blue methide ion, made by successive two-fold dilutions to cover the entire range of diminishing blue color.) After the experiments had indicated that the reaction was always of first-order with respect to the colored ion, the procedure was simplified further. The time was taken merely between the mixing and the matching of a single color standard, which corresponded to one-sixteenth of the original concentration of the blue methide ion (i.e., the color standard was made by four two-fold dilutions of the original matching crystal violet solution.)

We made measurements with acetic acid at four temperatures: -53°C, -63°C, -76°C, and -82°C and from these we could calculate that the reaction was first-order with respect to the acid and the heat of activation for the reaction of fading of the blue methide ion was 8.6 kcal. According to our interpretation, then, this is the energy difference between the

secondary form B_s and the primary form B_p of the methide ion. We next measured the heat of activation for the same reaction for five additional acids, for which the reaction also proved to he bimolecular, and found the same value for the heat of activation within the limits of our experimental value—an average of 9.1 kcal. Such a result is to be expected from our interpretation that the heat of activation should be equal to the difference in energy between the primary and secondary forms of the hase. If the activation occurred only at the moment of collision between the reacting molecules, it would be hard to explain why the heat of activation or, in other words, the potential barrier in the activated complex, should be the same for such very different substances as alcohol (for which we also measured the heat of activation, indirectly, as described below) and our other acids—chloroacetic, furoic, α -naphthoic, lactic, and benzoic, as well as acetic acid.

I have recounted here in some detail only the central conclusions from this research. Lewis made many other deductions that are too involved to be easily described here, hut which can be enjoyed by reading the paper reporting this work. I shall merely sketch some, by no means all, of these conclusions. From some other of our measurements he was able to deduce the equilibrium constant for the reaction in which the blue methide ion is formed from the reaction of the hydroxide (or ethylate) with the trinitrotriphenylmethane, and the heat of activation, from which he found that the heat of activation for the reverse reaction (B, plus ethyl alcohol), corresponding to the difference in energy between the primary and secondary forms of the base, is 8.9 kcal, in good agreement with our direct determination for the six acids (9.1 kcal). He could deduce from our measurements that only one-eighth of the trinitrotriphenylmethane was in the form of the blue methide ion under the conditions of our kinetic experiments. He also concluded that our kinetic measurements with such a weak acids as phenol and boric acid suggest that these displace the solvent alcohol from the nitro groups in the blue methide ion to an extent depending upon their concentration, and that the ion with the phenol attached is less reactive than the corresponding alcohol compound.

Earlier on, I have alluded to the orange color produced immediately upon the addition of the strong acid HCl to a solution of the blue methide ion. We also found this upon the addition of the relatively strong trichloroacetic acid. Lewis found a ready explanation for this. When the blue ion has been formed and the central carbon has lost its power of acting immediately as a base, the basic power has, in a certain sense, been transferred to the three nitro groups. Therefore, a aufficiently strong acid should attach itself at one or more of the nitro groups and in this process the blue ion should act as a primary base.

We finished these experiments just before Christmastime in 1938. After a diversion in January to test another of his ideas experimentally, we began in Fehruary the process of writing our two papers on primary and secondary acids and bases for publication in the Journal of the American Chemical Society. Writing a paper with Lewis was a very interesting process. We did most of our work on this, extending sporadically over several months, on Sunday afternoons in our laboratory, Room 119 in Gilman Hall. The process consisted of Lewis, pacing back and forth with cigar in hand or mouth, dictating to me. I recorded his thoughts in longhand. However, his output was interspersed with discussions with me and even with experimental work when he wanted to check a point or simply wanted a break. His sentences were carefully composed, and the result was always a beautiful and articulate composition.

After we had finished the two papers up to the point of the summary of the second paper, he said to me that he was tired of this process, and suggested that I write this summary by myself. By this time I was familiar enough with his thought processes to make this feasible. I wrote the following, which

he accepted after no more than a glance at it and without changing a word.

Trinitrotriphenylmethide ion was expected and has proved to be a secondary base. In alcohol when this blue ion is added to any weak acid at temperatures between -30 and -80° the formation of the corresponding methane is slow and can be followed colorimetrically. The rate of neutralization was studied with numerous acids and under like conditions the rates diminish with diminishing acid strength. With the weakest acids the rates are not proportional to the concentration of acid, and this fact is explained. With the six acids of intermediate strength the rates were found proportional to the concentrations of blue ion and of un-ionized acid, and unaffected by neutral salts. In these cases the heat of activation was calculated from the temperature coefficient of the rates and was found approximately constant with a mean value of 9.1 kcal. By indirect methods the rate of neutralization by alcohol itself was determined. Here the heat of activation is found to be 8.9 kcal. The constancy of the heat of activation over the great range from chloroacetic acid to alcohol can hardly be explained by the theory of an activated complex. The value obtained is taken as a measure of the difference in energy between the primary and secondary forms of the base. The small departures from this constant value are attributed in part to experimental error, but especially to differences in the actual composition of the reacting ion. Several kinds of evidence are adduced to show that the actual composition of the blue ion depends not only upon the solvent but in several cases upon the presence of other solutes.

While the trinitrotriphenylmethide ion is a secondary base with respect to addition of acid to the central carbon, it is a primary base with respect to addition of acid to the nitro groups. In the presence of strong acids an orange substance is thus formed which contains more than one free hydrogen ion per molecule. The very slow rate of fading of the orange compound is studied, and an explanation is suggested for the large catalytic effect of water. Mono- and dichloroacetic acids give mixtures of the orange and blue substances and the rate of fading in these solutions leads to some of the conclusions already mentioned.

During January, 1939, Lewis and I worked to make an experimental test of an old, rather far out, idea of his. This is far afield from acids and bases, hut is, I believe, worth mentioning as a further illustration of the breadth of his intellect and interests. A number of years before (1930) he had published an article in Science magazine [71, 569] on "The Symmetry of Time in Physics." A consequence of this theory, as it applies to radiation, is that we must assign to the emitting and the absorbing atom equal and coordinate roles with respect to the act of transmission of light. A consequence of this, Lewis told me, is that the receiver or observer of the light (for example, the apparatus used for this purpose) is of importance equal to that of the emitter of the light and exhibits its own influence upon how the light manifests itself.

Lewis told me he wanted to test this hypothesis by setting up a Michelson interferometer to detect the interference fringes with different receivers or detectors of radiation and to thus determine if some properties of the radiation depend on the receiver or detector as it should if it conformed with his theory on the symmetry of time. He asked me to set up a Michelson interferometer in the darkroom off Room 301 at the southwest corner of the third (attic) floor of Gilman Hall. This room contained a spectrograph with which Lewis had made his spectrographic measurements mentioned earlier on rare earth samples.

I went to the Department of Physics and borrowed a Michelson interferometer which was ordinarily used for demonstration experiments in some of the physics lecture courses. In order to make this operate correctly I had to prepare some "half-silvered" surfaces on glass with a silver layer of such thickness that about one-half of the incident light would be reflected and the other half transmitted through the layer. Since Professor Axel Olson had some experience with this "half-silvering" process, I enlisted his help. Lewis and I detected the interference fringes with each of a number of different types of photographic film in order to see if we could detect any gross differences in the way the films reacted. We

| | TNB | TNT | TNX | TNM |
|---|-----|----------------------|---|---|
| + | + | + | + | |
| + | + | + | + | |
| | + | + | | |
| | + | + | | |
| | + | + | ? | |
| | | + + + + + + | + | + |

found some peculiar effects, which excited Lewis for a time, but my ekepticism prevailed when I was able to explain these as due to rather prosaic failures in our techniques and which we could correct to eliminate the effects. These negative results then convinced Lewis to go on to something else.

During the period from January to June, 1939, Lewis and I did scouting experiments with a wide range of indicators, acids, and bases. Many interesting observations were made that are not susceptible to summarization in a reasonably brief fashion. As always, there were moments of excitement. I recall a series of experiments, conducted with test tubes immersed in our acetone-carbon dioxide bath, on the development of color when trinitrobenzene and sodium phenolate were reacted in absolute ethyl alcohol over a range of temperatures below room temperature. We found that large excesses of NaOH were needed to produce the indicator color. This elicited some bizarre interpretations from Lewis. However, when these experiments were repeated on the vacuum line the action of NaOH was more reasonable. Apparently, in our open test tube experiments, large amounts of CO2 were absorbed in the alcoholic solution from our CO₂-cooled acetone bath!

Our research during this period did result in one coordinated project from which some interesting conclusions could be drawn. We made observations on the degree of development of color (a measure of the degree of reaction between these acids and bases) when each of the bases ammonia, methylamine, dimethylamine, triethylamine, or hydroxide is reacted with each of the acids m-dinitrobenzene and symmetrical trinitrobenzene, trinitrotoluene, trinitroxylene, and trinitromesitylene (25 combinations in all). At any point in the table corresponding to a given base and a given nitro compound the sign + indicates the formation of color.

We found with trinitrobenzene the intensity of color is least with triethylamine, greater with dimethylamine, and still greater with methylamine and ammonia. For the direct addition of the base to one of the ring carbons that is not attached to a nitro group, there is the possibility of double chelation of hydrogen atoms to nitro groups in the case of methylamine and ammonia, thus strengthening the acid-base combination. With the weaker acid, m-dimtrobenzene, methylamine, and ammonia-which are capable of double chelation-give good colors, while the two stronger bases, dimethylamine-which is capable of only one chelation-and triethylamine—where no chelation is possible—give no color at all. Thus our conclusion was that the stability of the colored compounds is greatly enhanced by chelation, and especially double chelation, in which the hydrogens of an aliphatic amine are attached to oxygens of the nitro groups. Similarly, we could deduce that the chief effect of introducing methyl groups into symmetrical trinitrobenzene is to diminish resonance between the nitro groups and the ring, and that this effect, which is very strong when the nitro group is ortho to two methyl groups, as in symmetrical trinitroxylene, becomes weak when only one ortho methyl is present, as in symmetrical trinitrotoluene. Trinitromesitylene, in which each nitro group lies between two methyl groups, showed no color with any base.

Lewis and I didn't write up this work for publication until about a year later due to the press of our other activities. When we did, of course, it was done by the same method of dictation with me serving as a scribe. Our publication, which included explanations for all of our observations, was entitled "The Acidity of Aromatic Nitro Compounds toward Amines. The Effect of Double Chelation" (J. Amer. Chem. Soc., 62, 2122

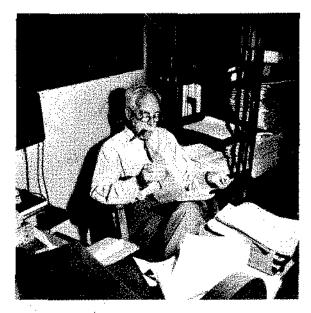


Figure 8. Gilbert Newton Lewis at work in his Gilman Hall Office.

(1940)).

During my last months with Lewis, April, May and June, 1939, he turned part of his attention toward spectroscopic observations on light absorption and the observations of fluorescence and phosphorescence in various colored organic substances. For this we used the spectrograph in Room 310, Gilman Hall, where Ted Magel, then a graduate student, was working. Lewis was now beginning his experimentation on the relation of energy levels in molecules to their emission of light and was already beginning to think in terms of the triplet state. Besides Magel, we were helped in these measurements by Otto Goldschmid, a volunteer research fellow and Ed Meehan, an instructor in the College of Chemistry. Melvin Calvin and Michael Kasha deal with this subject in their papers in this Symposium.

Also during this time Lewis was working with Melvin Calvin putting the finishing touches on their review paper "The Color of Organic Substances," which they mailed in August for publication in *Chemical Reviews*. Lewis had heen interested in the color of chemical substances for a long time and, in fact, this was the subject of his acceptance address in New York on May 6, 1921, when he received the Nichola Medal of the New York Section of the American Chemical Society. He had been working with Calvin, off and on, during much of the last year. I can recall looking in on them in Room 102, where they had their writing sessions, and finding them totally immersed in their piles of reference journals and notes.

During all of the time that I was working with Lewis he was, of course, serving as Dean of the College of Chemistry and Chairman of the Department of Chemistry. These positions would ordinarily entail heavy administrative duties, but he did not allow himself to be burdened by them. Nevertheless, I believe, he discharged his responsibilities very well (Fig. 8). He was efficient and decisive, highly respected by the faculty members in the College, and eminently fair in his dealings with them. To a large extent he ran the College from his laboratory. I recall that his efficient secretary, Mabel Kittredge, would come into our laboratory, stand poised with her notebook until she commanded his attention, describe clearly and briefly the matter that required his attention or decision. Lewis would either give his answer immediately or ask her to come back in a little while, after he had given the matter some more thought. This system worked very well in those days but might not be adequate today and certainly could only function then with a man of Lewis' ability.

Sometime in June, Lewis told me that he was putting me

on the faculty of the College of Chemistry as an instructor. In his whimsical way he expressed the opinion that he had been taking up "too much of my time." This was a revealing comment considering that I was supposed to be serving as his full-time research assistant. However, I have good reason to believe that he was not at all unhappy with my additional research and writing projects. He told me my salary would be

\$2200 per year, that of a third-year instructor. Thus, to my delight, he was giving me full credit for my two years in the capacity of his research assistant.

In conclusion, I want to say that I regard it as extraordinarily good fortune that I was granted the privilege of spending this time working so closely with Gilbert Newton Lewis.

Another Procedure for Writing Lewis Structures

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Many students have difficulty in learning to write Lewis structures for molecules and polyatomic ions. Several procedures for writing them are presented in general chemistry texts. I recently devised a scheme which has two uncommon features: (1) whether multiple bonds or expanded valence shells are present is first determined using the method described by Lever¹; (2) the dots representing electrons are entered before any hydrogen atoms are placed on the structure. The very simple procedure for writing a correct, or at least reasonable, Lewis structure for a molecule or ion containing only s-block and p-block elements can be summarized in a series of steps.

- Identify any monatomic cations. The rules for writing Lewis structures which follow are not needed for and do not apply to monatomic cations. Group I and Group II elements are almost always present as cations. Exceptions are Be in most compounds and the other elements of these two groups in organometallic compounds.
- 2) Determine the number of dots to be shown in the structure of a molecule or polyatomic ion. There is one for each s and p electron in the valence shell of each constituent atom; there is one more for each negative charge on an anion and one less for each positive charge on a cation.
- Evaluate 6y + 2 where y is the number of atoms other than hydrogen in the molecule or ion.
- 4) Compare the number of dots to be shown with 6y + 2.
 - a) If the two are equal, all atoms in the aggregate obey the octet rule, and there are no multiple bonds.
 Examples: PO₄³⁻, C₂H₆, CCl₄, Br₂, NH₄⁺, ClO₂⁻
 - b) If the number of dots to be shown is less than 6y + 2, either of the following holds.
 - There are multiple bonds in the atructure, a deficiency of two indicating a double bond and a deficiency of four indicating either a triple bond or two double hends.
 - ii) An atom of a Group I, II, or III element has less than an octet of electrons.
 - Examples: CH₂O, C₂H₄, N₂, CO₂, CO, BeH₂, LiCH₃
 - c) If the number of dots to be shown is greater than 6y + 2, the central atom has an expanded valence shell. Examples: SF₆, SeCl₄, XeF₂, ShF₆⁻⁻
- 5) Arrange the non-hydrogens in a likely fashion using the following principles as guides. Atoms of elements in Groups II, III, IV, and V are likely to be central atoms. If just one atom of some element and several atoms of some other element are present, the unique atom is likely to be central.
- 6) Enter the dots making use of the decision made in step (4). Start with the dots for any multiple bond, placing them between the central atom and one of its neighboring atoms. Then complete the octets for the atoms attached to the central atom. Finally enter dots for any pairs on the central atom.

7) Place the hydrogen atoms on the formula in a way which minimizes the number of atoms carrying formal charge and minimizes the magnitude of formal charges. Characteristics of atoms having zero formal charge when the octet rule is obeyed are given to the table.

 Group
 IV
 V
 VI
 VII

 Number of Shared Pairs
 4
 3
 2
 1

 Number of Unshared Pairs
 0
 1
 2
 3

The formal charge is more positive by one for each additional shared pair and more negative by one for each additional unshared pair.

Development of the Lewis structure of formic acid illustrates the procedure. Using step (2) one finds that the formula CH_2O_2 requires 18 dots to be shown. Steps (3) and (4) lead to the conclusion that one double bond is present. Carbon, a Group IV element, is central, and placing the dots on the formula as directed in step (6) gives the partial structure shown on the left below. A glance shows that the O on the right having two shared and two unshared pairs already has formal charge of zero. The other O and the C can have formal charge of zero if each shares a pair with H, and entering the H's completes the structure.

The procedure is not flawless, of course. The simple rules would have to be modified to account for cyclic structures, to allow correct placement of the single H of formate ion, and to deal with odd-electron structures. The rules do not lead to a decision about which atom is central in thiosulfate ion, and they do lead to an incorrect structure for phosphorous acid. The most serious flaw is that an incorrect choice of central atom (e.g., O in C_2H_4O) can occasionally cause the student to spend time developing a structure which cannot be properly completed.

These defects do not seriously impair the usefulness of this procedure. One should make sure that at the start students encounter only examples which are dealt with correctly by the simple rules. Students quickly become eware of the features possessed by correct Lewis structures, and one can then make modifications of the rules to extend the range of applicability of the procedure.

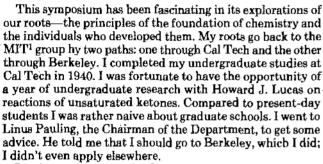
¹ Lever, A.B.P., J. CHÉM. EDUC., **49**, 819 (1972).

The Generalized Lewis **Acid-Base Theory**

Surprising Recent Developments

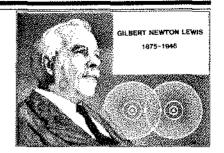
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Previous participants in this symposium have referred to Berkeley seminars chaired by G. N. Lewis and his succinct comments following each presentation. Joel Hildebrand tells a story about his first experience with the Berkeley seminars that illustrates the degree of interaction at all levels. He had just come from a university where professors' opinions were unquestioned. So he was terrified of what would happen when, after Lewis expressed an opinion, a graduate student brashly disputed him. Lewis turned his head toward the student and remarked: "A very impertinent remark, young man, but very pertinent." The discussions were very valuable to the graduate students. Professor William C. Bray was particularly an aid to the students. Whenever a speaker left any point not completely clear, Bray was sure to ask for clarification.

One of the advantages of Berkeley in those days was a smaller student body which afforded many opportunities for graduate students to speak at special seminars on a variety of topics not necessarily directly related to the student's research. I think I must have given a seminar each semester. This emphasis on a broad development goes back to G. N. Lewis' definition of physical chemistry-"anything that is interesting"-and for him that included economics, meterology, anthropology, and so on. William F. Giauque told a story at his retirement dinner about his graduate student days that illustratea the emphasis on breadth of preparation. He described how he made the round of the Department each week to follow the research progress of every graduate student. This emphasis upon a broad preparation made a strong impression upon me. When students come to me for advice on which directions to pursue, I point to a mobile in my office with six hands pointing in different directions. I point out that surprises in science arise frequently enough so that one should have a broad background in order to take advantage of these new unexpected directions. Although my first research was in organic chemistry with Lucas and I did my thesis work under Axel R. Olson on the effect of electrolytes upon the rates of aqueous reactions, I have since worked in the fields of ceramics, spectroscopy, astrochemistry, and metallurgy, as well as the general field of high temperature chemistry. Looking back, I realize that I could never have anticipated the directions that I would pursue, and I never regret the extra effort to prepare myself broadly.



The concepts of electron pair bonds and the Generalized Lewis Acid-Base Theory were so well developed at Berkeley that it came as a surprise to me to find out later that these ideas were not immediately accepted. Particularly, the acceptance of the generalized acid-base concept was much delayed. William Jensen will discuss in his paper² some of the problems that Lewis' ideas encountered, and he covers the impact of the acid-base theory in his recent book (1).

My introduction to a surprising application of Lewis' acid-base concepts first arose in the Manhattan Project. When I had completed my thesis in December 1942, Wendell M. Latimer approached me about working on an important secret government project. I agreed and he told me about the discovery of plutonium and the need to be prepared to handle and fabricate the metal before macroscopic amounts were available.

In this project, I worked with E. D. Eastman as well as Latimer, together with LeRoy Bromley, Norman Lofgren, and Paul Gilles. It was quite a jump from organic chemistry to the metallurgy of plutonium. To be sure that plutonium metal could be cast and fabricated and still maintain the desired purity, we concluded that CeS, a yet undiscovered compound, could provide a crucible material that would be resistant to attack by strongly electropositive metals. We were able to prepare the compound and fabricate crucibles that were highly resistant to attack by metals. The alkali and alkaline earth metals could be distilled from the crucibles without attack. However, one day when we wanted to calibrate our optical pyrometer against the melting point of platinum, we used a cerium sulfide crucible. The platinum chewed up the crucible. We found (2) that the platinum had reacted with the CeS crucible to form Ce₃S₄ and CePt₂. We had characterized the thermodynamic stabilities of CeS and Ce3S4 and realized the CePt2 compound would need an extraordinary stability for such a reaction to proceed.

We had also been working on an apparatus for the analytical determination of oxygen impurities in actinide metals by the vacuum fusion method, which involved dropping a uranjum sample into a molten iron bath in a graphite crucible and measuring the evolved carbon monoxide. We had difficulty due to the volatility of uranium, which acted as a getter for the carbon monoxide. In recognition of the capacity of platinum to reduce the thermodynamic activity of lanthanides and actinides, we replaced the iron by platinum. The vapor pres-

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¹ The history at the MIT group was covered in detail by Servos in a paper published last month as part of this Symposium (J. CHEM. EDUC., 61, 5 (1984)].

² The paper by Jensen will appear as part of this Symposium series

in the March issue.

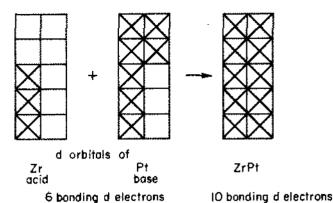
sure of uranium was so greatly reduced that we had no more trouble.

In the late forties, the Danish scientist Niels Engel spent a subbatical at Berkeley and introduced me to his theory (3) of metallic bonding, which was a combination of Lewis' electron bonding model, as used by Linus Pauling (4) for metals, with the relationship between electronic configuration and crystal structure discovered by William Hume-Rothery (5) in the late twenties. It was clear from Engel's model why platinum interacted so strongly with cerium and uranium. The classical example of a generalized Lewis acid-base reaction is the reaction of BF3 and NH3. BF3 does not have enough electrons to use all of the 2p orbitals of boron, and one orbital is vacant. NH3 has enough electrons to fill all of its valence orbitals, but only three pairs of electrons can be used to bond the three hydrogens and one pair is left nonbonding. By combining BF3 and NH3, the nonbonding pair of NH3 is shared with the vacant orbital of BF3, and all of the electrons and all of the valence orbitals are used in bonding. Exactly the same description can be given for the reaction of cerium with platinum or, in general, for the reaction of transition metals from the left-hand side of the Periodic Table with platinum group metals from the right-hand side of the Periodic Table.

If one starts with lutetium with only three valence electrons. and moves to the right toward Hf, Ta, W, and Re, the melting points and boiling points rise markedly as more electrons are available for bonding, until the d^5s and d^5sp configurations of W and Re, which utilize all of the d orbitals in bonding, are reached. If one moves on toward Os, Ir, and Pt, the melting points and boiling points drop, since additional electrons going into the d orbitals will produce nonbonding pairs. For example, in going from d^5sp Re to d^6sp Os, the number of bonding electrons per atom is decreased from seven for Re to six for Os, with a pair of electrons left nonbonding. For Pt with a d^7sp^2 configuration there are two pairs of nonbonding electrons, and only six of the ten valence electrons are used in bonding. However, if the platinum atoms had Ce or Hf neighbors, for example, with vacant 5d orbitals, the nonbonding electrons would bond the Hf and Pt atoms together, and one could approach the bonding effectiveness of W or Re because the orbitals and electrons were matched.

At the time these theories were put forth, no indication was found in the literature of extraordinarily stable intermetallic phases. It was generally stated that intermetallic compounds did not have very negative enthalpies or Gibbs energies of formation. In 1962, Bronger and Klemm (6) were able to demonstrate the high stability of lanthanide platinum phases by achieving the reduction of the lanthanide oxides by hydrogen in the presence of platinum. In 1966, I was teaching an inorganic laboratory course where each student was expected to do a minor research project. I had explained to the class the possible role of generalized Lewis acid-base interactions in metallic systems, and Gerald Stowe attempted a test of the stability of Zr-Pt compounds. He heated ZrC, which is one of the most stable carbides, with platinum. He found (7,8) that the platinum chewed up the zirconium carbide to form ZrPt₃. One could describe the reaction as an oxidation by platinum as the carbon was displaced to form graphite. For the formation of ZrC from the elements, $\Delta H^{\circ}/R$ is more negative than -24,000 K and the enthalpy of formation of ZrPt3 must be even more negative. The next year, Peter Riessenfeldt tried a more severe test. He used the method of Bronger and Klemm (6) of heating ZrO₂ in hydrogen at 1200°C in the presence of platmum. From the Gibbs energy of formation of ZrO₂, he could calculate that the amount of water formed by reduction to zirconium metal would be infinitesimal. However, with platinum present, water streamed out of the apparatus (9). From the weight loss and the volume of hydrogen gas, he was able to calculate that the activity of zirconium was reduced by almost a factor of 1020 by the presence of platinum.

METALLIC LEWIS-ACID-BASE INTERACTIONS



4 non-bonding d electrons

Figure 1. The utilization of nonbonding d electrons of Pt in bonding to Zr.

I had mentioned these results to John Margrave of Rice University, and I received a phone call from him a few weeks later about an accident that resulted from checking our results. In our experiments, the zirconium was already tightly bonded with either carbon or oxygen. Margave's student mixed hafnium and platinum powders and started heating. Nothing happened until about 1000°C, when diffusion rates became significant. Then the sample detonated and destroyed the apparatus, fortunately with no injuries. For the formation of HfPt₃ from the elements, a colorimetric determination (10) has fixed $\Delta H^{\circ}/R = -66$ kK. If one assumes $C_{\rm p}/R = 14$ for a mole of HfPt3, one can calculate that after the reaction started at 1000°C, the temperature would shoot up more than 4000°C. Such high stability is not an isolated example of strong acidbase reactions among metals. Grietje Wijbenga (11) has carried out a series of calorimetric and electrochemical measurements on intermetallic phases of uranium with Ru, Rh, and Pd. For the formation of UPd₃, $\Delta H^{\circ}/R = -66 \pm 4$ kK. Other examples of strong acid-base reactions in metallic systems have been summarized (12, 13). The formation of ZrPt₃ and similar intermetallic compounds is undoubtedly the cause of the so-called "hydrogen embrittlement" of Pt-Rh thermocouples in oxide protection tubes under reducing conditions.

Figure 1 illustrates the interaction of Zr with Pt showing just the d electrons and orbitals of Zr and Pt. Zr in the body-centered cubic structure (12) has the configuration d^3s , and Pt in the face-centered cubic structure has the configuration d^7sp^2 . Four of the d electrons of Pt are nonbonding in pure Pt. When Zr and Pt are combined to allow the electron pairs of Pt to utilize the vacant d orbitals of Zr, all ten d electrons of Zr and Pt can be used in bonding the nuclei together, resulting in an increase of four bonding electrons.

The strength of the interaction depends upon the degree of localization of the d orbitals. As nuclear charge is increased from Cr to W, for example, the increased nuclear charge has a greater effect upon the closed 5s,p electrons than upon the 5d electrons because of the greater penetration to the nucleus of the s and p electrons. Thus in going from Cr to W, the d orbitals become much more exposed, resulting in a much higher enthalpy of sublimation for W than for Cr. Also, as one moves from left to right in the Periodic Table, the d orbitals are at first rather expanded, but they contract with increasing nuclear charge as one moves to the right.

Due to crystal field effects, the d orbitals do not remain equivalent, and some contract more than others and become quite localized. Other orbitals expand and retain reasonable bonding ability. For the 3d metals from Cr to Ni, some of the orbitals are sufficiently contracted so that they can contain unpaired electrons whose interaction with adjoining atoms

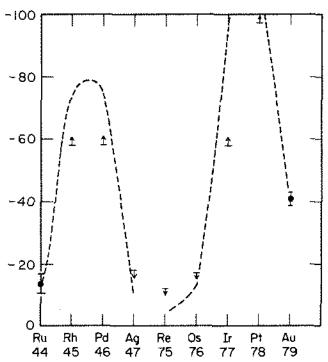


Figure 2. The limiting excess partial motal Gibbs energies of solution of Zr in kcal/mole in group VII to XI transition metals of the 4d and 5d periods.

is so reduced that they remain unpaired and magnetic as in the free gas. Thus, ferromagnetism is found for some of the 3d metals but for none of the 4d or 5d metals, for which the orbitals are sufficiently expanded to provide bonding interaction. However, the 4f orbitals are sufficiently localized to yield magnetic lanthanide metals. The 5f orbitals are sufficiently expanded so that magnetism does not occur until the heavier actinides. Since the strength of acid-base interactions using the d orbitals will depend upon the degree of localization, there should be substantial changes from the 3d to 5d metals. For the right-hand 3d metals, the nonbonding pairs are in the most localized orbitals and are not very basic. The base strength of metals of groups VIII to XI should increase from 4d to 5d. Figure 2 presents some results (12) on fixing the strength of acid-base interactions using ternary phase equilibria in a system involving graphite, zirconium, and platinum group metals. The excess partial molal Gibbs energy of Zr in the platinum group metals is indicated. The base strength of the 5d metals is substantially greater than that of the 4d metals. The base strength of Re is seen to be very small because the d^5sp configuration provides such a good match of orbitals and electrons that all are used in bonding. As one goes from Os to Ir to Pt, the number of nonbonding electrons increases and the base strength increases, but eventually the increasing nuclear charge will draw the nonbonding pairs in so closely that they cannot overlap efficiently into the vacant orbitals of Zr. Thus, the base strength of Au is significantly lower than that of Pt or Ir.

The above discussion has emphasized the role of the inner-shell d electrons and orbitals in the acid-base interactions because they play such a large role in the transition metal interactions. However, the acid-base interactions using outer shell s and p electrons is well established. It is recognized that the tetrahedral structure of GaAs corresponds to a donation of an electron pair from As to the vacant p orbital of Ga to form the sp^3 configuration corresponding to Ge.

Mixtures of metals cannot only undergo acid-base reactions when one of the metals has nonbonding valence electrons and the other has low-lying empty orbitals, but metals can show amphoteric behavior just as do the oxides and hydroxides. Palladium is a good example of this amphoterism. In the

ground state of the gaseous atom, the electronic configuration is d^{10} . If it stayed in that configuration, it should be a noble gas. However, in the pure metal form, it promotes d electrons to p orbitals to reach a configuration between $d^{7.5}sp^{1.5}$ and d⁷sp², corresponding to the face-centered cubic structure. With d^7sp^2 , only six electrons are used in bonding and four are nonbonding. The electron pairs cannot concentrate between the nuclei to provide bonding because of the Pauli Exclusion Principle. If an acid with vacant orbitals such as Zr or U is present, all of the electrons can be used in bonding. Aluminum has the ground state configuration s^2p in the gaseous state, which provides only one bonding electron. However, by promotion to sp^2 , all of the electrons can be used in bonding. Although the extra bonding due to two additional electrons offsets the promotion energy, the promotion energy penalty is quite high. If aluminum is added to palladium and the palladium remains in its d^{10} ground state, the aluminum can use all of its electrons without promotion by acting as a base and donating an electron pair to the vacant's orbital of the palladium. Thus, in the presence of a strong acid, such as uranium, palladium is a hase; whereas, in the presence of a strong base, such as aluminum, palladium is an acid. It is interesting that both Al and Pd have the cubic face-centered structure corresponding to 1.5 to 2 s,p electrons per atom according to the Engel correlation. However, the AIPd compound has the body-centered cubic CsCl type structure corresponding to 1 to 1.5 s,p electrons per atom. With all of the palladium valence electrons in the inner-shell d orbitals, the three s,p electrons of the aluminum are shared between Al and Pd for an average of 1.5 electrons per atom.

One normally considers aqueous H⁺ and OH⁻ as examples of very strong acids and bases. If one were to add 10 M HCi to an excess of 10 M NaOH at room temperature, the activity of H⁺ would be reduced by a factor of 10¹⁶. Dissolving Hf or U in an excess of palladium or platinum would reduce the activity of Hf or U at room temperature by a factor of more than 10⁹⁰. The strong acid-base reactions profoundly affect the chemistry of actinides, lanthanides, and transition metals from the left side with vacant d orbitals when added to the platinum group metals. This has been a most surprising extension of the Lewis acid-base concept.

Lewis' concept of acids and bases has not been readily accepted in the past, and there is still considerable resistance to the extension to metallic systems. For example, Mogutnov and Shvartsman (14) remark:

Evidently, from this point of view the strongest interaction between the components of an intermetallic compound can be expected if the transition-metal components lie at opposite ends of horizontal series of the Periodic Table. These ideas, with allowance for changes in the number of d-electrons and in nuclear charge as between the different elements, have provided satisfactory qualitative explanations of the peculiarities in the heats of formation of intermetallic compounds. However we note that Brewer's model of the formation of intermetallic compounds postulates electron transfer from "right-hand" to "left-hand" elements, which is opposite to the classical electronegativity concept.

On this basis of its being contrary to the classical electronegativity concept, they reject the Lewis acid-base model. However, they did not carefully read Pauling's account of the role of electronegativity under such circumstances. In his discussion (4) of the interaction of Ga with As, or Al with P to form the tetrahedral structure consistent with the sp^3 configuration, he remarks:

It is interesting that this effect involves the transfer of electrons to the more electropositive atoms (the stronger metals); that is, in the opposite direction to the transfer of electrons that takes place in the formation of ions in electrolytic solutions.

In the formation of $Cr(CO)_6$ from acidic Cr and basic CO, it is understood that the actual charge on the Cr does not correspond to the formal charge of -6. The reduction of

charge is described in terms of backbonding through higher orbitals. In the U-Pd interaction, the sharing of palladium electron pairs between the uranium and palladium nuclei must result in a movement of other bondings electrons away from the uranium interacting with the palladium. The important aspect of acid-base interactions in metallic systems is that electrons are not free to occupy all parts of physical space. They are primarily restricted to orbital volumes. The interaction of acids and bases makes it possible for the electrons to occupy allowed space and still interact with two or more nuclei.

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Gilbert N. Lewis and the Thermodynamics of Strong **Electrolytes**

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For this paper I have chosen to focus on the final period of Lewis' thermodynamic research before the publication of his remarkable book (1) which had such great influence. His emphasis in this period was on the peculiar properties of strong electrolytes. In view of my recent research in this area, it was of particular interest to examine the original papers of all of the leading investigators of that period and to note how various concepts were developed. But before proceeding to the detailed discussion of strong electrolytes, I wish to make a few remarks about my personal relationship with Lewis, and at somewhat greater length, to review the general nature of Lewis' contributions to chemical thermodynamics.

I had the good fortune to know Gilbert Lewis very well even though I never collaborated with him in a research project or publication. His influence through his leadership in seminars was very great, but in addition I had many personal discussions of scientific questions with him. He liked to talk with someone who maintained an independent viewpoint and I was willing, even as a very junior member of the department, to defend a viewpoint even if it differed from his. He had an enthusiastic interest in a wide variety of topics and a remarkable capacity to focus on the key questions. The chemical applications of quantum theory were still in their exploratory stages and our discussions often fell somewhere in that area. Although there were still very interesting questions in thermodynamics and especially in statistical thermodynamics, Lewis showed only limited interest in this area in the last decade of his life. He encouraged me to carry on my research and was pleased by the results obtained. But after the publication of his great book with Randall (1) in 1923, his personal interest in thermodynamics was no longer intense. Thermodynamics continued, however, to be a major area of research at Berkeley with support and encouragement by Lewis but



under the immediate leadership of Giauque, Latimer, Hildebrand, and others.

Classical thermodynamics (i.e., excluding the third law) was well established by 1900 when Lewis entered the field. Even the extension of the basic laws to systems of variable composition, primarily by Gibbs in 1876-78 (2), had occurred two decades earlier. But chemists were using thermodynamics only in very limited areas and often inexactly even then.

Lewis (3, 4) proposed new quantities, fugacity and activity, which were closely related to the familiar quantities pressure and concentration yet precisely defined in a manner to allow exact calculations. He also measured and encouraged others to measure the free energies of the most important chemical substances. Thus he brought into existence an extensive and accurate data base for the use of thermodynamics in chem-

Although the Gibbs equations utilizing the chemical potential are exact, most of the practical working equations in use in 1900 involved approximations of ideality for gases and solutions. If the properties of a gas, for example, are accurately known, one can relate the gas pressure to the chemical potential without use of the perfect gas law. However, the equations now seem different and more complex. By his definition of fugacity in 1901, Lewis obtained exact relationships of fugacities which had the same form as the familiar approximate equations in terms of pressures. Thus one can use the same form of equation in all cases and substitute pressures for an approximation or fugacities if the highest accuracy is required.

The situation for solutions is somewhat more complex than for gases but the relationships are essentially the same. Solubility products, ionization quotients, etc., retain their form but become exact relationships when activities are used.

As the third law of thermodynamics began to emerge, Lewis saw its importance to chemists. In his 1917 paper with Gibson (5) this was explained and implemented insofar as data then allowed. But of the greatest importance was the encouragement Lewis gave to Giauque, Latimer, and others to develop the low temperature facilities at Berkeley and to apply the third law to a variety of important substances. The simultaneous development of statistical thermodynamics by Giauque was a natural result of this program.

It is hardly possible to exaggerate the enormous influence of the thermodynamics book of Lewis and Randall. Lewis wrote it in a style easily readable and conveying enthusiasm and excitement yet at the same time precise and accurate. Not only were the important working equations derived from basic principles, but also a body of numerical values was assembled concerning the most important substances. Published in 1923 it was still in print and widely used in 1952 when the publisher persuaded Leo Brewer and me to undertake a revision. We left almost untouched the masterful presentation by Lewis of the basic ideas but added chapters on recent developments. The material on selected values for particular substances was, of course, completely replaced. We are pleased that our efforts gave renewed life to Lewis' presentation of the general concepts of thermodynamics. The revised edition is healthy after over 20 years and now 60 years after the first edition was published.

Since Gibbs died in 1903, not long after Lewis' first paper in 1899, it is not obvious whether they became personally acquainted or not, and I am sorry that I never asked Lewis about Gibbs. But E. W. Hughes did ask and thoughtfully gave others a report on the reply which I summarize. Hughes said that the question brought a happy smile and that Lewis said he had stopped over at New Haven on one of his many journeys between his home in New York City and Harvard while he was still a graduate student. Although completely unknown to Gibbs, he was warmly welcomed. Gibbs professed to be rather lonely at Yale where there were few, if any, others actively interested in his work. Lewis repeatedly suggested that he should not impose further on the time of the great man but Gibhs kept him engaged in conversation all afternoon. Thus it is clear that Lewis did have at least one long and friendly conversation with Gibbs.

Strong Electrolytes: A Puzzie

In the years just before and after 1900 a number of widely accepted natural laws were found to fail in explaining the now more accurately measured properties of real systems. The formulation of quantum theory and relativity in response to two of these situations is well known. The behavior of dilute solutions of strong electrolytes constituted another situation of this type, although in this case it was resolved by an improved application of established basic physical principles rather than a change in those principles.

The behavior of weak electrolytes, where the fraction ionized changed greatly with concentration, was explained satisfactorily by mass-action equilibrium-constant relationships in terms of concentrations, i.e., the Ostwald dilution law as it was then commonly called. We now know that this was only an approximation, but there was no clear discrepancy at the level of accuracy then available. For electrolytes such as NaCl or HCl, however, which were largely dissociated even at high concentration, there were two serious failures. First, the fraction associated could be determined from either conductance or freezing-point-depression measurements, and the results differed substantially—by roughly a factor of two. Second, and even more serious, was the failure of this fraction of association determined on either basis to be explained by the mass-action equilibrium expression. Apparent equilibrium constants for dissociation varied by more than a factor of ten for simple 1-1 electrolytes such as KCl at concentrations between 0.001 and 0.1 m. And Lewis pointed out, as an extreme case, K₄Fe(CN)₆ whose apparent dissociation K varied by five orders of magnitude from 0.0005 to 0.4 eq/l.

This failure of the widely accepted principles incorporated in the Ostwald dilution law was so surprising that for a decade or more the efforts of physical chemists were directed toward experiments of increased accuracy with the purpose of deciding whether this anomaly was really true, but there were no efforts to offer an explanation. One of the last papers of this type is that by Flügel (6) in 1912 working in Nernst's institute in Berlin. In his 1913 edition of "Theoretische Chemie" (7) Nernst acknowledged that this difficulty existed for strongly dissociated salts and acids, but he presented no discussion of possible explanations. By this time others, including Lewis, had already accepted the existence of the anomaly and were discussing the direction in which an explanation might be found. Some of these early proposals were ill-chosen, however. Thus in 1912 Lewis proposed that possibly the mobility of ions increased somewhat with increase in concentration, which is, of course, opposite to the truth as it eventually developed. Lewis promptly abandoned this idea, although the data he assembled at the time was useful in later work.

The simple idea that dilute, strong electrolytes were, for practical purposes, fully dissociated, is attributed first to Sutherland whose reasons were not very convincing. However, others supported this concept with better evidence and by 1920 it was widely accepted.

Strong Electrolytes: The Answer

In this paper I shall not examine the work of this earlier period in detail, rather I shall concentrate on the period just after the First World War, during which Lewis served as chemical staff officer to General Pershing in France. By that time Lewis was also very active in his theoretical work on the nature of the chemical bond which led to his book, "Valence and the Structures of Atoms and Molecules." Nevertheless, Lewis and his associates played a major role in the resolution of the "strong electrolyte anomaly" during the period 1919–21. While Debye and Hückel (8), in their masterful paper of 1923, are properly credited with the quantitative theoretical explanation, we shall see that many of the quantitative relationships, as well as the concepts, had been established earlier by Lewis and associates and by Bronsted.

In 1919 Lewis and Linhart (9) presented their treatment of the best freezing point data then available. They adopted the empirical equation which can be restated in more familiar symbols as

$$1 - \phi \simeq j = \beta m^{\alpha} \tag{1}$$

where ϕ is the osmotic coefficient, m is the molality, which is equivalent to the molar concentration for very dilute solutions, and α and β are empirical parameters. The function j is defined by the equation

$$j = 1 - \theta/\nu \lambda m \tag{2}$$

where θ is the freezing point depression, ν the number of ions in a formula unit, and λ is the molal lowering of the freezing point at infinite dilution which in turn is given by the heat of fusion of water, the temperature, etc. Except for a small correction which becomes negligible in the very dilute range, $j = 1 - \phi$.

We now know that eqn. (1) does represent the correct limiting expression with $\alpha = \frac{1}{2}$ and β given by the expression of Debye and Hückel which involves only the charges on the ions as well as solvent properties, T, etc. Thus for 1-1 electrolytes in water β depends on the temperature but not on the particular solute of that charge type, i.e., it is the same for NaCl, KCl, HCl, HNO₃, etc.

Lewis and Linhart plotted log j versus log m and found curves which became essentially straight lines below $0.02\,M$ with the slope determining α , and the intercept β . Their calculations were slightly revised and extended by Lewis and

Parameters for Equation (1) from Lewis and Linharl with Revisions and Extensions by Lewis and Randail

| | α | β | | |
|-------------------|---------|-------|--|--|
| NaCŧ | 0.535 | 0.329 | | |
| KCI | 0.535 | 0.329 | | |
| KNO ₃ | 0.565 | 0.427 | | |
| NatO ₃ | (0.500) | 0.417 | | |
| , KłO₃ | (0.500) | 0,417 | | |

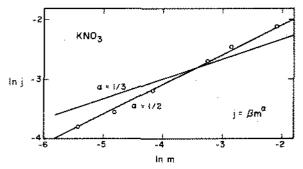


Figure 1. Tests of $\frac{1}{2}$ and $\frac{1}{2}$ for the exponent α with the freezing point data for KNO $_3$.

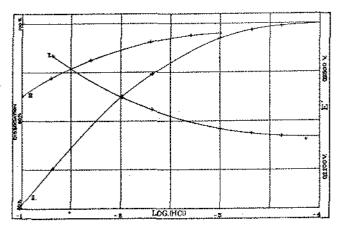


Figure 2. The approach (Curve i) of E'=E+0.1183 in m to E° as m approaches zero (from Linhart (11)).

Randall in 1921 (10) with the results shown in the table. In their 1921 paper Lewis and Randall drew the conclusion that α was $\frac{1}{2}$, within experimental error, for all 1-1 electrolytes.

The data for KNO₃ are shown in Figure 1 with lines drawn for α values of $\frac{1}{2}$ and $\frac{1}{3}$. The agreement with $\frac{1}{2}$ is excellent, although the best fit corresponds to a slightly larger value as shown in the table. The exponent of $\frac{1}{3}$ arises from lattice-type theories which were then current and still are reproposed from time to time although there is now overwhelming evidence, both theoretical and experimental, in favor of the exponent $\frac{1}{2}$.

While the number of examples in the table is not large, there were also data from electrochemical cells for HCl and from solubility measurements for TlCl in mixtures with several salts and acids. These experiments were related to the activity coefficient rather than the osmotic coefficient, but the two coefficients are related by thermodynamics which yields

$$\ln \gamma_{\pm} = -\left(\frac{\alpha+1}{\alpha}\right) \beta m^{\alpha} \tag{3}$$

Interpretation of the electrochemical ceil data for HCl is complicated by the fact that the standard potential for the ceil must also be determined by extrapolation to infinite dilution. Lewis encouraged his student Linhart (11) to extend the measurements of the ceil Pt, H₂|HCl(m)|AgCl,Ag to lower

concentration, and Linhart devised several improvements in electrode formulation and cell design which are unsurpassed even today. Accurate potentials were obtained to $0.000242\,M$ and a somewhat doubtful point was even found for $0.000136\,M$. From these high dilutions the extrapolation to infinite dilution is unambiguous as is shown in Figure 2 which is taken from Linhart's paper (11). Curve I and the right-hand ordinate scale give E' (= $E+0.1183\log m$) which extrapolates to E° . We need not be concerned with curves II and III. With this value of E° established, the data from slightly higher molalities fit eqn. (3) with $\alpha=\frac{1}{2}$.

Solubility measurements for TICl in mixtures with KNO₃, KCl, HCl, and TINO₃ were also carefully analyzed and indicated that in γ_{\pm} (TICl) depended on the one-half power of the

total molality of 1-1 electrolyte.

At this point let us examine the work of others, expecially Bronsted, before returning to another very important result of Lewis. It is interesting that Bronsted, working in Copenhagen, published most of his papers of this period in the Journal of the American Chemical Society (12). This indicates clearly his evaluation of the quality and leadership of American research in this field. In addition to some excellent experimental results, Bronsted's first major theoretical contribution was the recognition that the ordinary interparticle forces existing in nonelectrolytes as well as electrolytes would yield a linear term in concentration for either the osmotic or activity coefficient. This term would be specific to the particular electrolyte; he stated it as "the principle of specific interaction of ions." Bronsted's second major contribution was his conclusion that the special "electrostatic" term should not be specific to individual electrolytes but should depend only on the electrical charges. Thus in 1922 Bronsted (12) wrote

$$1 - \phi = f(c) + B_i c \tag{4}$$

where f(c) is a universal function and B_i a coefficient specific to the salt considered. (Bronsted used the symbol β which is here changed to B to avoid confusion with Lewis and Linhart's β .) Bronsted went on to show that a probable expression for the universal function was

$$f(c) = \beta c^{1/2} \tag{5}$$

with β about 0.32 for 1-1 electrolytes at 0°C. He acknowledges the earlier choice of $\frac{1}{2}$ for the exponent by Lewis and Randall. But Bronsted's contribution is very important because his inclusion of the linear term made it possible to fit the best experimental data with a universal value of β rather than one which varied slightly from solute to solute.

Among other investigators of that period, I will mention only Harned who continued work on electrolytes for many years and later, with Owen, wrote the comprehensive monograph, "The Physical Chemistry of Electrolyte Solutions." In a 1920 paper (13) he reported excellent measurements on several types of electrochemical cells and in interpretation used the equation (which in our symbols becomes)

$$\log \gamma_{\pm} = -\beta e^{\alpha} + Be \tag{6}$$

This equation is of the same general form as Bronsted's. With three freely adjustable parameters, Harned easily fitted his data. But the relatively small variation of β and α among several solutes undoubtedly encouraged Lewis and Randall in their choice of $\frac{1}{2}$ as the universal value of α and Bronsted in his further choice of a universal value of β .

The lonic Strength

The most remarkable contribution of the 1921 paper of Lewis and Randall (10) was the formulation of ionic strength as the quantity determining activity and osmotic coefficients in mixed electrolyte of various valence types. They define the ionic strength as

$$I = \frac{1}{2} \sum m_i z_i^2 \tag{7}$$

where m_i is the molality, z_i the charge in protonic units for the

ith species of ions, and the sum covers all ions present. With the factor $\frac{1}{2}$, I becomes equal to m for a single 1-1 electrolyte. Thus $I^{1/2}$ can replace $m^{1/2}$ (or $c^{1/2}$) in various equations, and they become applicable to mixed electrolytes including ions of various charges. The first evidence cited in support of this concept was the solubility of TlCl in BaCl2, Tl2SO4, and K₂SO₄. On the ionic strength basis these data were concordant with those already mentioned for TlCl solubility in other 1-1 electrolytes. Solubility data for Ba(IO₃)₂, CaSO₄, and La(IO₃)₃ in mixed electrolytes of various valence types were also successfully treated with ionic strength as the variable controlling the activity coefficient in very dilute solutions.

This combination of concentration multiplied by the square of the charge is, of course, the function which gives the concentration dependence in the theory of Debye and Hückel (8). But it had already been unambiguously identified and applied empirically two years earlier by Lewis.

It is not my purpose to review in any detail the derivations of purely theoretical equations for dilute electrolyte properties. It should be noted that Milner in 1912 (14) made a very significant attempt and that certain aspects of his results are nearly correct. But his analysis was so complex and his approximations were so difficult to evaluate that his work received only very limited attention. It clearly had more influ-

ence on Bronsted than on Lewis.

In contrast, the 1923 paper of Debye and Hückel (8) essentially solved this theoretical problem. By a remarkable choice of approximations, they obtained a simple final equation which retained all of the essential features for the limit of low concentration and a qualitatively correct indication of the behavior of somewhat higher concentration. Many further investigations were required to prove that the limiting law of Dehye and Hückel was theoretically exact. But the simplicity of the result encouraged its rapid acceptance as a guide to the extrapolation of experimental data to infinite dilution.

For comparison with the earlier equations of Bronsted and of Lewis and Randall, the Debye and Hückel equation for the osmotic coefficient of a pure electrolyte may be expanded with the first two terms as follows

$$1 - \phi = \beta c^{1/2} - B_i c + \dots$$
 (8)

This is exactly the 1922 formula of Bronsted, but Debye and Hückel give a theoretical expression for the coefficient β in terms of the charges on the ions, the dielectric constant of water, the temperature, and basic physical constants.

For the mean activity coefficient of a salt in a mixed electrolyte the leading term in the Debye-Hückel result may be expressed as

$$\ln \gamma_{\pm} = -A |z_{+}z_{-}| I^{1/2} \tag{9}$$

where I is the ionic strength as defined by Lewis and Randall. Again there is a theoretical value for the parameter A and the further dependence on charge type is given by the factor $|z_{+z_{-}}|$. But the dependence on the concentrations and charges of the various ions present is given by the quantity discovered by Lewis and Randall two years earlier.

Although Debye and Hückel in their original paper make comparisons with experimental freezing point data, they do not recognize or comment on the interpretative papers of Lewis and of Bronsted. In a later paper, Debye (15) does recognize the 1921 paper of Lewis and Randall and the fact that their "ionic strength" is exactly the function of charges and concentrations which appears in the Debye-Hückel theory. Surprisingly, Debye still does not recognize in his 1924 paper the very significant 1922 papers of Bronsted.

In conclusion, I want to emphasize my appreciation of Gilbert N. Lewis as a remarkably able scientist and leader and inspirer of other scientists. This particular vignette may also help remind later generations of the great contributions of Lewis to the nearly complete understanding and empirical representation of the peculiar behavior of strong electrolytes prior to the theory of Debye and Hückel.

The support of the Department of Energy, Office of Basic Energy Sciences, through Contract No. DE-AC03-76SF00098 is gratefully acknowledged.

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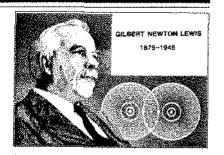
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Gilbert N. Lewis and the Beginnings of Isotope Chemistry

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In 1931 Gilbert N. Lewis became sufficiently intrigued by the challenge of separating isotopes by chemical means that he dropped his research program in theoretical science and started up an experimental program with the aim of separating isotopes on a small scale and then studying the differences in physical and chemical properties of the separated isotopes. It may be useful to review briefly the state of scientific knowledge, the interest in this subject in the scientific community, and some aspects of the Chemistry and Physics Departments at the University of California, Berkeley late in 1931.

Not long after the discovery of isotopes by Soddy in 1911, Fajans (1) recognized that there would be differences in the thermodynamic properties of isotopes in quantum solids. A more detailed study of this problem was made by Lindemann (2) as a result of the general question discussed by Aston and Lindemann as to whether there might be differences in equilibrium properties of isotopes in chemical reactions. Lindemann treated the case of a monatomic vapor in equilibrium with a Debye solid with and without zero-point energy. He made numerical applications for the isotopes 206Pb and ²⁰⁸Pb at 600°K. For the solid with zero-point energy there should be a 0.002% difference in vapor pressures (3) with $P(^{206}\text{Pb}) > P(^{208}\text{Pb})$. For the case of the nonexistence of a zero-point energy one predicts an effect two orders of magnitude larger than the zero-point energy case and an inverse vapor pressure isotope effect (VPIE). Lindemann failed to find any difference and through this study made a fundamental contribution to the concept of a zero-point energy in quantum mechanical systems bound by a potential.

In the late 1920's there were a number of important developments in the discovery of isotopy in the light elements. Many of these discoveries were made in Berkeley. Birge, in the Physics Department, discovered the heavy isotopes of carbon, ¹³C, and nîtrogen, ¹⁵N, in band spectra. Giauque and Johnston in the Chemistry Department, discovered the heavy isotopes of oxygen, ¹⁷O and ¹⁸O, in band spectra. This led Birge and Menzel (4) to revise earlier estimates of the natural abundance of a heavy isotope of hydrogen from 1/30,000 to 1/4500. The existence of a stable isotope of hydrogen of mass 2 had been predicted on the basis of studies of nuclear systematics by Harkins (5) at Chicago, Latimer (6) in Berkeley, and Urey at Columbia (7). In 1930, Peoples and Newsome (8) reported an unsuccessful attempt to separate the isotopes of chlorine by the distillation of chlorobenzene in a 6-m × 63-mm column, packed with 4-mm × 4-mm glass Raschig rings, which had been constructed in the laboratory of Herbert M. Evans in the Berkeley Biology Department.

As early as 1914, Otto Stern had arrived at the Lindemann equation for the difference in vapor pressures of a Debye solid. At his suggestion Keesom and van Dijk investigated the possibility of separating ²⁰Ne and ²²Ne by distillation at 24.6°K. They reported a partial separation in 1931 (9), a significant production of separated isotopes (10), and the measurement of their vapor pressures in 1935 (11).

In December 1931 Urey, Brickwedde, and Murphy (12) communicated their discovery of an isotope of hydrogen of mass 2, deuterium. As part of the evidence they showed that

HD was concentrated in liquid hydrogen by a factor of six when 6 l of the liquid were reduced to 2 ml by a Raleigh distillation near the triple point. This enrichment is consistent with an estimate of the vapor pressure ratio, $P_{\rm H2}/P_{\rm HD}$, of 2.5 made by Urey through the Stern-Lindemann theory. The Urey-Brickwedde-Murphy experiment was consistent with a natural abundance of deuterium larger than 1/30,000 and of the order of the Birge-Menzel value.

In December 1931 Lewis approached Ronald Tom Macdonald and invited him to become his research assistant to work on isotope separation. Macdonald had completed his thesis work with Gerhard K. Rollefson earlier in the year. He had not found employment and stayed on in Berkeley in the capacity of a teaching assistant. Macdonald began as Lewis' research assistant in January 1932. Berkeley was an outstanding center for research in physical chemistry in 1931. By American standards the Department of Chemistry was unusually well equipped and well staffed. Active fields of research included low temperature calorimetry, adiabatic demagnetization, thermodynamics of solutions of electrolytes and nonelectrolytes, electrical conductivity of ionic solutions, electrochemical cells, nuclear science, photochemistry, spectroscopy, magnetochemistry, inorganic chemistry, and physical organic chemistry. There was a particularly free exchange of ideas and research in progress through Lewis' Tuesday afternoon department seminar. Lewis had established close ties with members of the Physics Department, which was an outstanding center in band spectroscopy and nuclear physics. Lawrence and Livingston had built the first cyclotron (13). Lewis had developed a great interest in Lawrence's research. They had become close colleagues and Lewis did much to sponsor Lawrence's research at Berkeley.

isotope Separation

In this paper I will summarize Lewis' substantial accomplishment in isotope separation and isotope chemistry. I will not attempt to review each research in detail. A list of Lewis' publications in this area is appended to this paper for the interested reader. Rather I will summarize the major results and interpret them from the point of view of the development of the science and what they tell us about the research style and interests of Gilbert N. Lewis, a major figure in physical chemistry in the twentieth century and in the development of the University of California, Berkeley.

Lewis and Macdonald began their work in 1932 with attempts to separate the isotopes of lithium and oxygen (14-16). No description of that work has ever been published nor have I been able to get any clues, after a rather lengthy search process, as to what methods they tried. What is clear is that during this period they developed micro methods for the measurement of the densitics of crystals of lithium fluoride weighing milligrams and of small quantities of water. All of the work was carried out in room 119 Gilman Hail.

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A personal note might be appropriate at this point. I arrived in Berkeley in August 1941 from the State College of Washington to continue graduate studies. In Pullman I had conducted research with Otto Redlich, who had translated Lewis and Randall into German in the 1930's. I became acquainted with a young assistant professor of chemical engineering, Philip W. Schutz, who first worked with Lewis in the spring of 1934. He worked for the Shell Development Co. from the summer of 1934 through the summer of 1935, when he returned to Berkeley as Macdonald's successor as assistant to Lewis. Schutz came to Pullman as a faculty member in chemical engineering in 1937 and started up a research program on azeotropic solutions. He left Pullman in 1940 to accept a faculty position in chemical engineering at Columbia. When he left he gave me the only hand torch for blowing glass that existed in the Washington State College Chemistry Department. What a contrast I found when I arrived in Berkeley. Within two weeks of my arrival Lewis had accepted me as a research student. He asked a commitment to work seven days a week, approximately 14 hours a day, with minimum time off for courses and duties as a teaching assistant.

Lewis retired as Dean and Department Chairman at the close of the 1941 academic year. He agreed to consolidate his research on the third floor of Gilman Hall. He had as a research assistant David Lipkin, A National Research Council Fellow, Samuel I. Weissman, was nominally under his supervision. My first "research" assignment was to work with Lipkin in clearing out room 119. I carefully salvaged some stopcocks, ground joints and other vacuum apparatus. I collected a number of vials marked as samples of enriched 6Li (milligram crystals described by Lewis and Macdonald) and Macdonald's notebooks. I assembled these in my new home, 310 Gilman Hall, and asked Lewis what he wanted done with the samples and the notebooks. I had already squirrelled away the glassware and a complete set of reprints of Lewis' work on heavy water and deuterium that I found in room 119. I did as I was instructed; I disposed of the samples and the notebooks.

Why did Lewis start his program by attempting to separate the isotopes of lithium and oxygen? In retrospect the separation of the isotopes of these elements has proven among the most difficult in the science and technology of isotope separation. The pioneer experiments conducted by Lewis and Macdonald in 1934-35 on the concentration of ⁶Li in a countercurrent exchange column between Li-amalgam and LiCl dissolved in absolute ethanol has been the basis for much of the subsequent work on the separation of the lithium isotopes (17). Although ¹⁷O and ¹⁸O are currently separated by water distillation or cryogenic distillation of either CO or NO, none of these processes can be considered an elegant solution to the task of separating oxygen isotopes. It was obvious in 1931 that any differences in equilibrium chemical properties of isotopes or vapor pressure of isotopes1 would be associated with differences in zero-point energies. These differences would be the largest, for equal isotopic mass difference, in the light elements compared with the heavy elements. The differences would depend on chemistry through the correlation of zeropoint energy with the strength of the chemical bond and molecular vibration frequencies. Among the light elements, why did Lewis and Macdonald favor lithium and oxygen? What follows is pure conjecture on my part. Here there are questions of natural abundance, method of analysis, and chemistry. The primary analytical method used by Lewis and Macdonald depended on precision measurements of specific gravities and atomic weight. The 6Li/7Li ratio in natural lithium is 0.0813.

A 10% increase in this ratio will lead to a 0.027% decrease in the density of LiF; a 50% increase in this ratio will lead to a 0.13% decrease. The equivalent weight of a sample of $\rm Li_2CO_3$ enriched in $^6\rm Li$ by 1.5 above natural abundance is lower than a natural abundance sample by 0.031 equivalent weight units. With care one can obtain a precision of ± 0.004 in the determination of the equivalent weight of $\rm Li_2CO_3$ (16). The natural abundance of $^{18}\rm O$ is 0.2%. If waters of the same isotopic hydrogen content but different isotopic oxygen content are compared, a 1 ppm change in specific gravity corresponds to an absolute change of 0.002% in the $^{18}\rm O$ content. It is not difficult to measure the specific gravity of 1 g of water to 1 ppm.

As late as 1933, Lewis and Macdonald (13) were guided by the erroneous assumption that the natural abundance of deuterium was 1/30,000. Their successful experiments on the enrichment of deuterium by electrolysis, to be discussed shortly, convinced them that the true value was close to the Birge-Menzel value, 1/4500. In fact, they reported a value of 1/6500, which is very close to the currently accepted value for the average natural abundance of deuterium in fresh water. Natural water is 16 ppm denser than deuterium-free water at room temperature. An increase of 1 ppm in the density corresponds to a 6.3% enrichment in the natural abundance of deuterium. On the other hand if we assume the natural abundance of D/H to be 1/30,000, then natural abundance water is 3 ppm denser than deuterium-free water. An increase of 1 ppm in the specific gravity requires a 33% enrichment in the D/H ratio. These may be the reasons as to why Lewis and Macdonald began their work by trying to separate the lithium and oxygen isotopes.

In July 1932 Washburn and Urey (18) published qualitative results relating to the concentration of deuterium and 180 by the electrolysis of water. They claimed definite evidence for deuterium enrichment and gave little significance to their finding that ¹⁸O was actually depleted in the residue from electrolysis. Following the Washburn-Urey publication, a number of laboratories, including industrial producers (19). began at once to produce gram quantities of nearly pure D₂O by the electrolysis of water. Foremost among these were Lewis and Macdonald (14, 15, 20). In room 119 Gilman Hall were two large Burdette electrolytic cells which had been used to produce hydrogen for a number of years for Giauque's hydrogen liquefier. In January 1933 Lewis and Macdonald distilled water from the NaOH solution in one of these cells. They found it had a specific gravity 34 ppm larger than tap water. If this increase in density is entirely due to deuterium concentration, the cell contains water with a D/H ratio of about 1/2000. Lewis and Macdonald showed that the isotopic enrichment was entirely in the hydrogen and not in the oxygen. They had confirmed the findings of Washburn and Urey. Giauque was able to make an estimate of the total amount of water that had been electrolyzed in each of the cells. The amount of deuterium that had accumulated in the cells was some 3 to 4 times that to be expected if the D/H natural abundance were 1/30,000. At this point Lewis and Macdonald abandoned the 1/30,000 value for the natural abundance of deuterium.

Concurrent with the laboratory work on the electrolytic separation of deuterium, Lewis and Macdonald looked for an isotope effect in the diffusion of hydrogen gas through iron in the temperature range 500°-800°K (15). The method showed little promise and was dropped in favor of the electrolytic separation and water distillation. In the analysis of the diffusion experiment (15) Lewis gave a clear description of the physical basis of the isotopic difference in the rates of chemical reactions. He distinguished clearly between the classical term related to molecular collisions and diffusion, and quantum effects. The quantum effects discussed were the role of the zero-point energy on the activation energy and the unique possibility of large isotope effects in reactions of hy-

In the remainder of this paper we will treat the equilibrium vapor pressure isotope effect as a chemical reaction. This is justified both from the similarity of the statistical mechanical theory of the phenonema and the practical realization of isotope separation by chemical exchange and distillation in counter-current columns with reflux.

drogen associated with tunnelling through the activation barrier. Interestingly enough Lewis' son, Edward S. Lewis, has done important research demonstrating the existence of tunnelling in slow proton transfer reactions through the criterion of abnormally large H/D kinetic isotope effects (21).

The third method of concentrating deuterium studied by Lewis was the fractional distillation of water. Lewis' search for an enrichment of deuterium by the distillation of water was carried out in collaboration with Robert E. Cornish (22) using the 6-m still in Evans' laboratory which had recently been improved by Henriques and Cornish (23). Interestingly enough the latter workers had just made an unsuccessful attempt to effect a partial separation of the chlorine isotopes by the distillation of CH₂Cl₂ at 40°C. Lewis and Cornish concluded that not only was deuterium enriched in the liquid phase but ¹⁸O was also enriched in the distillation of water. This was later confirmed by Lewis (24) in the large distillation plant constructed hy Merle Randall (25).

Similar results to those obtained by Lewis and Cornish were obtained independently by Washburn et al. (26, 27) at the National Bureau of Standards. Washburn's work was communicated and his first paper was published prior to the communication of Lewis and Cornish. The distillation experiments from the Bureau and Berkeley (22) were communicated within a week of one another—15 May 1933 and 22 May 1933, respectively.

By the end of February 1933, Lewis and Macdonald had isolated 0.5 cc of 31% D₂O using the electrolytic method (14, 20). By mid-March 1933, they had prepared a second 0.5-cc sample containing 66% D₂O (14, 20). Further enrichment by the electrolytic method was continued to produce water with a deuterium content greater than 99%. With semi-micro amounts of water with a deuterium content in the range 30-99% available, Lewis and Macdonald proceeded to measure some of the physical properties of D₂O (28). The first properties studied were the freezing point, normal boiling point, and the density and vapor pressure as a function of the temperature. The vapor pressure data confirmed the earlier finding of Lewis and Cornish that the vapor pressure of D₂O is less than that of H₂O.

It was at once apparent to the Berkeley group that although the distillation fractionation factor was much smaller than the electrolytic separation factor ($[\alpha-1]$ {distillation at 50°C} = 0.05, $[\alpha-1]$ (electrolytic) ~ 4) the distillation process was a reversible one and the elementary effect could be easily multiplied in a distillation column. These considerations led to the decision to build a distillation plant at Berkeley for primary enrichment of deuterium by water distillation at about 60°C. The task was undertaken by Randall (25). The laboratory plant consisted of two columns each 22 m high. The primary column was 30 cm in diameter; the second stage column was 5 cm in diameter. Both columns were filled with scrap aluminum turnings. The packing material performed poorly and was chosen because of limitations of funds. In some later work the packing was replaced by small brass rings manufactured as shoe eyelets. The 30-cm column was discarded steel pipe from the University power plant. The entire construction of the first stage of the plant including purchase of materials, construction, installation, and preliminary operation was carried out in a period of 20 days. The project was in part a WPA project. The plant went into operation on 8 June 1933. It had a feed to the primary tower of 1 l ordinary water/min. Enriched water from the first stage was used as feed for the second stage column. The first stage performed particularly poorly. It achieved an overall enrichment of a factor of 2, which corresponds to an HETP of 5 ft. The second stage had an overall separation of 25, corresponding to an HETP of 14 in. The output of the distillation plant was further enriched by Lewis and Macdonald in their electrolytic plant. If the first column had achieved an HETP comparable to that of the second column, which is low by current practice, Randall's plant could have produced 125 g/d of 8% D₂O. If the

latter were then fed to a 4-stage electrolytic plant with recycle of the hydrogen from the first three stages, the Berkeley distillation plant supplemented by a small electrolytic plant could have produced approximately 10 g of >99% D₂O/d. The addition of a short stripping section to the top of the primary column would have increased the production of the facility by a factor of 5.

Although the water distillation plant did not perform in accord with expectations as a result of the failure of the packing, nevertheless, Lewis and Macdonald were soon producing on the order of 1 g/wk of >99% D₂O. They used part of the material in their own researches. They were extremely generous in making the material available to scientists all over the world. In the spring of 1933 Lewis furnished deuterium samples for nuclear research to Lawrence in Berkeley, Lauritsen at Cal Tech, and Rutherford at Cambridge (England).

The water distillation plant was subsequently improved by Randall and operated intermittently to produce ¹⁸O-enriched water for tracer studies carried out by Axel R. Olson and Samuel C. Ruben among others.

After Lewis concluded his researches on deuterium in mid-1934, he and Macdonald returned to the challenge of separating the lithium isotopes. They had abandoned the approach in their work two years earlier, whatever that may have been, and decided to achieve a separation by a countercurrent chemical exchange process. Some of the requirements for such a process are:

- a rapid, reversible chemical exchange reaction which leads to a preferential isotopic distribution in one of the chemical species;
- (2) a two-phase system—preferably a system in which one chemical species is entirely contained in one phase and the other species in the second phase;
- (3) quantitative reflux reactions through which the exchanging chemical species can be interconverted into one another and transferred quantitatively from phase to phase;
- (4) a simple method of countercurrent contacting and separating the two phases continuously.

The chemistry of lithium is simple. There are four general classes of compounds:

- zero oxidation state—Li(s), Li alloys,
- plus-one oxidation state—Li+ (solvated),
- (3) Li organics, and
- (4) lithium halide vapors.

Exchange reactions of organic lithium compounds are apt to be slow. Processes involving lithium halide vapors will require high temperatures; such processes will involve special container materials. The high temperature will necessarily mean a small chemical exchange separation factor. This leaves (1) exchange reactions between the 0 and the +1 oxidation states and (2) exchange reactions with no change in oxidation number. A change in oxidation number is more likely to be accompanied by a larger change in bonding of the lithium than reactions without a change in oxidation number, whether in the 0 or +1 oxidation state. One is led to focus upon the exchange reaction between the 0 and +1 oxidation states of lithium. Lewis was the original master of the method for carrying out this reaction. He conceived the solution to the problem of quantitative measurement of the equilibrium Li(s) = Li⁺(aq) + e⁻ in connection with the measurement of the standard electrode potentials of the alkali metals in aqueous solution (29). The actual potential of Li(s), Li⁺(aq) was determined by Lewis and Keyes (30). It involved the measurement of the cell potentials Li(s), Li(amalgam) and the half-cell potential Li(amalgam) LiOH(0.1M). The reactions are rapid and reversible. If Li(amalgam) and a solution of lithium ion are used, we have fulfilled all of the criteria for a chemical exchange enrichment process. The only unknowns are the single-stage enrichment factor and the column performance.

Lewis and Macdonald investigated two systems:

 ${}^{7}\text{Li}(\text{Hg}) + {}^{6}\text{Li}^{+}(\text{C}_{2}\text{H}_{5}\text{OH}) = {}^{6}\text{Li}(\text{Hg}) + {}^{7}\text{Li}^{+}(\text{C}_{2}\text{H}_{5}\text{OH})$

 $^{7}\text{Li}(\text{Hg}) + ^{6}\text{Li}^{+}((1)\text{C}_{2}\text{H}_{5}\text{OH}, (2) \text{ Dioxane})$

 $= {}^{6}\text{Li}(\text{Hg}) + {}^{7}\text{Li}^{+}((1)\text{C}_{2}\text{H}_{5}\text{OH}, (2) \text{ Dioxane})$

The solutions were each about 0.5 to 0.7 M. The anion in the ethanol solution was chloride; the anion in the ethanol-dioxane solution was bromide. The dioxane-alcohol solvent was tried in the hope that the irreversible reaction of the lithium amalgam with the ethanol would be slowed down by dilution with dioxane. They anticipated that the use of the dioxane solvent would lead to a higher separation than pure alcohol. It actually produced less separation and the final experiments were done with 0.6 M LiCl in ethanol. The system was studied in a countercurrent column 18 m high × 4 mm diameter constructed of glass by W. J. Cummings. A total of 101 of amalgam passed down the column in the form of droplets of 0.1 mm diameter. The droplets fell through the alcoholic solution and were collected in a reservoir at the bottom. There was an overflow tube at the top of the column. Thus the introduction of the amalgam provided for countercurrent flow of the LiCl solution. The amalgam that collected at the bottom was refluxed in 100-ml batches by titration with an alcoholic solution of HCl, and the latter was returned to the bottom of the column at 15-min intervals. Operation of the column to process the 10 l of amalgam required continuous attention and work for 24 h.

The isotope enrichment was determined by a precision intercomparison of the equivalent weights of Li_2CO_3 samples prepared from the amalgam at the top and the bottom of the column. In their third and final run this ratio was found to be 1.0023. The latter corresponds to a separation, S, of 2.3

$$S \approx \frac{(^6\text{Li}/^7\text{Li}) \text{ bottom}}{(^6\text{Li}/^7\text{Li}) \text{ top}}$$

The atomic weight determinations were later confirmed by mass spectroscopic abundance measurements by A. K. Brewer at NBS. The ⁶Li concentrates in the amalgam.

The experiment of Lewis and Macdonald was a tour de force. It was the first realization of a chemical exchange isotope separation process. The single stage separation factor for this exchange reaction has been measured by Palko, Drury, and Begun (17) and found to be 1.050; it was estimated to be 1.025 by Lewis and Macdonald. From the overall separation achieved by Lewis and Macdonald we estimate their HETP to be 1 m in excellent agreement with the determination by Lewis and Macdonald. The stage residence time was 15 s. They found that the reaction of lithium amalgam droplets with aqueous sodium chloride transferred 96% of the sodium ion to the amalgam after failing through a 1-m column.

After Lewis and Macdonald achieved a partial separation of the lithium isotopes, Lewis and Schutz carried out some experiments on the separation of the nitrogen isotopes. Those results have never been published.

Not only did Lewis and Macdonald achieve their objective of preparing gram quantities of enriched stable isotopes for the study of their chemical and physical properties, they contributed to the use of chemical methods of isotope separation. I have already described in detail their elegant enrichment of the lithium isotopes using nothing but simple chemistry for the enrichment process, the determination of the relative atomic weights for analytical purposes, a mastery of chemistry, and hard work. In their production of D₂O they demonstrated the effects of the magnitude of the single-stage enrichment factor and the stage multiplication process on the magnitude of the separation and the quantity of separated material produced. Interestingly enough, the Du Pont Company elected to produce heavy water in ton quantities at the Morgantown and Wabash River Ordinance Plants for the Manhattan District by a primary enrichment using water distillation followed by electrolysis. Concurrent with that effort groups at Columbia and Princeton Universities developed catalysts for the vapor phase isotopic exchange between water and hydrogen. The first industrial realization of the water-hydrogen exchange was achieved at Trail, B.C., where a large electrolytic hydrogen plant provided the reflux for the conversion of the water to hydrogen at the bottom of the chemical exchange tower.

Physical Properties of Heavy Water

As soon as Lewis and Macdonald accumulated about 0,3 ml of nearly pure D₂O they began to measure some of its physical properties (28, 31). To obtain the most accurate results in a minimum time Lewis enlisted the assistance of a number of graduate students in the Department. Thomas C. Doody was studying the electrical conductance of ionic solutions with a precision Jones and Bradshaw bridge under the guidance of Randall, He constructed a microconductivity cell and measured the relative mobilities of KCl in H2O and in D2O and HCl(H2O) and DCl(D2O) (32). William Maroney had a capacitance bridge for measurements of dielectric constants in connection with his work under Olson. Maroney measured the dielectric constant of D₂O relative to H₂O (33). Daniel B. Luten, Jr., a student of Stewart's, was following the rates of chemical reactions in solution by measurement of the index of refraction. He determined the index of refraction of D2O as a function of wavelength (34). Simultaneous determination of the density and refractive index of a water sample provided an isotopic analysis for both ²H and ¹⁸O in a sample of water (35). Lewis and Macdonald measured the specific gravity (28), the vapor pressure (28), and the viscosity (31) of D_2O as a function of temperature.

In August 1933, Wesley T. Hanson, Jr., who spent his first year as a graduate student in Berkeley working with Randall, changed his research supervisor and measured the vapor pressure of deuterium. We will review his work in a later section of this article. Philip W. Schutz completed his PhD thesis with Latimer and was an instructor in the Department for the spring semester of the 1933-4 academic year. He did not have his own research program, but rather was an assistant to Lewis and did some teaching. During this period Schutz measured the dissociation constants of a number of weak acids and bases in heavy water, and the vapor pressures of a number of deuterium compounds. This work will also be reviewed in later sections of this article. Contrary to the general tradition in the Department, there appears to have been little communication between Hanson, Macdonald, and Schutz. They worked in separate laboratories.

The early work from Lewis' laboratory on the physical properties of heavy water was very important and useful to his own work, to other workers in the field, and for the characterization of the differences between light and heavy water. The density difference is within 0.5% entirely due to the molecular weight difference. The molar volume of H_2O is 0.4% smaller than D_2O at 25°C. The dielectric constants and refractive indices of H_2O and D_2O , which depend on the electron configuration, nuclear charge, and molecular geometry, are expected and found to be nearly identical.

Lewis' measurements of the physical and chemical properties of heavy water and other deuterium compounds were all made on samples smaller than 1 ml of liquid. They recognized that their samples and solutions had impurities which they found difficult to remove. Some impurities came from the measuring vessels and could only be removed by rinsing with more than the world's snpply of heavy water at the time. However, it was Lewis' style not to make the ultimate measurement. He left that to others. In this work as well as in his other work, he wanted a measurement good enough to answer his questions. Kirshenbaum's compilation of the physical properties of heavy water (36) gives a complete compendium and evaluation of the determinations of the physical properties of heavy water through the later '40's. A summary comparison is given in Table 1.

What questions did Lewis ask of nature regarding the

Table 1. Some Physical Properties of D₂O

| | Lewis et al. | Accepted Value |
|---|-----------------|-------------------|
| Triple Point | 3.8°C | 3.82°C |
| Density (d ₂₅ 25) | 1.1088 | 1.10775 |
| Viscosity (η(D ₂ O)/η(H ₂ O) at 25°C | 1.232 | 1.232 |
| Diefectric Constant (25°C) ϵ (D ₂ O)/ ϵ (H ₂ O) | 0.990 | 0.9963 |
| Index of Refraction (25°C) $n(H_2O) = n(D_2O)$ | | |
| 5893 Å | 0.00465 | 0.004700 |
| 5461 | 0.00482 | 0.004832 |
| 4358 | 0.00526 | 0.005272 |

properties of deuterium? There were problems in phase equilibria (vapor pressures and triple points), the ionization of weak acids and hases, the growth of plants and organisms in heavy water, and finally a few pioneer studies in nuclear reactions. Lewis was a master of the application of thermodynamics to chemical problems including the behavior of electrolytic solutions. Recall, he invented the activity coefficient and discovered the principle of ionic strength, later explained in the famous paper by Debye and Hückel. His interest in the nuclear properties of the deuteron undoubtedly stemmed from his interest in Lawrence's work as well as earlier nuclear work done in the Chemistry Department by Gibson, and by Latimer and Libby. The work on the biological properties of heavy water reflect Lewis' penchant to explore natural phenomena and carry out research in fields in which he had no prior training.

Vapor Pressure isotope Effect

The measurement by Lewis and Macdonald (28) of the vapor pressure of $\rm D_2O$ as a function of the temperature showed a very large temperature coefficient for the logarithm of the vapor pressure ratio ($\rm ln P_{H_2O}/P_{D_2O}$). The large temperature coefficient of the isotopic vapor pressure ratio was attributed by Lewis (15) to the hydrogen bonding in water. The zeropoint energy associated with the hydrogen bonding is principally responsible for the vapor pressure isotope effect. The hydrogen-bonded structure of water is broken as the temperature increases. Thus the temperature coefficient of $\rm ln(P_{H_2O}/P_{D_2O})$ will be greater than the T^{-2} law applicable to small quantum effects.

Typical of Lewis' approach to a field of investigation was the construction of a theory based on the results of an experiment. The theory had to be a predictive one. From the theory Lewis would design a few crucial experiments to test the theory. In the case of the vapor pressure isotope effect he predicted that a test could be made between two factors which have a profound effect on the vapor pressure isotope effect, temperature and zero-point energy, by the study of the isotope effect in HCl and acetic acid. A summary of these results is given in Figure 1. The vapor pressure isotope effect in the liquid at the triple point is smaller in HCl (37) than in water. The vapor pressure isotope effect in NH_3 - ND_3 measured by Taylor and Jungers (38) is consistent with the qualitative analysis of the water data. The larger vapor pressure isotope effect at the triple point in ammonia compared with water is a consequence of the lower triple point temperature and the fact that there are three D/H substitutions in ammonia compared with two in water. When one corrects for these two factors, one finds that the zero point energy difference per hydrogen bond in ammonia is smaller than in water. The latter is consistent with the weaker association in liquid ammonia compared with liquid water and the fact that the melting point of ammonia is significantly lower than ice.

On the basis of the above argument, Lewis predicted that the vapor pressure of the deutero-form of a hydrogen-bonded substance whose vapor is associated would be larger than that of the protio form. This prediction was confirmed by the results of Lewis and Schutz (39) on the vapor pressure ratio of

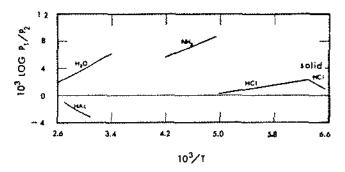


Figure 1. Plot of $10^3 \log_{10}(P_{\text{HuX}}/P_{\text{DuX}})$ versus $10^3/7$ (from Ref. (15)).

CH₃COOH to CH₃COOD. The vapor phase association will certainly reduce the vapor pressure isotope effect. Since the association in the vapor phase is smaller than in the liquid, association per se in the vapor cannot lead to an inverse isotope effect. While a detailed analysis of the vapor pressure isotope effect in acetic acid has not yet been made, it is safe to presume that the inverse isotope effect is associated with the customary red shift in the O-H stretching vibration in the liquid compared with the vapor. The red shift in the liquid lowers the heat of vaporization of the deuterium compound relative to the protium compound and leads to the inverse vapor pressure isotope effect.

In the measurement of the hydrogen isotope fractionation factor in the distillation of water, Lewis and Cornish (22) were surprised to find that the fractionation factor was about one half that to be expected from the vapor pressure data of Lewis and Macdonald (28) on the vapor pressures of pure $\rm H_2O$ and $\rm D_2O$. They recognized that in dilute solutions of $\rm D_2O$ in $\rm H_2O$ the deuterium is present in the form of HDO. Assuming statistical distribution of protium and deuterium between the species $\rm H_2O$, HDO, and $\rm D_2O$ they arrived empirically at the rule of the geometric mean, $\rm ln(P_{H_2O}/P_{HDO}) \simeq \frac{1}{2} \ln(P_{H_2O}/P_{D_2O})$. The theoretical foundation for this intuitively obvious prediction did not come until two decades later (40).

In addition to three of the substances shown in Figure 1, H₂O, HCl, and HAc, Lewis and Schutz measured the vapor pressures of HCN and DCN (41). Earlier I mentioned the work of Lewis and Hanson on the vapor pressures of solid and liquid H₂ and D₂. In none of these investigations did Lewis attempt anything other than a qualitative understanding of the phenomena based on the zero-point energy concept. No molecular theory of the condensed phase isotope effect existed at the time. In fact it was the absence of such a theory, particularly with respect to the liquid state, that made these studies interesting to Lewis. In his Madrid lecture (15) Lewis states, "On the other hand, it is often these very cases which defy the analysis of mathematical physics that are of the most interest to chemists." The defiance lasted less than 30 years (45). In the last 20 years the analysis of vapor pressure isotope effects through the statistical mechanics of interacting systems has yielded interesting information about intermolecular forces, the coupling of intermolecular with intramolecular forces, hindered rotation in solids and liquids, and the structure of monatomic and polyatomic fluids (46-50).

Conceptually the measurement of the vapor pressure of a one-component system as a function of the temperature is a simple type of measurement. All one needs is a pure sample held at a known, fixed temperature and a pressure-measuring device, frequently a mercury column. If one is interested in the difference in vapor pressures of isotopes not only must the samples be chemically pure, but also of high isotopic purity. In most cases it is advantageous to bring samples of the separated isotopes into thermal contact with one another and measure both the absolute and differential pressures. It is the type of experiment which appealed to Lewis. The experiment

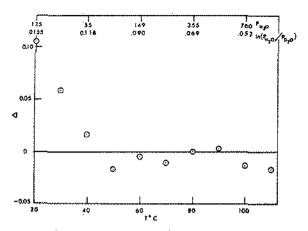


Figure 2. Relative differences between currently accepted values of the H/D isotope effect on the vapor pressure of water and values determined by Lewis and Macdonald (28).

$$\Delta = \frac{\ln(P'/P)_{\text{accepted}} - \ln(P'/P)_{\text{Levels}}}{\ln(P'/P)_{\text{bacepted}}}$$

is simple in principle and yields information of interest to chemists. We will review the results obtained by Lewis with recent data.

In Figure 2 we compare the logarithm of the vapor pressure ratio, $\ln(P_{\rm H_2O}/P_{\rm D_2O})$, measured by Lewis and Macdonald (28) with recent data (47). The quantity plotted, Δ , is

$$\Delta = \frac{\ln(P'/P)_{1} - \ln(P'/P)_{L}}{\ln(P'/P)_{1}}$$
 (3)

where $\ln(P'/P)_1$ is the accepted literature value, $\ln(P'/P)_L$ is the Lewis value, and P' denotes the light isotopic species. If we ascribe all the difference to errors in measurement of the pressure difference, $\delta\Delta P(\Delta P=P'-P)$, we obtain the results shown in Figure 3. Apart from the data at and above $100^{\circ}\mathrm{C}$, the measurements show a root-mean-square deviation of 0.06 mm in the measurement of the pressure difference, which is of the order of the accuracy obtainable with conventional mercury manometers.

Lewis and Hanson found the vapor pressures of mixtures of H₂ and D₂ to obey Raoult's law at 18.65°K (42). The excess enthalpies of mixing of such solutions have now been measured (51). The nonideality arises from the difference in the molal volumes, 28.2 and 23.5 cm³ mol⁻¹ for liquid H₂ and D₂, respectively at 20°K. The excess free energy and enthalpy of mixing per mole are 1.71 and 2.90 cal mol⁻¹ at 50 mol %. A 50 atom % mixture in equilibrium with respect to H2, HD, and D₂ would show an excess vapor pressure of 4.7 torr above the Raoult law value. The preparation of Lewis and Hanson's mixture is not described in their paper, and it is not clear to what extent disproportionation had been established in their samples. They failed to detect any difference between the vapor pressure of a sample of n-D₂ condensed in a clean glass tube and one condensed in a tube containing charcoal (presumably ortho-deuterium). At 20°K the ortho-deuterium has a vapor pressure of 223.1 torr compared with 219.9 torr for n-D₂ (52). Henson constructed three cryostats before he could get any reliable measurement of the vapor pressure difference between H₂ and D₂ (53). The final cryostat employed thinglass tubes (0.1-mm wall) directly immersed in a liquid hydrogen bath. The tubes were joined in a bundle by copper wire to promote thermal equilibrium between the H₂ and D₂ samples. Pressures on a mercury manometer were read to ± 0.5 mm Hg. The results of these measurements are compared with Grilly's data (54) in the form of Δ and $\delta\Delta P$ plots in Figures 4 and 5, respectively. Above the triple point of D_2 (18.72°K) the agreement between the data of Lewis and Hanson and those of Grilly are within the accuracy of the former mea-

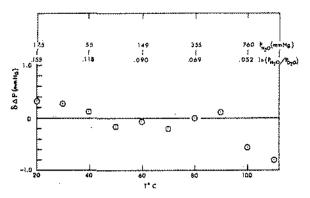


Figure 3. Comparison between accepted values of the absolute difference in vapor pressure between $\rm H_2O$ and $\rm D_2O$ and those measured by Lewis and Macdonald.

$$\delta\Delta P = (P_{\rm NgO} - P_{\rm DgO})_{\rm accepted} - (P_{\rm HgO} - P_{\rm DgO})_{\rm Lowis}$$

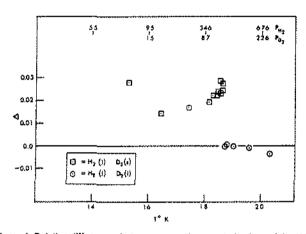


Figure 4. Relative differences between currently accepted values of the H/D isotope effect on the vapor pressure hydrogen and values determined by Lewis and Hanson (43, 44).

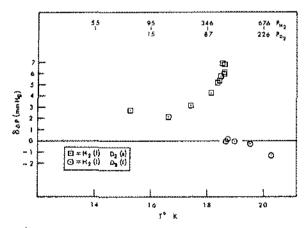


Figure 5. Comparison between accepted values of the absolute difference in vapor pressure between ${\sf H}_2$ and ${\sf D}_2$ and those measured by Lewis and Hanson.

surements. Below the triple point of D_2 Lewis and Hanson report a significantly higher vapor pressure for D_2 than does Grilly. The method of comparison developed here reduces to second-order any difference in vapor pressure from a difference in temperature scales (cf. Lewis and Hanson report the triple point of D_2 to be 18.66°K). The fact that the absolute pressure of D_2 reported by Lewis and Hanson is larger than Grilly's measurements and that this difference increases with temperature can be explained by the thermal leak in Lewis

| | Triple-Point Pre | Triple-Point Pressures (mm) | | |
|---|------------------|-----------------------------|--|--|
| | HCI | pcı | | |
| Giauque and Wiebe (1928) | | | | |
| (158.91°K) | 103.71 | | | |
| Lewis, Macdonald and | | | | |
| Schutz (1934) | *** | 91,3 | | |
| Clusius and Wolf | | | | |
| (1947) (158.91°K) | 103.60 | 93.7 | | |
| Vapor Pressure Ratio at the Triple Point of DCI (158.44°K) (InP'/P) | | | | |
| Lewis, Maodonald, and | | | | |
| Schutz (1934) | 0.051 | | | |
| Clusius and Wolf (1947) | 0.077 | | | |

and Hanson's experiment. Liquid H_2 makes good contact with the vessel wall; solid D_2 does not. The heat capacity of solid D_2 is smaller than that of liquid hydrogen. Even a symmetric heat leak to the H_2 and D_2 samples will lead to an increase in the vapor pressure of D_2 relative to H_2 compared with the true value at the temperature of the reference liquid H_2 sample.

In Table 2 we compare measurements of the triple point temperatures and pressures of HCl and DCl carried out in a number of laboratories (55–57). Note the excellent agreement in the triple-point pressures measured by Clusius and Wolf (57) with the earlier measurements by Giauque and Wiebe (55). The disagreement between the DCl triple-point pressures measured by Lewis, Macdonald, and Schutz and those of Clusius and Wolf, as well as the sign of the temperature dependence of $\ln(P_{\rm HCl}/P_{\rm DCl})$ solid reported by Lewis et al. (see Fig. 1), cast doubt on the DCl data of Lewis, Macdonald, and Schutz.

The magnitude of the vapor pressure ratio of (HCN/DCN) liquid measured by Lewis and Schutz (58) is in agreement with recent data of Appleton and Van Hook (59). The sign of Lewis and Schutz' temperature coefficient of $\ln(P_{\rm HCN}/P_{\rm DCN})$ is opposite that of Appleton and Van Hook.

While the measurement of the vapor pressure of a onecomponent system is one of the simplest physical measurements, to measure it with sufficient accuracy to obtain significant isotope effects requires great care (60). It cannot be done on the time schedule that Lewis set out for himself and his limited number of students and assistants. We will return to the time schedule later in this article.

Dissociation of Weak Acids and Bases in H₂O and D₂O

With 0.25 g of D₂O Lewis and Doody (32) determined the conductivities of D2O and of solutions of KCl and HCl, each 0.017 M. The D₂O was not sufficiently pure for measurements of its electrical conductivity. In fact, at the time of the measurements there was not enough D2O available to permit one rinse of the microconductivity cell prior to the actual measurements. The good agreement of the results of Lewis and Doody with those of later workers (61, 62), who had an order of magnitude more D2O available to them, is shown in Table 3. The ratio of the conductivity of an inert strong electrolyte, KCl, in H₂O compared with D₂O solvent is in good agreement with Walden's rule. According to Walden's rule the ratio of the conductivity of a given salt in two solvents is equal to the ratio of the viscosities of the two pure solvents. The viscosity ratio of H₂O relative to D₂O at 25°C is 1.232. Interestingly enough we note that the ratio AHCl(H2O)/ADCl/(D2O) is definitely larger than that expected from Walden's rule. This result proves that there is a kinetic isotope effect in the proton mobility in water. The latter observation warrants investigation of the temperature dependence of the conductivity ratio. Such measurements could add additional understanding of the mechanism of proton transfer in aqueous solutions.

Lewis and Schutz (63, 64) determined the dissociation

| | 5°C | 25°C |
|--------------------------------|--|-------|
| • | AKCI(H _E O) | |
| | AKCI(D ₂ O) | |
| Lewis and Doody (1933) | 1,212 | 1.162 |
| La Mer and Nachod (1941) | 1.270 | 1.210 |
| | <u>Λ</u> ΗCI(H ₂ O) ΛDCI(D ₂ O) | |
| | | |
| Lewis and Doody (1933) | 1.476 | 1.390 |
| Longsworth and Macinnes (1937) | | 1.362 |

Table 4. Dissociation Constants of Weak Electrolytes K_H/K_D

1. CH₃COOH/CH₃COOD

Lewis and Schutz (1934)

Le Mer and Chittum (1936)

2. CICH₂COOH/CICH₂COOD

 Lewis and Schutz (1934)
 2.71

 McDougall and Long (1962)
 3.08

 3. NH₄DH/ND₄OD
 Lewis and Schutz (1934)
 1.65

 Salomea, Schaleger, and Long (1964)
 4.06

constants of CH₃COOH, CH₃COOD, ClCH₂COOH, ClCH₂COOD, NH₄OH, and ND₄OD by measurements of the electrical conductivity of solutions in the concentration range 0.03 to 0.14 M. The degree of dissociation was calculated from the ratio $\Lambda_c/(\Lambda^+ + \Lambda^-)_c$, where Λ_c is the equivalent conductances of H⁺(D⁺) and A⁻ at the concentration c. The ratio

$$\frac{(\Lambda^{+}_{H^{+}} + \Lambda^{-}_{A^{-}})_{H_{2}O}}{(\Lambda^{+}_{D^{+}} + \Lambda^{-}_{A^{-}})_{D_{2}O}}$$

was assumed by Lewis and Schutz to be independent of concentration at low concentration of the weak electrolyte and independent of the type of anion. With these assumptions, the equivalent conductance ratio is just the value determined by Lewis and Doody (32) for HCl in H2O compared with DCl in D₂O. La Mer and Chittum (65) later showed that the slow dependence of the conductance ratio on the concentration of dissolved electrolyte is in accord with the Onsager conductance equation (66). The low sensitivity of the equivalent conductance ratio for a strong protio-acid in H2O to a strong deutero-acid in D_2O on the acid anion is a consequence of the fact that the anion transference number is in the range 0.10-0.20. Lewis and Schutz established the reliability of their method by the good agreement of their values for the dissociation constants of CH₃COOH, ClCH₂COOH, and NH₄OH with accepted data in the literature. A comparison of their dissociation constant ratios, $K_{\rm H}/K_{\rm D}$, with more recent data (65, 67, 68) is given in Table 4.

Lewis and Schutz's values for the $K_{\rm H}/K_{\rm D}$ ratios are lower than the more recent data. The agreement of Lewis and Schutz's values of $K_{\rm H}/K_{\rm D}$ for acetic acid and chloracetic acid with the data of La Mer and Chittum (65) and McDougall and Long (67), respectively, is within the approximations made in deriving the dissociation constants from conductance data and the additional possibility of small corrections which may need to be applied to the data of Lewis and Schutz for protium contamination of their deutero acid solutions. In the case of NH₄OH Lewis and Schutz had little basis from which to estimate the Λ_0 , the equivalent conductance at infinite dilution, of ND₄OD. It is difficult to reconcile their data with the $K_{\rm H}/K_{\rm D}$ ratios reported by Salomaa, Schaleger, and Long (68).

From the limited data available to them, Lewis and Schutz concluded that the ratio of $K_{\rm H}/K_{\rm D}$ decreases with the strength of the protio acid. Further study (69) of $K_{\rm H}/K_{\rm D}$ ratios has substantiated the conclusion reached by Lewis and Schutz

with the important qualification that the ratio depends not only on the base strength of the conjugate base but also on the base type (70).

Biology of Heavy Water

A characteristic work style that Lewis had developed by the time he carried out his researches on heavy water was to work with a small number of assistants. But he always reserved some exploratory experiments which he carried out by himself. In the heavy water research these experiments were designed to test a hypothesis put forward by Lewis that D_2O would not support life and would be lethal to higher organisms. This was to be Gilbert N. Lewis' first experimental research in the biological sciences.

In the first experiments Lewis found that tobacco seeds, which germinate infallibly in four days in ordinary water, did not germinate in three weeks in $D_2O(71)$. If the seeds were then removed from the D₂O and placed in ordinary water, germination took place in an abnormal way after one week. "The sprouts were extremely thin, and this sickly growth came to an end after a few weeks" (72). On the other hand, seeds placed in 50% D₂O showed normal development, albeit at a slower rate than in H₂O. Lewis found that yeast did not ferment nor did mold develop in media with the H2O replaced by D_2O . On the basis of these preliminary observations he was led to predict that microorganisms would not grow in D_2O_2 particularly after all the exchangeable hydrogen had been replaced by deuterium. He showed that D₂O was lethal to flatworms. Flatworms exposed to D₂O for less than 4 h and then returned to H₂O have a reasonable chance of survival. Lewis tried an inconclusive test of the effect of heavy water on a warm-blooded animal, a mouse. All that can be deduced from that experiment was that a 10-g mouse out-smarted Gilbert N. Lewis in 1933. The mouse drank 0.54 g of 87% D₂O and 0.26 g of 71% D₂O in 3 h. For this valuable beverage the mouse put on a little show. Lewis and Macdonald's D₂O production could not keep up with the mouse's thirst. The scarcity of heavy water posed a barrier to research on the biological effects of heavy water.

Cheap heavy water for experimental research hecame available in the mid-1950's. A large program was organized by J. J. Katz (73) at the Argonne National Laboratory. They were successful in growing green algae in pure D_2O . The morphology of algae grown in D_2O differs significantly from that grown in H_2O . They also grew E. coli (strain K-12) using fully deuterated glucose as a substrate in 99.6% D_2O . The growth rate is about five times slower than in H_2O . Studies were also carried out by Thomson, in particular, which showed that when the D_2O content of the body water of mice reaches 20% severe physiological effects become manifest; 30% D_2O is lethal, Similar results are found in dogs.

Katz took advantage of the ability to raise algae in D₂O to prepare a wide spectrum of deuterium compounds through biosynthesis.

We still lack a real understanding of the effect of deuterium on the growth of simple and higher organisms. Replacement of protium by deuterium changes rates of chemical reactions, equilibria and therefore the pH(pD) of physiological solutions, the viscosity of the medium, structure of nucleic acids, etc.

Nuclear Studies with Deuterium

As soon as Lewis and Macdonald prepared a small amount of 50% D_2O , Lewis and Ashley (who later married W. F. Giauque) determined the spin of the deuteron to be 1 (74). The determination was made from the relative intensities involving the odd and even rotational levels in the molecular spectrum of D_2 . Subsequently, Lewis collaborated with E. O. Lawrence in the study of nuclear reactions produced by the acceleration of HD+ to 2 MeV in the cyclotron. They found the deuteron to be an effective projectile for the disintegration of nuclei of the light elements. Bombardment of targets of

 NH_4NO_3 gave alpha-particles with a range of 6.8 cm (75). Bombardment of LiF yielded two sets of alpha-particles, with ranges 8.2 and 14.5 cm, respectively. The latter corresponds to an energy of 12.5 MeV and is in good agreement with the value obtained from mass relations for the reaction

$${}_{1}^{2}H + {}_{3}^{6}Li = 2{}_{2}^{4}He$$

Protons with ranges up to 40 cm were observed in the bombardment of a variety of targets, including gold, with 0.6–1.3-MeV deuterons (76). All of the nuclear reactions observed in this work must be assigned to reactions of the deuteron with light elements, either present in the target per se or in the pump oil in the dees of the cyclotron. The kinetic energy of 1.3-MeV deuterons is inadequate to penetrate the coulomb barriers of any but first row element nuclei. The energy is greater than the threshold for the reaction

$${}_{6}^{12}C + {}_{7}^{2}H = {}_{7}^{13}N + {}_{1}^{1}N$$

Examination of any of the targets would have revealed the 10-min position activity of $\frac{13}{7}$ N, and along with it, artificial radioactivity would have been discovered.

Retrospective

Some 200 scientific papers dealing with deuterium were published in the three-year interval between Urey's discovery and the time he received the Nobel prize in 1934. Urey, who received his PhD degree in Berkeley in 1923, was the first of the California school to receive a Nobel prize. Between February 1933 and July 1934 Lewis published 26 out of the 200 publications on deuterium. By the criterion of number of publications it was the most productive period in Lewis' career. By any criterion Lewis made a substantial contribution to the development of isotope chemistry that took place in the 1930's. These include his preparation of pure D2O, his work on isotope separation by distillation, electrolysis and chemical exchange, the effect of deuterium on the vapor pressures of protolytic substances, the effect of deuterium on the ionization constants of weak electrolytes, and some pioneer experiments on the biology of heavy water and nuclear reactions of the deuteron.

In all of these researches, except for the nuclear reaction studies, Lewis was guided by the application of qualitative arguments concerning the role of zero-point energy on the chemical and physical properties of substances. I have mentioned earlier that the problems Lewis and associates investigated reflected his areas of interest, expertise, and the scientific activity within the Chemistry Department at the time. It is of interest to mention some of the other major areas of research undertaken at other research centers with deuterium in the period 1931-34. These included the effect of deuterium on the equilibrium in gas reactions and comparisons with calculations from statistical mechanics, kinetic isotope effects in gases and liquids, use of deuterium as a tracer and in the study of reaction mechanism, and structural studies of molecules using deuterium substitution (particularly vibrational spectroscopy).

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I have been aided in the preparation of this paper by discussions with a number of people who were at the Chemistry Department at Berkeley during 1931–34. Of these, special thanks go to Daniel B. Luten. Most of the literature survey necessary for this study has been carried out by Liu Ting-Hai. I also am pleased to acknowledge the access to library facilities in Berkeley. Finally, it is a pleasure to thank K. S. Pitzer and G. T. Seahorg for supplying me with useful information from the records of the Department of Chemistry.

Appendix:

Publications by Gilbert N. Lewis on Isotope Chemistry and Properties of Deuterium

"The Isotope of Hydrogen," J. Amer. Chem. Soc., 55, 1297 (1933). "Concentration of H² Isotope" (with R. T. Macdonald), J. Chem. Phys., 1, 341 (1933). "Separation of the Isotopic Forms of Water by Fractional Distillation" (with R. E. Cornish), J. Amer. Chem. Soc., 55, 2616 (1933).

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- "The Mobility of Ions in H2H2O" (with T. C. Doody), J. Amer. Chem. Soc., 55, 3504
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The Effect of Neutral Ions on Acid-Base Balance

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That neutral ions affect acid-base balance is well documented by numerous case studies in the medical literature. How the neutral ions manifest this influence is often overlooked or misinterpreted. The most common errors made are failure to consider the equilibria established between proton (H+) donors and acceptors in the aqueous environment of the extracellular fluids and the role of the kidney in maintaining electroneutrality while selectively resorbing and secreting ions across the tubular membranes. The purpose of this article is to illustrate such errors and to clarify the role of neutral ions in acid-base balance.

Aqueous Ionic Equilibria

In water, H⁺ and OH⁻ will always be present and in dynamic equilibrium as a result of water's self-ionization. The presence of other aqueous ionic species may affect this equilibrium and thus produce a surplus of H⁺ over OH⁻ ions or vice versa. This interaction of water with aqueous ions is referred to as hydrolysis. An ionic component in water may be neutral, acidic, or basic because of its relative ability to bind or donate protons.

Of the common ions in body fluids, Na⁺, K⁺, Ca²⁺, and Cl⁻ are neutral. Acidic ions include $H_2PO_4^-$ and NH_4^+ , and basic ions consist of HCO_3^- , HPO_4^{2-} , proteinate anions, and organic acid anions. The most prevalent as well as most crucial species in determining intercellular acid-base balance are K⁺, Na⁺, Cl⁻, and HCO_3^- .

Acid-base homeostasis is regulated by three systems in the body. They are (1) the bicarbonate-carbonic acid buffer system, (2) the respiratory system, and (3) the renal system. Most allied-health chemistry courses consider the first two systems in some detail, but failure to investigate the synergism of all three mechanisms often leads to confusion. The kidney has the greatest capacity for maintaining balance in the body. Its compensatory action is particularly important in chronic disorders. The kidney functions by selectively secreting and absorbing ions across the tubular membranes and does so primarily through the movement of neutral species such as Na⁺, K⁺, and Cl⁻.

As the concentrations of neutral ions change, the ultimate effect may be a change in blood pH. Failure to consider the interrelationship between electrolyte changes and pH changes has led to a misinterpretation of the nature of these ions and their role in acid-base balance.

Errors from the Literature

A quick perusal of a few books and articles yielded numerous errors. The ones cited are not the only ones found but have been included to emphasize incorrect interpretations of solvent system equilibria or failure to recognize kidney function.

In the article, "Reviewing Acid-Base Balance" (1), the following paragraph appeared:

If the body fluid becomes too acid, (pH below 7.35), the buffer carbonic acid immediately gives off hydrogen ions to swing the chemical equations to the bicarbonate side, and thus raise the pH toward normal.... If the hody fluid becomes too alkaline, with a pH higher than 7.45, the hnffer bicarbonate immediately takes on a hydrogen ion to swing the chemical equation to the carbonic-acid side and lower pH toward normal.

This is indeed unusual chemistry in that the correction for

Normal Concentrations of Electrolytes and Carbon Dioxide in Blood

| HCO₃ [™] | 22-26 mEg/l | |
|-------------------|---------------|--|
| Na ⁺ | 135–145 m£q/! | |
| CI | 95-105 mEq/t | |
| K+ | 3.5~5.0 mEq/I | |
| CO ₂ | 24-32 mEq/l | |
| Hq | 7.35-7.45 | |
| | | |

acidemia is to liberate more of the strongest possible acid, while the correction for alkalemia is to remove the strongest possible acid, namely H⁺.

Some comments regarding chloride ion are even more convoluted. From Guthrie's "Introductory Nutrition," (2):

As a part of hydrochloric acid, chlorine is necessary to maintain the normal acidity of the stomach contents needed for the action of gastric enzymes. It is an acid-forming element, and along with the other acid-forming elements phosphorus and sulfur, [it] helps to maintain acid-base balance in the body fluids.

From "Fluids and Electrolytes: A Practical Approach," (3) comes the following:

Note that the terms hydrogen-ion donor and acceptor are not synonymous with the terms cation and anion. Sodium and potassium are neither bases nor acids; the cation ammonium is a weak acid; the anions chloride and sulfate are weak bases. . . .

Another citation is from the chapter, "Water, Electrolytes and Acid-Base Balance," in the prestigious "Modern Nutrition in Health and Disease," (4), p. 381:

... Sodium, potassium, magnesium, calcium and chloride ions as such do not function as buffers and are neither acids nor hases. They are "aprotes" since they neither donate nor receive protons.

Then on pp. 385 and 388, respectively, the author contradicts himself by stating as a cause of metabolic acidosis and metabolic alkalosis:

Increased intake of acid, e.g., acidifying salts such as NH_4Cl and $CaCl_2\dots$

... The common causes of metabolic alkalosis are a loss of body acid, particularly loss of chloride ion, and excess of base, usually sodium, and the loss of significant amounts of potassium.

Depending, then, on the published source, the chloride ion is variously termed acidic, hasic, neutral, or maybe acidic. This confusion results from failure to consider solution concepts and kidney function.

Kidney Function and Electrolytes

A brief review of kidney physiology is necessary to show the interrelationships between changes in electrolyte concentrations and acid-base balance. Under normal conditions greater than 99% of the water, and the Na⁺, Cl⁻, and HCO₃⁻ ions are resorbed from the glomerular filtrate. A fairly constant 93% of the K⁺ is resorbed (5). Approximately 65% of the reabsorptive and secretory processes that occur in the tubular system take place in the proximal tubules. An active transport mechanism resorbs Na⁺. Water and anions (mostly Cl⁻) follow due to osmosis and the membrane electrical potential, respectively (6). Some solutes such as glucose, protein and amino acids are completely resorbed in the proximal tubules

as well. The osmolality of the tubular fluid remains equal to that of the surrounding interstitial fluid due to the free permeability to water.

In the loop of Henle the osmolality increases by perhaps fivefold because of the counter-current mechanism and the hyperosmolality of the interstitial inner medullary fluid. The net effect is that another 15-20% of the solutes in the glomerular filtrate are resorbed.

The remainder of the resorption of solutes (mainly Na⁺) and water occurs in the distal and collecting tubules under the action of aldosterone and antidiuretic hormone (ADH), respectively. Since the concentration of Na+ is greater than that of any single anion (see table), the resorption of this ion is accompanied by a combination of passive anion transport or active cation exchange (K+ or H+) to maintain electroneutrality throughout. The tubules are poorly permeable to bicarbonate ion; prior to resorption it must first be combined with H^+ , which forms H_2CO_3 . This is enzymatically decomposed by carbonic anhydrase found in the luminal tubular epithelium. The CO₂ formed is highly lipid-soluble and diffuses rapidly into the peritubular capillary blood. It is important to remember that passive anion transport occurs predominantly in the proximal tubules accompanying Na+ active transport and active cation exchange occurs predominantly in the distal and collecting tubules. There is an inverse relationship between Na+ concentration and K+ and H+ as the exchange occurs. Further, there is an inverse relationship between K⁺ and H⁺ concentrations as competition across cell membranes, as well as competition in active secretion into the urine, occurs.

Examples of Neutral Ion-Acid Base Disturbances

A most perplexing example of the often overlooked interrelationships between neutral ions and acid-base imbalance was the case of infants who failed to grow due to feeding of an infant formula grossly deficient in chloride (7). Infants given this Ci- deficient formula exhibited metabolic alkalosis, which was surprising in the absence of severe vomiting or diuretic administration. These infants exhibited a normal to low Na+ serum level, a slightly lowered K+ concentration, and definite, although not severe, hypochloremia (85–90 mEq/l). Two laboratory findings provided a clue to the imbalance created by Cl⁻⁻ deficiency; an aldosterone concentration almost 30 times normal and undetectable urine Cl-.

Although essentially 100% of available chloride was resorbed, it was insufficient to allow normal resorption of Na+ in the proximal tubules. Because of this much larger quantities of Na+ were required to be resorbed in the distal tubules which accounted for the enormously high aldosterone concentration. Accompanying the abnormal resorption pattern of Na+, more HCO3-, which is not resorbed very well, was produced to maintain electroneutrality in the presence of insufficient Cl., and more K⁺ and H⁺ secretion occurred distally to complete Na+ resorption. This led to retention of base and secretion of acid and to hypokalemic, hypochloremic, metabolic alka-

Next, consider the seemingly paradoxical situation of metabolic alkalosis with production of an acid urine which is corrected by administration of a neutral salt. Metabolic alkalosis is a common disorder in hypertension, cardiac failure, or recovery from surgery (8). Common factors in such cases

are diminished extracellular volume and chloride depletion. Again Na⁺ resorption requires HCO₃⁻ to maintain electroneutrality, thus HCO₃⁻⁻ cannot be excreted. Since H⁺ is secreted in the final stages of Na⁺ resorption and HCO₃⁻ is efficiently recaptured through carbonic anhydrase action, this leads to retention of base and loss of body acid into the urine which further exaggerates the existing alkalosis. Since respiratory compensation through hypoventilation is poor if operative at all, fluid electrolyte replacement is usually needed. Specifically, solutions of the neutral salt KCl are required. The fluid corrects volume depletion, while Cl - can be resorbed to allow HCO3 excretion, and K+ secretion allows retention of H⁺. Thus, excretion of excess base and retention of acid will promptly restore acid-base balance.

For the final example to demonstrate neutral ion-acid base interrelationships, consider the effect on the concentration of neutral K+ during treatment of an acid-base imbalance. Careful monitoring of the patient is required to prevent a life-threatening hyperkalemia from reverting to an equally serious hypokalemia during correction of metabolic acidosis.

In response to an acidotic state, H⁺ will move into the cells in exchange for K+. This leads to K+ wastage in the urine, hyperkalemia and a depletion of total body potassium, the degree of which is not reflected in serum values (9). Hyperkalemia, particularly in the presence of diminished urine output, can lead to abrupt cardiac arrest. An example of such a condition would be the osmotic diuresis accompanying hyperglycemic, diabetic ketoacidosis (10) or sodium wasting associated with a low carbohydrate diet or during fasting (11). As the acidosis is corrected by administration of glucose and insulin in the diabetic or refeeding the starved patient, potassium secretion into the urine and exchange of H+ from the cells for potassium may result in a hypokalemia severe enough to require potassium supplementation. If unchecked this hypokalemia can lead to serious cardiac arrhythmias,

Summary

By considering the equilibria established in aqueous systems such as body fluids, the competition among the electrolytes for donating or accepting protons allows classification of the solutes as acidic, basic, or neutral ions. Coupled with a knowledge of kidney function, this information allows development of the interrelationships between electrolyte and acid-base balance in the body. Only then can the influence of neutral ions such as Na+, K+ and Ci- on acid-base homeostasis be comprehended.

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The Bonds of Conformity

W. A. Noyes and the Initial Failure of the Lewis Theory in America

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My own interest in the chemical side of the electron theory arose from an accident. Some twenty years or so ago (1898), I had occasion to perform the old Hofmann experiment... The tube is filled with chlorine, and when a solution of ammonia is added, this chlorine should combine with an equal volume of hydrogen and liberate the nitrogen with which the hydrogen was combined.

Thus, William Albert Noyes (1857-1941) described to an audience at the Franklin Institute in 1918 (1) how he first became interested in the role of the electron in chemistry.

W. A. Noyes and several of his American contemporaries were among the first chemists to utilize the electron to explain organic structure and reactions. Their theoretical framework proved to be faulty, yet it did show that in the emerging American organic community there was an interest in combining theory with empirically derived experimental evidence. European organic chemists at this time were chiefly concerned with synthetic chemistry, and theory was not considered to be of any great importance, except in England. Ironically, the early interest of American chemists in the electronic interpretation of organic chemistry proved to be a major factor in why G. N. Lewis' electronic theory initially failed in his native country. Through the papers and letters of W. A. Noyes (2), we will attempt to show why this happened.

William Albert Noyes obtained his PhD in 1882 with Ira Remsen at Johns Hopkins after undergraduate studies at Grinnell College. Graduate education at Johns Hopkins was organized in form and substance along the Germanic model that Remsen had been exposed to in his studies with Fittig at Göttingen (1869–72). In contrast to Remsen's lack of interest in theoretical organic chemistry, Noyes, early in his career, combined both fields along with an abiding interest in chemical education.

Noyes' career involved academic and government posts including service at Minnesota (1882–1883), Rose Polytechnic Institute (1886–1903), National Bureau of Standards (1903–1907), and finally the directorship of the chemical laboratories of the University of Illinois (1907–1926). In addition, among his accomplishments were the first editorships of Chemical Abstracts (1907–1910), Chemical Reviews (1924–1926), and The American Chemical Society Scientific Monographs (1919–1944). Noyes was also editor of the Journal of the American Chemical Society from 1902–1927. This was a crucial period for the Journal, as Noyes helped in the merger of Remsen's American Chemical Journal into the Journal of the American Chemical Society.

In 1901, when Noyes was at Rose Polytechnic, he assigned as a senior thesis project the problem of the course of the ammonia-chlorine reaction. The reaction was found to yield nitrogen trichloride and Noyes rationalized the results as follows:

If we suppose what seems not inherently improbable, that all reactions involving the decomposition of molecules are preceded by ionization of the parts of these molecules, it would follow that elementary molecules ionize into positive and negative parts (3).

At this point, Noyes was applying the concept of ionization that Arrhenius had postulated in 1887. In 1904, in his

Silliman lectures at Yale, J. J. Thomson discussed the arrangement of electrons in atoms and their role in chemical bonding. Thomson's model was a modern form of Berzelius' dualism in which the chemical bond was formed by "loss or gain of corpuscles of electricity which created charged species" (4). Noyes later in 1904 at the International Congress of Arts and Sciences held in St. Louis stated:

If, however, we accept the theory of electrons, it is evident that the electrons must be present in the molecule of an electrolyte no matter in which manner it is formed. It is but a step further to the conclusion that the electrons are involved in every combination or separation of atoms and indeed, may be the chief factor in chemical combination (5).

The concept of the electron as the basis of bonding was also appreciated by other American organic chemists. Over the next two decades attempts to apply the electropolar hypothesis to organic reactions were made by Julius Stieglitz (1867–1937) at Chicago, Harry S. Fry (1878–1949) at Cincinnati, and K. George Falk (1880–1953) and James F. Nelson (1876–1965) at Columbia. These chemists along with Noyes formed a distinct group who used what would become known as the electron theory of valence as the basis of their rationalization of organic structure and reactivity.

Falk and Nelson (6) used the electron theory for the explanation of physical and chemical properties of organic compounds. Fry (6) wrote several papers as well as a monograph on aromatic substitution using the electron theory. Stieglitz (6) thought that with the electron theory he had discovered the basis of why molecular rearrangements occur in certain organic compounds. Noves himself did not contribute much in the way of applications to organic chemistry per se but considered the larger problem of proving the worth of the electropolar theory of chemical bonding. His eminence in American chemistry was viewed as an imprimatur by his colleagues in pressing their views against their critics. Their views quickly generated a wide variety of criticism. Typical of Noves' work in this era (1912) was his paper on "Possible Explanation of Some Phenomena of Ionization by the Electron Theory" (7).

Structural formulas for compounds such as ammonium hydroxide and nitric acid in use during this period as shown below gave no clue as to why these compounds behaved as bases or acids.

When we write the formulas in the light of the electron theory, as shown in this diagram, we see that the negative oxygen of the hydroxyl may be held strongly by the positive nitrogen atom of the nitro group (NO₂), while it is not held so strongly by the nitrogen atom of the ammonium group (NH₄). The nitrogen atom of the latter group has lost four electrons and gained one, if we assume a localization of valence electrons (7).

Implicit in the electron theory was the belief that if a bond was formed by electron transfer from X to Y to produce the product X^+Y^- , the reverse process could also occur to produce X^-Y^+ . These two compounds were referred to as electronic isomers or electromers. Noyes attempted to produce the pair $N^{+3}Cl_3^-$ and $N^{-3}Cl_3^+$ in order to prove the electron theory of valence. The compound $N^-Cl_3^+$ had already been prepared, and Noyes stated that if the other electrons could be prepared then:

The discovery of such a compound would make it seem probable that electrical charges are present in compounds and are not merely found during ionization of compounds in solution. This would give support to the hypothesis that atoms are held in combination by electrical forces (8).

The attempts to prepare the electromer N⁺³Cl₃⁻ or for that matter other electromeric pairs always failed, but this did not dim the enthusiasm of Noyes and his circle for the hypothesis. The intrinsic problem with the theory can be viewed as follows. How do you treat bonding in ethane, for instance? Is one carbon positive and the other negative? As Stewart Bates remarked in 1914.

It is difficult to conceive of two methyl groups in ethane as being so different from one another as would be the case if one of the molecules is positive and the other negative. In the vast number of reactions, two halves of such molecules react in an identical manner (9).

The electron theory fails totally when applied to organic compounds, in which polarity does not exist.

Yet Noyes, Stieglitz, Fry, Falk, and Nelson persisted against their detractors. To their credit these classically trained chemists were pioneers in the early development of physical organic chemistry in America. There was much interest in their ideas internationally as evidenced by an entire chapter devoted to the electron valence theory in Heinrich's "Theories of Organic Chemistry." The 1921 edition translated into English by Treat Johnson of Yale was used extensively in graduate courses here and abroad in the 1920's. There is no mention at all of the Lewis theory in the text and the only reference is in a footnote.

By 1914 J. J. Thomson had modified his views concerning valence (10) to include nonpolar bonds. These could be formed by two similar-sized atomic spheres overlapping with the electrons shared equally. Thomson envisioned tubes of force emanating from the electron of one atom somehow anchoring itself to the nucleus of another atom and vice versa. This would lead to a nonpolar bond with the minimal number of electrons being two.

In 1915 two significant papers concerning bonding came across Noyes' desk as editor of the *Journal of the American Chemical Society*. One was by Albert Parsons (1889--), and the other by Gilbert Newton Lewis (1875-1946). Both offered a comprehensive rationale for how all types of bonds found in both organic and inorganic molecules could be understood on a single theoretical basis.

Parsons' conception of valence involved the production of magnetic moments by the circulation of electrons in atoms. These magnetons, as he called them, were located at the corners of a cube and could be shared in a variety of ways to produce the gradation in polarity found in F₂ and HF, for example. Noyes was forced to reject the paper because, as he recalled later (2a), the Canadian physical chemist, William Lash-Miller, as one of the reviewers, had insisted that it was physics and not chemistry. Julius Stieglitz, a member of Noyes' circle, however, strongly recommended its publication (2a). Noyes saw merit in Parsons' idea, as did G. N. Lewis, in whose department Parsons worked, and he arranged to have it published in the Smithsonian Institution's Miscellaneous Collections (11).

Noyes' response to the magneton theory can be found in a lecture on valence delivered in 1917 and reprinted in the Journal of the Franklin Institute in 1918.

The magneton theory of the structure of the atom has also been developed and elaborated by Parsons. It cannot account for ionization, where, if we accept the electron theory at all, electrons must be transferred completely from the positive atom or group to the negative (12).

The Lewis paper which was accepted and appeared in April 1916 issue of the Journal of the American Chemical Society was entitled simply "The Atom and the Molecule" (13). In this paper Lewis described how by treating the chemical bond as an electron pair one could rationalize all the various types of chemical bonds as one continuum. Interest in the Lewis theory in America among organic chemists was minimal in the next decade.

We shall now try to probe the reasons for this lack of interest by looking at the way Noyes reacted to the Lewis theory. His problems mirrored the difficulties other American organic chemists had with Lewis' theory. One of the first recorded reactions of Noyes to the Lewis theory was his address to the AAAS meeting held in Baltimore on December 27, 1917. His lecture was later reprinted in *Science* in 1919.

G. N. Lewis has proposed the hypothesis that carhou compounds are not held together by polar valences because they do not readily ionize. It seems possible that this is true in some cases, but it is difficult to believe that there is any essential difference between the reaction of methyl iodide with silver nitrate and that of potassium iodide with the same agent (14).

In February 1917, Noyes himself published in the Journal of the American Chemical Society some new ideas about bonding in a paper, "A Kinetic Hypothesis in Explaining the Function of Electrons in the Chemical Combination of Atoms" (15). The assumption was made that a single valence electron in rapid motion would bind two atoms by the interaction of the negative electron with the two positive nuclei. For carbon atoms, Noyes drew the following picture:



Why did other organic chemists have such difficulty with the electron-pair concept? One reason for this was G. N. Lewis himself. From all indications it appears that Lewis had little interest in organic chemistry. In his 1916 paper as well as his 1923 monograph "Valence and the Structure of Atoms and Molecules" few if any substantial examples of application to organic molecules can be found. Lewis was aiding by these omissions the chasm that was perceived to exist between physical and organic chemistry by their respective practitioners. Further evidence comes from the way Lewis built the department at Berkeley which he took over in 1912. He recruited a group of highly innovative inorganic and physical chemists but seems not to have done the same for organic chemistry as Melvin Calvin (16) relates "From that time on, all the rest of the department of chemistry were homemade." Gerald E. K. Branch was the only member of the department publishing in the area of organic chemistry between 1916 and 1926. His work for the most part was synthetic in nature, though he did do some kinetic studies. However, his papers do not use or mention the Lewis theory during this period. Branch in the 1930's would become one of the leaders of physical organic chemistry in America, however, primarily through his close contacts with C. K. Ingold which commenced in that period.

Lewis' work also could not have appeared at a more inopportune time in terms of its heing accepted. European chemistry had come to a virtual standstill because of the war. With America's entry into the war Lewis himself was eliminated from further work in electron pair bonding because he joined the chemical warfare service. When he returned from France in 1919 he devoted his research efforts to thermodynamics and not to the electron pair bond.

In 1919, Irving Langmuir (1881–1957) at the General Electric Company took up where Lewis had left off. His series

of three papers appearing between 1919 and 1920 further amplified the electron pair concept and introduced the octet concept in detail (18). Langmuir was a tireless proselytizer for the electron pair and he gave many talks here and abroad. One of these speaking engagements was at the University of Illinois where Noyes was the head of the department. This occurred in 1919 and was the result of a correspondence that had been taking place between Langmuir and Noyes concerning valence. Noyes at the time was preparing his "A College Level Textbook in Chemistry" and was eager for "criticism of this chapter (valence), and a statement of those parts of the chapter which seem inconsistent with the facts which are known about chemical combination (2c)."

The following is from a letter dated May 6, 1919, from Noyes to Langmuir and shows clearly the conceptual problems Noyes was having:

According to your theory, methyl iodide is a non-polar compound, while ammonium iodide and sodium iodide are polar, but methyl iodide reacts as readily with silver nitrate as do the other compounds, and in the reaction the iodine is almost always replaced by a negative atom of the group in normal double decomposition, while by your theory it should be replaced with equal ease by negative or positive atoms. Your theory supposes that in the combination of two atoms, the valence electrons are drawn together... how do you account for it? (2c)

In response to these points raised by Noyes, Langmuir wrote on May 9, 1919:

The octet theory indicates in methyl iodide a pair of electrons is held in common between the carbou atom and the iodine atom and in this respect differs radically from sodium iodide. . . The fact that methyl iodide reacts so easily with silver nitrate simply indicates that the iodine atom is capable of detaching itself readily from the CH₃ group leaving the latter temporarily positively charged, and that in such a condition that it reacts readily with a negative group (2c).

As to the reason why two electrons form a stable pair, Langmuir could only allude to what he believed to be well-known chemical facts that support the electron pair acting as a single bonding unit. In one particular instance Langmuir writes "the isomerism of nitrogen, phosphorous, and sulfur compounds etc., is completely explained by the octet theory, always considering however that a pair of electrons which is shared between two atoms acts as though it is concentrated at a point. This not only explains optical isomerism of substances such as amine oxides of the type ONR, R₂, R₃, but also explains the isomerism of tervalent nitrogen compounds such as ketoximes, diazo compounds, etc. (2c)."

The last known letter from Noyes to Langmuir dated May 23, 1919, contains the following:

I can see no reason, other than your theory, for thinking that in the reaction between methyl iodide and silver nitrate an iodine atom which is not negative becomes so during the reaction and that a nitrate ion which is negative changes to a group that is not negative. It seems to me much simpler to suppose that methyl iodide undergoes a trifling ionization and that the reactions are alike instead of radically different (2c).

The depth of commitment Noyes and his contemporaries had to the electropolar school of valence could not be changed ensily. A 1920 paper by Eustace Cuy entitled "The Electronic Constitution of Normal Carbon Chain Compounds" (19) is based on the assumption "that carbon compounds are polar in nature and that carbon atoms in a chain tend to assume alternately positive and negative charges" (19). No mention of Lewis-Langmuir theory is made, and this is not an isolated example. The intellectual hurdles the Lewis theory faced in its acceptance against the well-entrenched, but fallacious, electropolar theory were enormous.

Noyes, although skeptical like the majority of his colleagues of the electron-pair bond, sought in the early 1920's to provide experimental evidence either for or against the concept. In 1921 (20), he reported again on his attempt to prepare the electronic isomer of NCl₃ where the nitrogen would be in the plus three state. As he stated "the question of whether there is a transfer of an electron from one to another in all forms of chemical combination or whether this occurs only in the so-called 'polar' compounds, and the question of whether atoms are held together by a single electron or by pairs of electrons may well still be open" (20), and this would be settled by this investigation. He was quite convinced at the time of the existence of Cl⁺ from his earlier studies of N⁻³Cl₃⁺ and if he could prepare N⁺³Cl₃⁻, then it would yield Cl⁻ and thus show the validity of the electron theory he had supported.

This compound could not be prepared, and the most Noyes was willing to conclude was as follows:

So far as negative results have values, the experiments favor Professor Lewis' hypothesis that electrons are held jointly by two atoms rather than the view that electrons are transferred from one atom to the other when atoms combine (20).

Noyes carried on an active and extensive correspondence with G. N. Lewis (2a,b). Even by 1923, Noyes still did not fully understand the value of the Lewis theory in organic chemistry. On June 4, 1923, (2a) Noyes wrote to Lewis the following upon review of the galley proofs of the Lewis monograph "Valence and the Structure of Atoms and Molecules":

This leads me to the suggestion that the separation into positive and negative parts takes place in the immediate presence of some reacting element or compound. This, as you will see, places the emphasis nut on the condition of the element in the compound, but on its condition during its transfer from one compound to another. In light of your theory of pairs of electrons, this seems to be an almost necessary corollary of that theory. In accordance with this tendency of elements to separate from others with or without the pair of electrons, it seems to me perfectly proper to designate some atoms as positive and others as negative (2a).

Even such a succinct statement of Lewis' position as occurs in a letter dated July 27, 1923, (2a) did not change matters significantly.

You seem to intimate that I have made a distinction between polar and non-polar bonds. Never have I done this, nor do I see the slightest occasion to, whether the bonded atom is hydrogen or any other. In cases of complete ionization, we have the bond broken and it ceases to exist, but I recognize one type of bond which is the electron pair. In so far as it shifts from the electrical center of gravity it makes the molecule more polar, I think it would be rather unfortunate to perpetuate the misleading terms polar and non-polar bond (2a). (These terms had been introduced by Langmuir).

In the above cited letter of June 4, 1923, Noyes made the following comment about the electron-pair bond, "I have not found in your book one clear statement of any forces, other than static ones hetween electrons and positive nuclei and magnetic forces between electrons." Noyes in retrospect in a letter dated September 9, 1932, to Robert Robinson, stated that in this period the major difficulty he had with the Lewis theory was that it was "very artificial and I was repelled by it" (2a).

The year 1923, however, marked a turning point in the use of the Lewis theory in organic chemistry. During the preceding seven years in America, the electron pair theory had been met with either indifference or skepticism as to its usefulness. Applications of the Lewis theory by physical and inorganic chemists of Lewis' circle had been published. Except for a very few tentative uses by organic chemists such as James B. Conant (21) of Harvard and Wallace Carrothers (22) of Illinois, most American chemists were content simply to ignore electron considerations of bonding. However, on the other side of the Atlantic in England a lively interest had been growing in the use of the Lewis theory. This may have heen sparked by

Langmuir's series of lectures on the electron pair bond in 1919 at the British Association for the Advancement of Science meeting in Edinburgh. A small but influential group of chemists began using the Lewis theory as a focal point of their research efforts.

Robert Robinson (1886-1975) and Thomas Martin Lowry (1883-1935) were the leaders of this group. They would later be joined by Christopher K. Ingold (1893-1970) who would expand the work started by Lowry and Robinson. Both Lowry and Robinson had matured in an environment which looked upon chemistry as a truly organic subject. The melding of physical and organic chemistry was initiated by Lowry's mentor H. E. Armstrong (1848-1937) and continued by Robinson's colleague Arthur Lapworth (1872-1941), also an Armstrong student.

Lowry in 1923 organized a two-day symposium at Cambridge entitled "The Electron Theory of Valence" (23) with J. J. Thomson as the chairman and G. N. Lewis as the keynote speaker. The first day of the meeting was devoted to the physical aspects of the theory and the second day was reserved for the applications to organic chemistry.

In his opening address on the second day, T. M. Lowry stated:

But it was, I believe, left to G. N. Lewis to complete the electronic theory of valence by finding a mechanism for the non-polar bond of organic chemistry, namely a sharing of electrona in order to make up for a shortage in the number required to provide each atom with an independent stable group (29).

There followed papers by Lowry, Robinson, and Lapworth which show a remarkable understanding of the Lewis concept of bonding and its role in organic chemistry. Noyes, who seems to have been the only American organic chemist present, contributed to the discussion with his analysis of amine oxides. The basis for Noyes' contribution was the work of Lauder Jones, one of the members of the American electropolar school and a colleague of Harry Shipley Fry at the University of Cincinnati, In 1914, Jones proposed that the nitrogen atom in amine oxides forms a double bond with oxygen (24). The double bond was viewed as having nitrogen simultaneously donating and accepting a pair of electrons. Noyes used the analogy of hydrogen peroxide where the cleavage of the peroxide linkage results in one oxygen being positive and one negative. He then proposed the following formula for trimethylamine oxide:

(CH₃)₃N¹;O

The position of the colons, which are used to represent pairs of electrons, is intended to indicate that one pair clings to nitrogen and the other to the oxygen in the reactions of the compound; The union between oxygen and the nitrogen has all of the usual characteristics of a double union between oxygen and carbon.... The manner of writing this formula indicates that in reactions the upper pair of electrons always remains with nitrogen while the lower remains with oxygen.... (23).

Later in the day G. N. Lewis corrected Noyes erroneous pentavalent nitrogen in amine oxides by postulating that the bond between nitrogen and oxygen was a single bond in which nitrogen donates the electron pair to form the bond. Lewis offered for proof for his structure that amine oxides add a proton to the oxygen in absolute alcohol, "a phenomenon which could hardly be explained on the theory of quinquivalent nitrogen" (23).

Noyes came away from the symposium still not totally convinced of the worth of the Lewis theory. He could not have failed to have been impressed by the enthusiasm and ingenuity of the English in the application of the electron pair concept. His continued commitment to the electropolar theory is evident from a short note in the December, 1923 issue of the

Journal of the American Chemical Society (25), in which he tries to reconcile the Lewis electron pair with the electron theory of valence. Noyes saw the need for the use of the electron pair but could not see how it could be used in the reactions of organic molecules which seemed to involve ions. He, therefore, stated that if one assumed "that when the molecule separates into two atoms, in a reaction with some compound, the pair of electrons usually remains with one of the atoms, which is therefore negative while the atom which separates without the pair is positive" (25). Thus, he believed both views of bonding could live together in harmony.

The desire to use the Lewis theory in American chemical education was expressed in 1925 by Morris Kharasch. Before the Division of Chemical Education he argued for the use of electron theory "to put a soul into the teaching of organic Chemistry" (26). Yet Kharasch was reluctant to subscribe fully to Lewis' theory himself as he stated "that considerable caution must be exercised in the interpretation of organic

reactions from this new standpoint" (26).

In his textbook "Organic Chemistry" (1926) Noyes refers to the work of Lewis as it can be used for the "interpretation of some of the phenomena of organic chemistry." He then returns to reiterating his positive-negative approach to reaction mechanism in which every atom in a bond is potentially either a positive or negative ion but not necessarily by cleavage of the pair. Thus, even at this junction there was less than total understanding of what Lewis had done. A small number of organic chemists in America appreciated the usefulness of the Lewis theory but their influence was practically nil at the time. They themselves were still not totally familiar with how to use it. A good example of this is the work of Howard Lucas (1885-1963). Lucas published a series of three papers in 1924 and 1925 concerning electron displacement in aliphatic compounds (27). The focus of this series was an effort by Lucas to show that the notion of alternating polarity in carbon chains, such as represented in the work of Cuy (19) previously mentioned was impossible. In the view of Lucas "the properties of many classes of organic compounds can be accounted for satisfactorily on the basis of electron displacement" (27a).

Lucas uses the dot notation of Lewis to explain the course of addition of HI to propylene, acrylic acid, and dimethylallene. In the case of acrylic acid displacement by "the strong pull of carboxyl on the electron pair, is toward the carboxyl as shown.

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which may be written CH₂‡=CH+-COOH. When hydrogen iodide adds, iodine goes to the beta position:

$$CH_{2}^{++}CH^{+-}COOH + H^{+} + I^{-} \rightarrow I^{-+}CH_{2}^{+-}CH^{+-}COOH$$

The assumption of alternating polarity of carbon atoms is unnecessary." Lucas appreciated the simplicity of explaining reaction mechanism by the Lewis theory but his use of the +, - formulae created confusion as to whose ideas he was using.

By 1925 in the U.S. there was an appreciation by a small group of organic chemists of the need to use and teach the Lewis theory. However, the theory had made little headway and was for all intents and purposes a failure in the country of its origin. In England by 1925 Robinson had almost completed his study on the application of the Lewis theory to the chemistry of conjugated systems. His work would result in a comprehensive theory of organic reactions on an electron basis utilizing the electron pair as the focus (28).

Why did the Lewis theory succeed in England and not in America? Earlier both Robinson and Ingold had been infatuated with other theories of bonding such as partial valence and strict polarity. However, they were not as rigid in their views as most of their American counterparts. They could see that the Lewis theory could explain so much of organic chemistry without resorting to untenable hypotheses such as an electropolar bond in carbon chains. In contrast to their American colleagues who were well along in their careers, Robinson and Ingold in particular were still very young and vigorous.

Several unique factors existed in England which contributed to the adoption of the Lewis theory. Among these one can point to the limited number and proximity of educational centers in England as well as the hierarchical organization of university departments. In America those who were interested in the application of electron theory to organic chemistry were widely dispersed: Lucas in California, Noves in Illinois, and Conant in Massachusetts. In England, the short distances between the major centers of electronic theory; Oxford, Cambridge, Manchester, and London assured that frequent and direct communications occurred. Numerous meetings and symposia such as the Faraday Symposium of 1923 could be organized and attended by leaders in the field without involving major commitments of time and resources.

Graduate education in America in the period of 1919-1925 was dispersed over some forty colleges and universities. In England only a handful of universities offered the opportunity to qualify for the PhD or DSc. The spread of new ideas was more likely to take place when student density was so highly concentrated. There was only one professor of organic chemistry in each of the major British chemistry departments. Thus, they had tremendous power and influence as contrasted to those who were part of the more democratic organization of American chemistry. This hierarchical system aided in the spread of new ideas, Robinson and Ingold generally would staff their section with former students who would carry on a close collaboration with their mentors. Thus, those who were familiar with the new electronic interpretation were bound to spread further the Lewis theory as they participated in training a new generation of students.

The excellent correlations that were obtained between theory and experimental facts by the English school (29) as it became known in America made it impossible for the bulk of American organic chemists to ignore the Lewis theory any further after 1926. With the rise of a new generation of American chemists, the Lewis theory was readily adopted during the 1930's. Noyes himself was able to overcome his

difficulties and produce several excellent review articles which extolled the merits and the use of the Lewis theory (30). In 1934 (31), Noyes corrected Robinson for his sloppy use of symbolism and nomenclature in Robinson's 1932 pamphlet outlining the latter's electronic theories. The Lewis theory finally had succeeded in America!

Acknowledgment

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Computer Workshops for College Teachers

The Committee on Computers in Chemical Education of the Division of Chemical Education in cooperation with Project SERAPHIM is sponsoring the following workshops for high school chemistry teachers. The purpose of these sessions is to provide teachers with an opportunity to evaluate currently available computer software.

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ContactRita Barichievich

April 7, 1984

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demical principles revisited

Edited by DAN KALLUS Midtand Senior High School 906 W. Illimois Midtand, TX 79705

The "6N+2 Rule" for Writing Lewis Octet Structures

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Lewis octet structures (LOS's) constitute an overwhelming majority of the structures that students encounter in a course in general chemistry, organic chemistry, or biochemistry. Hence, the writing of LOS's corresponding to a given molecular formula is an important exercise for them. The ability of students to write these structures correctly, and then to calculate the formal charges of the atoms involved, is a prerequisite to understanding such topics as acidity and basicity, resonance, molecular geometry, structural isomerism, and reactivity. Thus, if Lewis structures are written for all of the oxyacids of chlorine, their observed increase in acidity as more oxygen atoms are attached to the chlorine atom can be rationalized by an increase in formal charge of the central atom in passing from HClO to HClO₂ to HClO₃ to HClO₄, Determination of the structure of an organic compound from elemental analysis and spectral data requires the ability to choose among a set of isomeric Lewis structures. Despite the unquestionable necessity of learning how to write Lewis structures, many textbooks do not give any procedures for writing such structures. Some textbooks do provide equations or rules, but they appear to be unnecessarily complicated and too difficult to be remembered (1-5). An earlier article in THIS JOURNAL gave rules that are useful for writing resonance structures (6).

The "6N+2 Rule"

We recommend a set of instructions for writing LOS's which incorporates as a central feature the application of a simple rule, which we call the "6N+2 Rule." The basis of the rule is illustrated in Figure 1 in which LOS's of progressively larger polyatomic molecules or ions, each containing only single bonds and no rings and each having been stripped of its hydrogen nuclei, are depicted. A dash is used here to represent a bonding pair of electrons, whereas dots are used to denote lone pairs. It will be noted that the initial atom has (2+6) valence electrons and the further addition of each heavy atom (i.e., an atom other than hydrogen) is accompanied by the incorporation of six valence electrons into the structure. Thus, the "6N+2 Rule" states that 6N+2 valence electrons are required to write an all-single-bonded, noncyclic Lewis octet structure, where N= number of heavy atoms in the molecule.

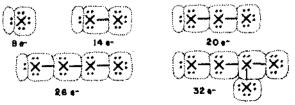
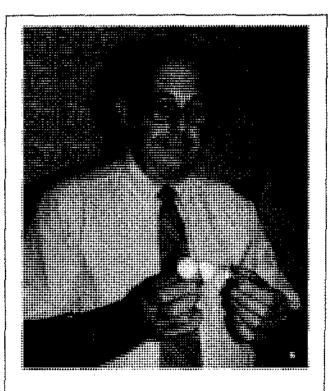


Figure 1. All-single-bonded, noncyclic Lewis actet structures.

This rule leads to quickly recognized "magic" numbers of valence electrons (8, 14, 20, 26, 32, 38, etc.) for compounds devoid of multiple bonds or rings.

Now, an extra bond can only be introduced into any allsingle-bonded, noncyclic Lewis octet structure that is shown in Figure 1, without violation of the Octet Rule, at the expense



This feature is almed as a review of basic chemical principles and as a reappraisal of the state of the art. Comments, suggestions for topics, and contributions should be sent to the feature editor.

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Kallus' achievements in teaching chemistry won him the 1976 ACS Regional Award in High School Chemistry.

Figure 2. Formation of an extra bond at the expense of two lone pairs of electrons and resulting in multiple bonds and/or rings.

of two lone pairs, as shown in Figure 2. In other words, each extra bond, by serving the same purpose as two lone pairs, leads to a reduction in the total number of valence electrons required for a Lewis octet structure by two. Hence, if a given compound has less than (6N+2) valence electrons, it must, within the framework of a Lewis octet structure, accommodate this shortage by forming one extra bond for each deficiency of two valence electrons, resulting in the production of multiple bonds and/or rings1 (one double bond or ring for each extra bond, and one triple bond for two extra bonds). (If non-octet structures are allowed, then a compound can accommodate fewer than (6N+2) valence electrons by utilizing three-center bonds as in B2H6, by incorporating atoms that are relatively stable with fewer than eight electrons in their valence shell as in BF₃, Ag(NH₃)₂+ or LiCH₃, or by employing more unconventional structures as in $Fe(C_5H_5)_2$. Of course, the "6N+2 Rule" would not apply to an ionic compound considered as a single entity but rather to each covalently bonded fragment (ion).)

If hydrogen atoms are added to any of the structures written in Figure 1, the total number of valence electrons is still (6N+2) because each new bond (to a hydrogen nucleus) replaces one lone pair, as shown in Figure 3. Therefore, the "6N+2 Rule" ignores hydrogen atoms and N simply represents the number of heavy atoms.

Figure 3. The addition of hydrogen atoms at the expense of lone pairs of electrons with no change in the total number of valence electrons.

Instructions for Drawing LOS's

We can now recommend rules for drawing all "chemically reasonable" LOS's for a given formula of a covalent compound or of an ionic fragment, if the compound is ionic. These rules for "chemically reasonable" LOS's are intended to be brief, easily understood statements that exclude most structures normally considered to be unstable while retaining most structures corresponding to stable compounds. Their basis lies in the principle that the absolute value of the formal charge² of all atoms in stable compounds tends to be zero, i.e., it takes energy to separate unlike charges. Thus, oxygen linked

by two bonds, nitrogen by three bonds, and carbon by four bonds each have zero formal charge.

Rules for Writing Lewis Octet Structures

Divide the compound into its ionic or molecular fragments and for each fragment follow the steps described below:

- Calculate V, the total number of valence electrons in the fragment.
- Calculate A, the number of valence electrons required for an all-single-bonded, noncyclic Lewis octet structure, using the "6N+2 Rule", where N is the number of non-hydrogen atoms.
- 3) Calculate EB, the number of extra bonds, by subtracting the answer in step (1) from that in step (2) and dividing the resulting difference by 2: EB = (A V)/2; for example, if A minus V is 4 electrons, then EB = 4/2 = 2, and there must be either 2 double bonds, or 1 triple bond, or 1 double bond and 1 ring, or 2 rings present in any octet structure.
- 4) Arrange the heavy atoms (atoms other than hydrogen) in all possible unique and "chemically reasonable" ways, ntilizing double and triple bonds and rings, if any, to account for the extra bonds
- Add all hydrogen atoms, starting first with carbon, then add lone pairs until all heavy atoms have an octet (four pairs).
- 6) Check to see that the total number of electron pairs in the structure is equal to the number of valence electrons present (step (1)) divided by 2, viz., V/2. (Note: These two quantities will agree with each other, unless a mistake has been made in one of the earlier steps.)

Rules for Writing the Most "Chemically Reasonable" Arrangement of Atoms in a Lewis Octet Structure

- Hydrogen atoms may never form more than one covalent bond; therefore, they must occupy a terminal or peripheral position.
- 2) Carbon atoms nearly always form four bonds in stable compounds; hence, they almost never have lone pairs (common exceptions include CO, CN⁻, carbanions, and compounds containing the --NC (isocyanide) group).
- In stable structures, nitrogen usually forms three bonds and oxygen forms two bonds; however, there are several exceptions; e.g., NH₄+, H₃O+, O₂²⁻, HNO₃, HN₃, etc.
- e.g., NH₄+, H₃O+, O₂²⁻, HNO₃, HN₃, etc.
 4) Oxygen-to-oxygen bonds (peroxide linkages) are rather unstable;
 i.e., O—O bonds are to be avoided, if possible.
- 5) Symmetrical arrangements are most common.
- 6) If the molecule or ion is of the form AB_n, it is quite common for A to occupy a central position bending to all of the B atoms. [However, B will be the central atom if its covalency or electrovalence is higher than that of A. For example, N₂O is N—N—O rather than N—O—N.]

Rule for Calculating the Number of Valence Electrons

For the atoms belonging to the A subgroups in the Periodic Table, the number of valence electrons is simply equal to the number of

¹ According to IUPAC Rules, the definition of the number of rings in a polycyclic compound is the minimum number of cuts that must be made in the compound in order to convert it into an open-chain compound. This definition is precisely in agreement with the number of rings calculated by application of the "6N+2 Rule" to a polycyclic system (see example (4)). The agreement follows from the fact that the extra bonds introduced into a noncyclic structure to produce a polycyclic system, as in Figure 2, could be the very bonds that are required to be cut in the reverse process by IUPAC Rules.

² Formal charge is computed by dividing *bonding* electrons equally between bonded atoms. Thus, formal charge equals the group number of the element minus the number of electrons in the form of lone pairs on the atom minus the number of bonds.

$$FC = GN - 2LP - B$$

where FC is the formal charge of atom, GN is the group number of element, LP is the number of lone pairs on the atom, and B is the number of bonds attached to the atom. For example, there are no formal charges on the atoms in HOCi, but there are formal charges present in HClO.

the group. Thus, the number of valence electrons present in a molecule is equal to the sum of the number of atoms of each kind multiplied by the group number of each atom. For an ion, the net charge must be taken into account; that is, negative ions coutain extra electrons and positive ions are deficient in electrons.

Examples

 C_2H_5F

$$V = (2 \times 4) + (5 \times 1) + (1 \times 7) = 20$$

 $A = (6 \times 3) + 2 = 20$
 $EB = (20 - 20)/2 = 0$

Hence, no multiple bonds or rings are present and the LOS is

Note that

is obviously "chemically unreasonable" since carbon has a lone pair and consequently forms only three bonds.

CO2

$$V = (1 \times 4) + (2 \times 6) = 16$$

 $A = (6 \times 3) + 2 = 20$
 $EB = (20 - 16)/2 = 2$

Possibilities: 2d; 1d + 1r; 2r; 1t

("d" denotes double bonds, "r" denotes rings, and "t" denotes triple bonds.)

The LOS, then, requires two extra bonds. The possibility of incorporating two rings is not allowed with three atoms, while one ring and une double bond would require a peroxide linkage. Thus, the allowed LOS's are

The last two resonance structures are of higher energy because of non-zero formal charge, which should be readily apparent to students because oxygen has more than or less than two bonds.

$C_2H_4O_2$

$$V = (2 \times 4) + (4 \times 1) + (2 \times 6) = 24$$

 $A = (6 \times 4) + 2 = 26$
 $EB = (26 - 24)/2 = 1$
Possibilities: 1d; 1r.

Hence, a LOS must have I double bond or 1 ring. Possible "chemically reasonable" LOS's are

1,3-dioxetane (1r)

Note here that the method leads to several interesting structures corresponding to $C_2H_4O_2$ that elementary students can easily write. However, they would need more experience in chemistry to appreciate

not stable (1r)

the fact that the last two LOS's are unstable. The formulation of additional rules at this point, however, would probably be unwise.

 C_6H_6

+1r: 14 + 2r

$$V = (6 \times 4) + (6 \times 1) = 30$$

 $A = (6 \times 6) + 2 = 38$
 $EB = (36 - 30)/2 = 4$
Possibilities: 4d; 3d + 1r; 2d + 2r; 1d + 3r; 4r; 2t; 1t + 2d; 1t + 1d

Among the various LOS's that correspond to the requirement of EB = 4 are the following:

While the presence of one and two rings in cyclohexatriene and Dewar benzene, respectively, will be easily discerned by students, it may not be immediately apparent to them (nor even to experienced chemists unfamiliar with the nomenclature of polycyclic hydrocarbons) that benzyalene and prismane are considered to be tricyclic and tetracyclic, respectively (see Footnote 1).

(4r)

Na₂SO₄

If Na_2SO_4 is considered as a single entity, $V = (2 \times 1) + (1 \times 6) + (4 \times 6) = 32$ $A = (6 \times 7) + 2 = 44$ EB = 6Possibilities: Many.

(1d + 3r)

It is immediately seen to be unreasonable to write an LOS for this entity because it would entail the placing of eight electrons around sodium and a large number of multiple bonds or rings. Since this compound is ionic, it must be divided into its ionic fragments before the "6N+2 Rule" is applied. Thus, consideration of Na₂SO₄ as 2Na⁺ plus SO₄²⁻ leads to the writing of a LOS for SO₄²⁻. For SO₄²⁻,

$$V = (1 \times 6) + (4 \times 6) + 2 = 32$$

 $A = (6 \times 5) + 2 = 32$
 $EB = (32 - 32)/2 = 0$
Hence, the LOS is

Note: Sulfur may expand its valence shell to reduce the high formal charges in the octet structure. This consideration leads to the Lewis non-octet structure

NoHAOn

$$V = (2 \times 5) + (4 \times 1) + (3 \times 6) = 32$$

 $A = (6 \times 5) + 2 = 32$
 $EB = (32 - 32)/2 = 0$

If N₂H₄O₃ represents a covalent molecule, then our rules would lead, for example, to the following LOS as one of several alternative structures:

Note: Consideration of $N_2H_4O_3$ as a single entity led to EB=0 and to the conclusion that this molecule must have all single bouds and no rings.

However, another way to satisfy the requirement of zero extra bonds is to have a double bond in one part of the compound and to have a compensating zero bond in another part (namely, two ionic fragments). Thus, consideration of this formula for an ionic compound leads to the writing of separate LOS's for NH4+ and NO3". Although no definite rules can he given to indicate to students which atoms should be grouped to form the two ions, the students might, as an aid in the present example, use rule (6) for writing the most "chemically reasonable" arrangement of atoms in LOS's, namely, molecules or ions of the form AB_n . For NH_4^+ ,

$$V = (1 \times 5) + (4 \times 1) - 1 = 8$$

 $A = (6 \times 1) + 2 = 8$
 $EB = 0$
Hence, the LOS is

For NO₃⁻,

$$V = (1 \times 5) + (3 \times 6) + 1 = 24$$

 $A = (6 \times 4) + 2 = 26$
 $EB = (26 - 24)/2 = 1$

Since peroxide linkages are to be avoided, a cyclic structure is not written, and, even though two of the oxygen atoms have a formal charge of -1, a "chemically reasonable" LOS (resonance structure)

Non-Octet Structures

Lewis structures in which more than eight electrons surround an atom are possible if this atom is that of an element found in the third row or a subsequent row of the Periodic Table. For such structures, the total member of valence electrons required to insure the absence of multiple bonds or rings will exceed that calculated by the "6N+2 Rule." Hence, the "6N+2 Rule" is not applicable to these non-octet Lewis structures. However, the following generalization of the rule

could be used in such cases; the total number of valence electrons required to write an all-single-bonded, noncyclic Lewis structure is $(2 + 6N_8 + 8N_{10} + 10N_{12} + ...)$, where N_8 , N_{10}, N_{12}, \ldots are the number of atoms surrounded by 8, 10, 12, ... electrons, respectively, and again hydrogen atoms are ignored. The presence of multiple bonds and/or rings will be required in molecules which have fewer than the total number of valence electrons given by this formula. Although one may not be able to predict which atoms will expand their octets and to what extent, the generalized rule provides a student a way of discovering alternative non-octet Lewis structures.

The "6N+2 Rule" is inapplicable as well to molecules such as B_2H_6 , $C_2H_5^+$, $C_2H_5^-$, $C_2H_4^-$, $C_2H_4^+$, etc., which have three-center bonds or are carbonium ions or free radicals and hence cannot have Lewis octet structures. However, if students try to apply the "6N+2 Rule" to B₂H₆, for example, they will immediately notice that this molecule must have some exceptional bonds.

Conclusion

Most textbooks treat bending from the standpoint of atomic and molecular orbitals. Such an approach to bonding makes this subject unduly complicated for elementary students. In fact, the authors believe that an overemphasis has been placed on quantum mechanics and molecular orbital theory in introductory chemistry courses, and this is presumably the reason why many textbooks do not provide rules for writing LOS's. Lewis structures are fundamentally so important that students should be introduced very early to them, and the "6N+2 Rule" and other rules given here should facilitate the ability of students to master this topic. In order not to give students the impression that the Lewis theory of structure is completely divorced from quantum theory, we point out that there are parallels to the Lewis theory in the Floating Spherical Gaussian Orbital technique, an ab initio quantum mechanical method of calculation introduced by A. A. Frost (7). Frost's method focuses directly on localized core, bonding, and nonbonding orbitals and predicts structures in agreement with Lewis theory, valence shell electron pair repulsion theory (8), and Bent's Tangent Sphere model (9), and leads to a nonempirical electronegativity scale (10).

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applications and analogies

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Diagonal Relationships—Descriptive or Theoretical?

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It is well known to inorganic chemists that certain diagonally related pairs of elements (e.g., lithium and magnesium, beryllium and aluminum, and boron and silicon) possess a surprising number of similar properties.² This behavior is generally explained by Fajans' Rules, namely that polarizability is a function of charge and of size of the charged species. The result is that the members of each of the above pairs are more similar to each other than would be expected simply from their positions in the periodic table in adjacent families. There are two areas where an understanding of this phenomenon is useful; as an aid to remembering periodic properties and as an aid to devising methods of analysis in certain cases.

When I was a bench chemist I received a request for a direct determination of the free (elemental) beryllium in fairly pure beryllium metal. The major impurity was beryllium oxide. Other impurities were small and were determined spectrographically. As any bench chemist knows, analyses of highpurity metals are generally made by determining the impurities and then finding the purity from the difference. However, in this case a direct determination was stipulated. It was essential that an acceptable method be used and that a result be obtained in a reasonable time. A research project was out of the question. There were just too many different types of samples waiting for analyses.

Reference to the standard treatises was of no help. Nor were the chemists of the beryllium producers of any assistance. The thought then occurred, based on the concept of diagonal relationship, that perhaps a method for the determination of free aluminum could be found in the monographs published by the aluminum producers. Eureka!

A relatively simple method was described for the determination of metallic aluminum in aluminum skimmings and dross. It was readily adapted to beryllium with little change. The sample was reacted with sodium hydroxide solution in a closed system. The evolved hydrogen gas forced an equal volume of water into a beaker. The volume of the hydrogen was determined by weighing the water. This was compared with the volume of hydrogen obtained under the same conditions at the same time from a standard sample of aluminum (since no standard beryllium was available) and the free beryllium was calculated from this ratio. (If other elements and compounds (silicon, aluminum, zinc, etc.) which also evolve gases under the same test conditions are present in more than

negligibly small amounts, suitable corrections must be made.)

There are other cases in which a method for one member of a pair of diagonally related elements can be applied to the other under appropriate conditions. One that comes immediately to mind is the spectrophotometric method for beryllium or aluminum using the ammonium salt of aurin tricarboxylic acid. Another is the determination of Na₂O in borates or silicates by titration with strong acid.

An Analogy for the Leveling Effect

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In most introductory chemistry courses the discussion of relative strengths of acids inevitably leads to a description of the leveling effect of certain solvents. Our experience has been that most students have some difficulty appreciating how variations in the relative basicity of the solvent permit determination of the relative acidity of a series of acids which are equally dissociated in a leveling solvent.

The strength of a Bronsted acid in solution is usually measured by the position of the dissociation equilibrium

HX + Solvent → Solvent -- H+ + X-

However, the basicity of the solvent (or the acidity of its conjugate acid Solvent—H⁺) clearly plays a central role in determining the magnitude of the equilibrium constant. The classic example of this effect is the relative acidity of HClO₄, HNO₃, and HCl in water and in acetic acid as solvent. All three acids are equally strong (essentially fully dissociated) in water. However, in acetic acid (a less basic solvent than water) the acid strength (measured as the extent of dissociation) increases in the order HCl < HNO₃ < HClO₄. Thus, although the three acids are not inherently equally strong, they appear equally strong in water for it is sufficiently basic to dissociate each one fully. In this context, water is described as having a "leveling" effect on the acids' strengths. We have found that the following analogy helps bring home the point.

Imagine a father and his young son (representing the more and less basic solvents, respectively) are in the kitchen fixing lunch. In front of them is a series of jars and bottles, each fitted with a screw cap, including a half-filled jar of peanut butter, a new bottlé of ketchup, and a large unopened jar of jelly. We know from experience that the father could readily dissociate each cap from its container with little difficulty. If his young son were to attempt the same feat, he would find it easy to dissociate the peanut butter jar, for it had been opened previously. He would have to struggle with the ketchup bottle, but the cap would eventually yield to his small hand. However, try as he will, he would be unable to budge the top on the jelly jar. Thus, while the father sees all the containers as easy to dissociate, the son experiences quite a range of difficulty opening them. Of course, asking the father to pull the cap off a soda pop bottle with his hare hands, like water trying to dissociate methane, would prove that even he has limits!

³ "Analysis of Aluminium and its Alloys," The Eritish Aluminium Co., London, 1941, pp. 120–121.

¹ Present address; 10411 Forest Ave., Fairfax, VA 22030.

² Brown, G. I., "Introduction to Inorganic Chemistry," Longman, London, **1974**, pp. 182–183; Puddephatt, R. J., "The Periodic Table of the Elements," Clarendon Press, Oxford, **1972**, pp. 54–55.

Equilibrium Binding and Steady-State Enzyme Kinetics

An Approach Emphasizing Their Commonality

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Two commonly recurring requirements in chemistry and molecular biology are the measurement of equilibrium binding (or dissociation) constants and the experimental determination of the two parameters which govern steady-state enzyme kinetics. The major purpose of this article is to show that these two apparently unrelated problems have a great deal in common. The equations and their error analysis can be cast in identical forms. Thus, if the solution of one problem is taught, the solution of the other is also. Various methods of data analysis are evaluated.

Steady-State Enzyme Kinetics

For a single-substrate, enzyme-catalyzed reaction the simplest model is

$$E + X \xrightarrow{h_1} EX \xrightarrow{h_{col}} E + Product$$
 (1)

where X is substrate. The steady-state approximation may be applied to EX and the conservation relation

$$[E]_0 = [E] + [EX]$$
 (2)

is valid; $[E]_0$ is the total enzyme concentration. It follows that the velocity of the reaction v $(M \, s^{-1})$ is given by

$$\frac{v}{[E]_0} = \frac{k_{\text{sat}}}{1 + \frac{K}{[X]}}$$
(3)

leading to a rectangular hyperbolic plot (Fig. 1). In eqn. (3), $k_{\rm cat}$ (s^{-1}) is the turnover number and $K = (k_{-1} + k_{\rm cat})/k_1$ is the Michaelis constant in M units. The maximum velocity (for $[X] \rightarrow \infty$) is $k_{\rm cat}$ [E]0. For any smaller value of v only a fraction of the maximum velocity f is attained

$$f = \frac{v}{k_{\text{cat}} [E]_0} \tag{4}$$

Therefore eqn. (3) may be expressed as

$$f = \frac{1}{1 + \frac{K}{|\mathbf{X}|}} \tag{5}$$

For steady-state enzyme kinetics the Michaelis constant K is not a dissociation constant; and the more elaborate the model the more obvious this statement becomes. Nevertheless, K has an important property of a dissociation constant: the larger the value of K, the larger [X] must become in order that $v \to k_{\rm cat}$ $[E]_0$.

Equilibrium Binding

The system

$$\mathbf{E} + \mathbf{X} = \mathbf{E}\mathbf{X} \tag{6}$$

may represent, for example, binding of ligand or inhibitor by an enzyme or formation of a charge-transfer complex. The dissociation constant K (in molar units M) is

$$K = \frac{[\mathbf{E}][\mathbf{X}]}{[\mathbf{E}\mathbf{X}]} \tag{7}$$

The conservation relation, expressed in terms of total con-

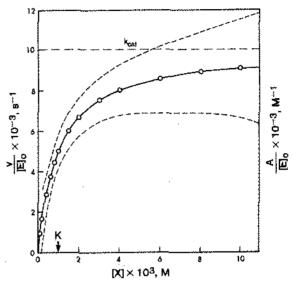


Figure 1. Rectangular hyperbolic plot of steady-state enzyme kinetic data (left ordinate). For equilibrium binding data use the right ordinate and replace $K_{\rm cat}$ by $\epsilon_{\rm EX}$. Error limits in K are shown by the dashed lines; these limits are somewhat deceptive for small (X) because of the steepness of the curve.

centration of enzyme $[E]_0$, is eqn. (2). For weak binding and large enough [X]

$$[\mathbf{X}]_0 = [\mathbf{X}] \tag{8}$$

If only EX absorbs light of a given wavelength then

$$A = \epsilon_{\text{EX}} [\text{EX}] \tag{9}$$

where A is the absorbance and $\epsilon_{\rm EX}$ the molar absorptivity. (The units of $\epsilon_{\rm EX}$ in eqn. (5) are M^{-1} since unit path length is included.) If $[{\rm EX}] \to [{\rm E}]_0$ then

$$A_0 = \epsilon_{\text{EX}} [E]_0 \tag{10}$$

and $\epsilon_{\rm EX}$ may be determined independently. However, for weak binding both K and $\epsilon_{\rm EX}$ are unknown until the performance of accurate experiments and data analysis. The above equations may be combined into the form

$$\frac{A}{[E]_0} = \frac{\epsilon_{EX}}{1 + \frac{K}{[X]}} \tag{11}$$

A plot of $A/[E]_0$ versus [X] is a rectangular hyperbola as shown in Figure 1. The fraction of total enzyme which has X bound to it, f, is

$$f = \frac{[EX]}{[E]_0} = \frac{A}{\epsilon_{EX} [E]_0}$$
 (12)

Substitution of eqn. (12) into eqn. (11) leads to eqn. (5), which was derived for steady-state kinetics.

The Common Equation

Equation (5), which leads to a rectangular hyperbolic plot whether the data are for equilibrium binding or steady-state enzyme kinetics, can be expressed conveniently in at least four other ways to obtain K:

Table 1. Type of Analysis of the Common Equations for Steady-state Enzyme Kinetics and Equilibrium Binding a

| Form of | | Form of | Type of least- | Names associated with | | |
|--|---|-----------------------|------------------|---|-----------------------|--|
| equation | Plot | Plot | squares analysis | Kinetics | Equilibrium | |
| $f = \frac{1}{1 + \frac{K}{ X }}$ | f versus [X] (Fig. 1) | rectangular hyperbola | nonlinear | | Deranleau-Neurath (2) | |
| $\frac{1}{f} = \frac{\kappa}{ X } + 1$ | $\frac{1}{I}$ versus $\frac{1}{[X]}$ (Fig. 2) | straight line | linoar . | Linewoaver-Burk (3) | Benesi-Hildebrand (4) | |
| $\frac{[X]}{f} = (X) + K$ | $\frac{[X]}{f}$ versus [X] (Fig. 3) | straight line | linear | Hanes (5) | Scott (6) | |
| $\frac{t}{[X]} = -\frac{t}{K} + \frac{1}{K}$ | $\frac{f}{[X]}$ versus $f(Fig. 4)$ | straight line | linear | Eadie-Hofstee (7~9) | Scatchard (16) | |
| | f versus log [X] (Fig. 5) | sigmoidat | nonlinear | • | Bjerrum (1) | |

⁼ Fraction of maximum velocity

$$\frac{1}{f} \approx \frac{K}{[X]} + 1 \tag{13}$$

$$\frac{[\mathbf{X}]}{f} = [\mathbf{X}] + K \tag{14}$$

$$\frac{1}{f} \approx \frac{K}{[X]} + 1 \tag{13}$$

$$\frac{[X]}{f} = [X] + K \tag{14}$$

$$\frac{f}{[X]} = -\frac{f}{K} + \frac{1}{K} \tag{15}$$

Finally, a plot of f versus $\log |X|$ may be employed (1). All of the forms of eqn. (5) (eqns. (13-15)) may be cast into the appropriate form for steady-state kinetics or equilibrium binding by substituting for f using eqn. (4) or (12). All of the methods are summarized in Table 1 and Figures 1-5. The parameters used to construct Figures 1-5 are listed in Table 2.

A more detailed discussion of errors is given below. However, at this point it is important to realize that experimental points should be as evenly spaced as possible as a function of f in order to obtain maximum accuracy in the analysis (11). There are several useful criteria to determine which is the best form to plot. The computer age has changed one of these cri-

Table 2. Parameter Values in Figures 1-5

| ···· | · · · · · · · · · · · · · · · · · · · |
|------------------------------------|---------------------------------------|
| Kinetics | Equilibria |
| K = 10 ⁻³ M | $\dot{K} = 10^{-3} M$ |
| {E}₀ = 10 ⁻⁶ M | $\{E\}_0 = 10^{-4} M$ |
| $k_{\rm cat} = 10^4 {\rm s}^{-1}$ | $\epsilon_{\rm EX} = 10^4 M^{-1}$ |

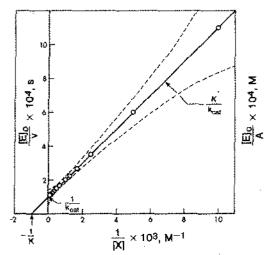


Figure 2. Lineweaver-Burk plot of steady-state enzyme kinetic results (left ordinate). For Benesi-Hildebrand plot of equilibrium binding data use right ordinate and replace k_{cat} by ϵ_{EX} . Note how the experimental points (which are spaced fairly evenly as a function of f) are jammed together near the ordinate.

teria. No longer is it necessary to cast the data into the form of a straight line equation because analysis of a curve is now just as easy. Therefore, the rectangular hyperbola, analyzed directly (see ref. (2) for an example involving equilibrium binding), and the semilog plot both deserve a higher priority. Of the two curves, the experimental points are better spaced along the curve in the semilog plot (Fig. 5 compared to Fig. 1), and the errors are shown more clearly. The semilog plot is symmetric with the value of K occurring at the inflection point, but there is no intrinsic change in the rectangular hyperbolic plot in the region of [X] = K. The subject of fitting polynomial equations to curves has been reviewed exhaustively (12), and thus its specifics will not be discussed here.

To a certain extent in the Hanes (Scott) plots and particularly in the Lineweaver-Burk (Benesi-Hildebrand) plots (Figs. 2 and 3) the experimental points are spaced unevenly. The plots are open-ended along both axes. Therefore, select data might make a superb-looking but virtually useless linear blot. The negative abscissa intercepts in Figures 2 and 3, which are also shown in many textbooks, deserve comment. They serve one purpose only: to point out that there would be advantages to having experimental points lie along the hypotenuse of a triangle. The hypotenuse (slope) and its two ends (two intercepts) would define both parameters to be determined and the self-consistency of their values. This does occur in the Eadie-Hofstee (Scatchard) plots in Figure 4. However, the negative intercepts in Figures 2 and 3 do not contribute to the analysis nor to its self-consistency.

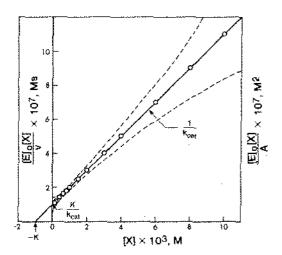


Figure 3. Hanes plot of steady-state kinetic data (left ordinate). Scott plot of equilibrium binding data (right ordinate and k_{cat} replaced by ϵ_{EX}).

Table 3. Assessment of the Relative Merits of Various Types of Plots of Steady-State Kinetic and Equilibrium Binding Data a

| | Rating (on 6-pt. | Points well | . Errors accurately and clearly | range of | ccessible expti, pts. ed along | Clear v represer of one or b and k _{oa} | ntation both of K |
|---|---------------------|----------------|---------------------------------------|----------|--------------------------------------|---|----------------------|
| Type of Plat | scale) | spaced | displayed | one exis | two axes | one | both |
| Eadle-Holslee (Scatchard) | 6 | + | + | + | + | + | + |
| Semilog (Bjerrum) | 4 | + | + | + | | + | _ |
| Rectangular hyperbola (Deranleau-Neurath) | 3 | + | +(?) | + | | | |
| Hanes (Scott) | 2 | +(?) | | | | + | |
| Lineweaver-Burk (Benesi-Hildebrand) | 1 | - | | *** | | + | |

^{*} A "+" sign indicates that the type of plot exhibits the given characteristic; a "-" sign, that it does not

The rectangular hyperbola and semilog plots (Figs. 1 and 5) show the full accessible range of experiments along one axis, but only the Eadie-Hofstee (Scatchard) plots (Fig. 4) do so along both axes. These considerations are tabulated in Table 3 which includes an evaluation of the relative merits of the different types of plots on an arbitrary scale.

Error Analysis

In the error analysis to follow we shall concentrate upon K. Errors in $\epsilon_{\rm EX}$ and $k_{\rm cat}$ become small provided f can be made sufficiently large. Errors in [X] should also be negligible.

Equation (13) may be rearranged to

$$K = [X] (1/f - 1)$$
 (16)

The differential of eqn. (13) is

$$-\frac{\mathrm{d}f}{f^2} = \frac{\mathrm{d}K}{|\mathbf{X}|} \tag{17}$$

In error analysis the - sign becomes \pm . Division by K and substitution of eqn. (16) leads to

$$\frac{\mathrm{d}K}{K} = \pm \frac{\mathrm{d}f}{f(1-f)} \tag{18}$$

For a constant error in f, one can readily show that a plot of dK/K versus f is symmetric with a minimum value at f=0.5 (see (13) and Figure 1 of ref. (11), which is based on a more complicated but essentially equivalent equation). The values

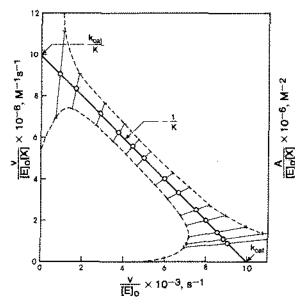


Figure 4. Eadle-Hofstee plot of steady-state kinetic experiments (left ordinate). Scatchard plot of equilibrium binding data (right ordinate, $k_{\rm cat}$ replaced by $\epsilon_{\rm EX}$ and v replaced by A in the abscissa).

of f, K, and [X] are interrelated, for example through eqn. (16). Therefore, a plot of dK/K as a function of $\log [X]$ is also readily obtained as shown in Figure 6. In addition, this plot is symmetric and is of greater practical value since $\log [X]$ is obtained prior to data analysis; f is only obtained after. The minimum error occurs where [X] = K.

Each value of dK/K is a single-point determination. In other words, if only one experiment were performed with a 2% error in f then the percent error in calculating K can be read from Figure 6. Of course the percent error in K can be reduced by performing many experiments. A good rule-of-thumb for these experiments can be deduced from Figure 6: vary [X] from K/10 to 10K. One wants to cover as broad a range of [X]

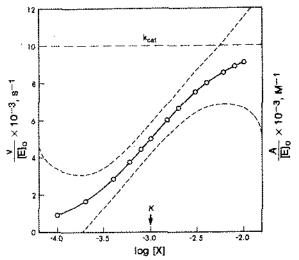


Figure 5. Semilog plot of steady-state kinetic data (left ordinate). Bjerrum plot of equilibrium binding results (right ordinate and $k_{\rm cat}$ replaced by $\epsilon_{\rm EX}$).

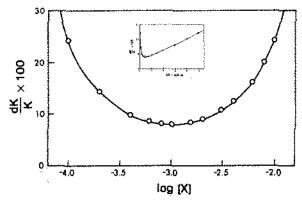


Figure 6. Relative errors in K as a function of log [X]. Inset: dK/K versus (X). It is assumed that the error in I is constant at 2% (eqn. (17)).

as possible, but there is little value in experiments performed outside these limits. This rule-of-thumb is comparable to one which states that 75% of the range of f should be covered (11,

In all of the plots (Figs. 1-5) we have shown the single-point error limits in K corresponding to 2% error in f. The error bars are vertical for Figures 1-3 and 5 and are not shown. In Figure 4, errors in f influence z- and y-values of each point equally so the error bars are symmetric with respect to the origin (11). The maximum y-axis value in Figures 1 and 5 is $k_{\rm cat}$ (or $\epsilon_{\rm EX}$) which is proportional to f. Therefore, assignment of errors on a fixed scale to individual points is readily performed. The same applies to Figure 4 along both axes which leads to the error symmetry described above. Error bars in the two reciprocal plots (Figs. 2 and 3) are misleading since the percentage error scale varies with the y-value.

Extensions

The equilibrium binding analysis is readily extended to NMR chemical shift data where $f = \delta/\delta_0$ (11). If both E and EX absorb light

$$A = \epsilon_{\mathbf{E}}[\mathbf{E}] + \epsilon_{\mathbf{E}\mathbf{X}}[\mathbf{E}\mathbf{X}] \tag{19}$$

The value of ϵ_E is determined readily in the absence of [X].

With introduction of the conservation relation (eqn. (3)) it can be shown that A should be replaced by $[A - \epsilon_{\rm E} | {\rm E}]_0]$ in Figures

Adherence to the equations for Figures 1-5 is evidence for Michaelis-Menten kinetics or 1:1 binding. The theory may be extended for effects such as positive or negative cooperativity, allostery, and multiple-binding sites. It is assumed in this paper that pH, ionic strength, and temperature are controlled accurately; otherwise apparent complications are introduced into simple systems.

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Papers are being invited for the Eighth Biennial Conference on Chemical Education which will be held August 5-10, 1984 at the University of Connecticut, under sponsorship of the Division of Chemical Education. Both oral presentations and poster sessions will be used. Oral presentations should be for 20 min or less. To be considered for inclusion in the program, a typed abstract of the proposed paper must be submitted on an official ACS abstract form, available from Dr. Robert Bohn, Department of Chemistry U-60, University of Connecticut, Storrs, CT. 06268.

General and contributed papers are solicited. Related papers will be grouped into symposia, as appropriate. Symposia scheduled include

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Deadline for receipt of complete abstracts is February 15, 1984. All abstracts are to be sent to Conrad Stanitski, Program Chair, Randolph-Macon College, Ashland, VA 23005.

A computer graphics contest will be held in conjunction with the Conference. Information is available from Don Rosentbal, Department of Chemistry, Clarkson College, Potsdam, NY 13676.

The Evaluation of Strain and Stabilization in Molecules Using Isodesmic Reactions

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Heats of Formation, $\Delta H_i(g)$ (1-3)

We commonly discuss the stability of compounds relative to the standard states of the component elements (graphite, H₂, etc., at 25°C, 1 atm pressure), which are arbitrarily assigned heats of formation of 0.0 kcal/mole.

REFERENCE:
$$mC$$
, $n/2$ H₂ $\Delta H_f \approx 0$ O_2 $CO_2 + H_2O$

$$\Delta H'_{comb}$$

$$\Delta H_f = ?$$

$$COMPOUND C_{m}H_{\pi} O_2$$

$$\Delta H_{comb}$$

Since the compound can seldom be formed directly from the elements, the heat of formation is often determined from heats of combustion: $\Delta H_{\rm f} = \Delta H'_{\rm comb} - \Delta H_{\rm comb}$. In combustion experiments the samples are usually liquids or solids. Since we are interested in *intra*molecular energies only, we must correct $\Delta H_{\rm comb}$ or $\Delta H_{\rm f}$ for the heat necessary to overcome intermolecular forces in the sample, which is the heat of vaporization (or sublimation): $\Delta H_{\rm f}({\rm g}) = \Delta H_{\rm f}(1) + \Delta H_{\rm v}$.

 $\Delta H_{\rm f}(g)$ becomes more exothermic (negative) in homologous series as the number of bonds increases; CH₄, ~17.8 kcal/mole; C_2H_6 , -20.0; C_3H_8 , -25.0, etc., yet the larger molecules are not less reactive. A similar problem exists with cyclopropane $[\Delta H_f(g) = 12.7]$ relative to benzene $[\Delta H_f(g) = 19.8 \text{ kcal/mole}]$. The less endothermic value does not reflect greater stability. This seems to imply that we can compare only isomeric compounds, but, in fact, we can consider non-isomers if we choose some other reference state. One could use values of C-C and C-H bond dissociation energies, and examine deviations of the compounds from bond additivity, but there are no unique values for BDE's, even in unstrained compounds. The energies of hypothetical models can be calculated, but the results depend on the assumptions made and the method (a few experimental thermochemical data for benzene have been interpreted as demonstrating stabilization of <20 to >40 kcal/ mole).

Isodesmic Reactions

These reactions, introduced by Pople (4), "are examples of (hypothetical) chemical changes in which there is retention of the number of honds of a given formal type (C—H, C—C, C—C) but with a change in their formal relation to one another." The following are examples. For the reaction, $\Delta H = \Sigma \Delta H_f(g)$ (Products) $-\Sigma \Delta H_f(g)$ (Reactants).

Numerous quantum and thermochemical errors cancel, so "the energies of isodesmic reactions measure deviations from the additivity of bond energies." The enthalpies of reaction (calculated from independently measured heats of formation)

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and to the Robert A. Welch Foundation (Grant E-136) for additional support.

represent the strain in cyclopropane and the resonance stabilization of benzene. We can thus relate the energy of a molecule to the energies of a few simple reference molecules.

The choice of reference molecules is significant. Comparison of $\Delta H_f(g)$ values for a series of methyl derivatives (CH₃X, X $-NO_2$, -OH, $-NH_2$, $-OCH_3$, -H, -CN, $-CO-CH_3$, and -COOH) with the corresponding ethyl derivatives shows differences of 2.3-7.9 kcal/mole, whereas the primary alkyl derivatives beginning with ethyl have quite uniform methviene increments (CH₃CH₂X versus CH₃CH₂CH₂CH₂X differences are 4.7-5.3 kcal/mole/CH₂) (2). Similarly, $\Delta H_1(g)$ of tert-butyl and the isomeric 1-butyl derivatives differ by 1.9-10.9 kcal/mole. It is therefore desirable to include in isodesmic reactions reactants and products with alkyl groups of two carbon atoms or more, and to convert reactants with primary, secondary, or tertiary functional groups to products with the same structural features. Chlorocyclopropane and chloroethylene, for example, are secondary derivatives which should be converted into the simplest secondary chloroelkane, 2-chloropropane. (Note that C-1 of chloroethylene forms only one carbon-hydrogen bond, and two carbon-carbon bonds, and, in this sense, is a secondary carbon. Similarly, 1-chloro-1-methylcyclohexane, chlorobenzene, and chloroacetylene should give tert-butyl chloride as one of the products.)

Improved methods using these principles have been proposed by Bock (5) (homodesmotic reactions), and by Dill, Greenberg, and Liebman (6) (group separation reactions), and will be used in the following discussion. We will also illustrate a related method, metathetical isodesmic reactions.

Strain Energies of Cycloalkanes

Cyclopropane consists of three methylene groups (—CH₂—) in a strained ring. In a hypothetical reaction with ethane the methylene groups will be transferred to propane:

$$\Delta H_{\rm f}({\rm g}) = 12.7 \pm 0.1 \ (3) \ 3(-20.1 \pm 0.05) \ 3(-25.0 \pm 0.1)$$

 $\Delta H({\rm reaction}) = 3(-25.0) - 12.7 - 3(-20.1) = -27.4 \ {\rm kcal/mole}$

Since the reaction is exothermic we are converting a strained reactant to an unstrained one. The strain energy is $-\Delta H(27.4 \pm 0.3 \text{ kcal/mol})$. The "conventional ring strain energy" (CRSE) derived from bond energy additivity schemes (2) is 27.5 kcal/mole.

Other cycloalkanes can be involved in similar reactions:

| | ΔH (Group | |
|-----------------------------------|-----------------------|------|
| Ring | Separation) | CRSE |
| c-C ₃ H ₈ | -27.4 ± 0.3 kcal/mole | 27.5 |
| c-C₄H ₈ | -26.4 ± 0.4 | 26.5 |
| c-C ₆ H ₁₀ | -5,a ± 0.5 | 6.2 |
| C-C ₆ H ₁₂ | 0.1 ± 0.5 | 0.0 |
| C-C7H14 | -6.0 ± 0.6 | 6.2 |
| c-C ₁₀ H ₂₀ | -12.1 ± 0.9 | 12.3 |
| <i>c</i> -C₁₅H₃e | -1.5 ± 1.2 | 1.8 |
| c-C ₁₆ H ₃₂ | -1.5 ± 1.3 | 1.8 |

In all cases $-\Delta H$ and the CRSE are in excellent agreement.

Alkenes

Energies of cycloalkenes or branched alkenes can be related to simple alkanes and alkenes (5), or to alkanes only (6). In the latter (group separation) method =CH₂ or -CH₂— of an alkene is changed to propane, -CH= becomes isobutane, and

becomes neopentane. The number of hydrogen atoms attached to a carbon atom remains unchanged. Aromatic C—H groups are similarly converted to isobutane, and substituted aromatic carbon atoms (C—X) become tert-butyl-X, by reaction with ethane.

A traditional view of alkene stability is based on heats of hydrogenation (7,8).

carbon atom of ethylene has two carbon-carbon bonds, and two C—H bonds). But even in the alkanes this would be a \sim 7.1 kcal/mole transformation. The *unique* stabilizing effects of a methyl group attached to ethylenic carbon (whether hyperconjugation or other factors) is not 7.7-5=2.7 kcal/mole, but rather, 7.7-7.1=0.6 kcal/mole, and this is the quantity that isodesmic reactions evaluate. The remaining 2.1 kcal/mole of stabilizing effect is common to alkanes and other homologous series, and cannot result from a "special" electronic interaction of the methyl group and π electron system.

Aromatic Compounds

Resonance and hyperconjugative interactions of substituents with aromatic rings is an old concept of organic chemistry (9, 10) which is more readily demonstrated for charged and

There have been many years of discussion of how the methyl group of propylene stabilizes that compound by 2.7 kcal/mole relative to ethylene. Similarly, additional methyl groups attached to the ethylenic carbons lead to additional stabilization, although cis methyls also contribute some steric destablization. The most stable alkenes are those with the least exothermic heats of hydrogenation.

To gain insight into the problem, let us consider $\Delta H_i(g)$ for alkanes: propane (-25.0 kcal/mole), butane (-30.2), 2methylpropane (-32.1), pentane (-35.0), 2-methylbutane (-36.8), and 2,2-dimethylpropane (-40.0). If we insert a methylene group into a primary C-H bond of propane or butane, $\Delta H_i(g)$ of the resulting products (hutane and pentane) are 5 kcal/mole more exothermic. In the insertion of CH₂ into the secondary C—H bond of propane, $\Delta H_f(g)$ of the product 2-methylpropane is 7.1 kcal/mole more exothermic. CH2 insertion into the tertiary C-H bond of 2-methylpropane produces 2,2-dimethylpropane, and $\Delta H_{\rm f}(g)$ becomes 7.9 kcal/mole more exothermic. This is equivalent to saying that branched alkanes have more highly exothermic values of $\Delta H_{\rm f}({
m g})$ than do the normal isomers, possibly because the former have a larger number of strong primary C-H bonds.

With alkenes each CH_2 insertion into the primary (methyl) C—H bonds in the series propene \rightarrow 1-butene \rightarrow 1-pentene changes $\Delta H_f(g)$ by the usual -5 kcal/mole. But the change from ethylene to propylene is -7.7 kcal/mole. This, however, involves CH_2 insertion into a secondary C—H bond (each

radical intermediates than for the ground states of neutral molecules. However, the heats of hydrogenation of benzene derivatives (to the cyclohexanes) vary with the substituent. This has been taken of evidence of conjugation, although the effect of methyl substitution is somewhat less than in alkenes. The cyano group appears to have a destabilizing effect.

$\Delta H(hydrogenation) \Delta H(isodesmic)$

However, enthalpies of the isodesmic reactions are essentially identical, demonstrating that neither methyl, hydroxyl, phenyl, nor cyano substituents promotes significant net stabilization, although cancelling stabilizing and destabilizing effects may be occurring.

Metathetical Isodesmic Reactions

An alternative, and somewhat more accurate treatment of aromatic reactions involves a metathetical relationship (11). Since only two reacting molecules and two product molecules are involved, the uncertainties in ΔH (reaction) are relatively small compared to group separation reactions involving many molecules.

A compound which does show stabilization is

The reaction is unfavorable (endothermic) primarily because of the stabilization of styrene.

The data demonstrate that no net stabilization occurs in cvclopropyl cyanide, 1,1-dimethylcyclopropane, or cyclopropylamine. Only in cyclopropylbenzene is there a substantial (3.0 kcal/mole) stabilizing effect.

Other Compounds

Isodesmic reactions are not a substitute for various semiempirical or ab initio methods of calculating molecular energies but may be used in conjunction with these methods (4, 6). Isodesmic reactions can, simply and conveniently, permit the estimation of strain and conjugation energies based on experimental (or calculated) heats of formation. The versatility can be further illustrated with examples of cyclic ethers, a highly branched hydrocarbon, bicyclic hydrocarbons, and acetylenes, and is limited only by the availability of thermochemical data for the compound of interest and appropriate reference compounds.

Conjugation in Cyclopropane Derivatives

The cycloheptatriene-norcaradiene equilibrium

$$\bigcap_{R}^{R} \rightleftharpoons \bigcap_{R}^{R}$$

favors the norcaradiene only when the groups R are π electron acceptor groups such as -CN or phenyl. In a 1970 article (12), Hoffmann noted the ability of cyclopropane to enter into π -type conjugation with neighboring π electron systems such as cyano, and this is believed to be involved in the stabilization of cyano-substituted norcaradienes. Others have supported the concept of cyclopropane conjugation. Dill, Greenberg, and Liebman (6) calculated (at the STO-3G level) the following stabilizations of cyclopropanes by substituents: CH3, 2.4 kcal/mole; CN, 5.8; and NH2, 2.9. With the help of some new thermochemical data we recently measured (13), we may examine isodesmic reaction enthalpies for some cyclopropane derivatives:

Conventional ring strain energies (CRSE) of the cyclic ethers (2) and the steric repulsion energy (SRE) of 2,2,4,4tetramethylpentane (2) are very well reproduced by $-\Delta H$ values of the isodesmic reactions, as are the CRSE values of spiropentane, bicyclo[3.1.0]hexane, bicyclo[1.1.0]-butane, bicyclo 4.2,0 octane, and cubane. Acetylenes are stabilized by 2 kcal/mole per alkyl group, a value much larger than that for alkenes, but much less than that implied by heats of hydrogenation.

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Recommended Format for the Periodic Table of the Elements

American Chemical Society Committee on Nomenclature K. L. Loening, Chairman

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A change in the use of the letters A and B to designate subgroups of elements in the periodic table made by publishers of periodic charts of the elements late in the 1970's brought to a head a problem in the use of these letters that has been around a long time. Although acknowledged by an occasional publication, this problem went unrecognized by the great majority of chemists. However, many did become concerned when new periodic charts appeared using A and B differently than on earlier charts, even though this change was an attempt to conform with the recommendations given in the 1970 IUPAC (International Union of Pure and Applied Chemistry) "Nomenclature of Inorganic Chemistry." The difference was noted by the Nomenclature Committee of the ACS Division of Inorganic Chemistry early in 1979 and publicized in the Division's Fall Newsletter (October 1979) where comments and suggestions to solve the problem were requested.

On behalf of the Nomenclature Committee of the ACS Division of Inorganic Chemistry, W. C. Fernelius and W. H. Powell prepared a thorough review of the problem which was presented to the ACS Committee on Nomenclature at its meeting in November 1981. The ACS Committee on Nomenciature adopted the interim position that the letters A and B should no longer be used in any way to designate element subgroups in the periodic table, recommended publication of the report as soon as possible, and asked the Nomenclature Committee of the ACS Division of Inorganic Chemistry, under the chairmanship of T. D. Coyle (Inorganic Materials Division, National Bureau of Standards, Washington, DC, 20234), to develop an alternative method for designating subgroups of elements in the periodic table. The report, "Confusion in the Periodic Table of the Elements," was published in THIS JOURNAL, 59 [6], 504 (1982), and was presented by Fernelius at the Seventh Biennial Conference on Chemical Education. August 8-12, 1982, in Stillwater, Oklahoma. In each case, comments and suggestions to solve the problem were earnestly solicited.

In still another effort to publicize the problem as widely as possible, thereby generating as many comments and suggestions for a solution as possible, the paper "The Periodic Table: Historical Road to Confusion" was presented in the symposium "The Periodic Table in Chemical Education" at the ACS National Meeting in Seattle, Washington, March 24, 1983. This symposium was co-sponsored by the ACS Divisions of Chemical Education, Chemical Information, and Inorganic Chemistry, and the ACS Committee on Nomenclature.

The comments and suggestions arising from all of the above efforts combined with opinions and suggestions from various committees and other groups produced a large number and variety of possible schemes for designating subgroups of elements in the periodic table. Fortunately, for the most part they could be grouped into just a few hasic formats: those that were purely arbitrary; those distinguishing between main, representative, or characteristic elements and transition elements: and those reflecting electronic structure. Accordingly, four periodic table formats were considered thoroughly at a meeting of the Nomenclature Committee of the ACS Division of Inorganic Chemistry in Washington, D.C., on August 29, 1983; and the one shown below was selected for recommendation to the ACS Committee on Nomenclature as the official periodic table format of the American Chemical Society. The Nomenclature Committee of the ACS Division of Inorganic Chemistry was satisfied that this recommended format met all the minimum requirements for subgroup designations. It provides an unequivocal designation for each subgroup in the 18-column periodic table. In addition, it distinguishes the "d-block" elements and provides a means for identifying the "f-block" elements. There is a notational relationship with the Mendeleev subgroups, similar to the former "A" and "B" subgroups, e.g., former subgroups 3A and 3B are now 3d and 13; the same units digit is retained. Further, this recommended format is fully compatible with the current tentative position of the IUPAC Commission on Nomenclature of Inorganic Chemistry.

On November 14, 1983, the ACS Committee on Nomenclature concurred with the Nomenclature Committee of the ACS Division of Inorganic Chemistry by approving the periodic table format shown below.

Recommended Format for the Periodic Table of the Elements

| 1 | 2 | 3d | 4 d | 5d | 6d | 7d | 8d | 9d | 10d | 11 d | 12d | 13 | 14 | 15 | 18 | 17 | 18 |
|----|----|--------|------------|----|----|-----|----|----|-----|-------------|-----|----|----|----|----|----|----|
| н | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | В | С | N | Q | F. | Ne |
| Na | Mg | | | | | | | | | | | Αi | Si | Р | S | CI | Ar |
| ĸ | Ca | Sc | TI | ٧ | Cr | Mrs | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Яb | Sr | Υ | Zr | Nb | Mo | To | Ru | Rh | Pd | Ag | Cd | ln | Sn | Sb | Te | 1 | Χe |
| Cs | Ba | La* | Hf | Ta | W | Re | Os | lr | Pt | Au | Hg | TI | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac** | | | | | | | | | • | | | | | | |
| 3ŧ | | - *Ce | Pr | Nd | Pm | Sm | Eв | Gd | Τb | Dy | Но | Er | Tm | Yb | Łu | | |
| Ŭ. | | └ ••Th | Pα | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | | |

Atomic Volume and Allotropy of the Elements

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The periodic law of D. I. Mendeleev is one of the great organizing themes of science. Mendeleev (1) considered four aspects of matter which represent measurable properties of the elements and their compounds: (1) isomorphism, (2) the relation of specific volumes, (3) the composition of salts and (4) the relations of the atomic weights of the elements. Thus, specific volume and its components of density (g cm⁻³) and atomic volume (cm³ mol⁻¹) were central to the development of the periodic law.

The density and the atomic volume of the elements have been surveyed numerous times over the past century. However, they have not been surveyed to take account of the ap-

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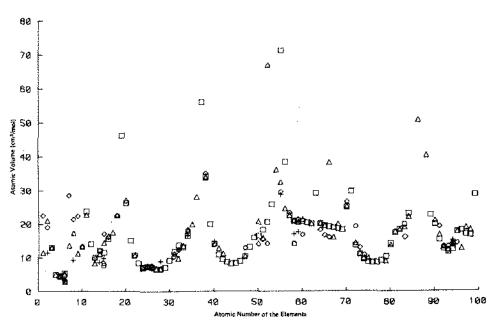


Figure 1. Atomic volumes of the allotropic forms of the elements.

Allotrope stable at room temperature and atmospheric pressure.

A lifetrope stable at lowest temperature and/or pressure. (For elements which do not have an allotrope stable at a temperature lower than room temperature, the symbol represents the next allotrope of the element at increasing temperature and/or pressure.)

♦ + \(\Delta \) \(\Omega \) Allotropes in order of increasing temperature and/or pressure.

The atomic volumes are graphically represented for the allotropes of elements whose structures have been studied.

The difference in atomic volume for different alfotropes of an element on the graph does not represent a change in atomic volume due to a structural transition. The symbol represents the atomic volume of an element's alfotrope under whatever conditions it was studied. Metastable alfotropes, alfotropes formed by unusual means (e.g., thin films), and alfotropes whose proper positions on the element's phase diagram are not clear are the last alfotropes to be represented on the graph for a given element.

Only the most commonly known allotropes of sulfur, boron, and phosphorus are represented, because of the large number of allotropes for these elements.

The radon atomic volume is for the liquid at its normal boiling point.

plication of modern X-ray methods to the structure of the elements and to phase transformations as a function of temperature and pressure reported over the past 15 years.

The extensive summary of X-ray data of Donnay and Ondick (2) contains a wealth of material. It was the primary reference for the present survey. The present survey started out to include detailed descriptions of all allotropic forms of the elements. This proved to be much too ambitious an undertaking. Thus the present paper presents what are believed to be reliable values of the atomic volume of the form of the solid element thermodynamically stable at 1 atm and room temperature (usually 298K). Exceptions, such as the low-boiling gaseous elements, are noted. In addition the allotropic forms of the elements under other conditions of temperature and pressure are noted and referenced. Other references, thought useful, were Donohue's fine book (3) on the structure

of the elements and Sanderson's book (4) on the periodic law. The present paper is an updating of some of the information in those books.

The structure, phase transitions, and atomic volumes of the various families of the periodic table are discussed below. A table and a graph (Fig. 1) of the atomic volumes at one atmosphere and room temperature accompany the discussion. In addition, the graph also shows values of the atomic volume of allotropic forms of the elements stable at other temperatures and pressures

The Characteristic Elements

The Alkali Metals, Group IA

The crystal structure of the alkali metals at room temperature and atmospheric pressure is a body-centered cubic crystal. The members of this family show large increases in their atomic volume as the atomic number of each successive member increases. This trend is common to all the other elemental groups to varying extents.

Cesium not only has the largest atomic volume of the alkali family but also the largest atomic volume of any element. Incomplete structural transitions occur in both lithium and sodium at low temperatures from their bodycentered cubic structure to a hexagonal close-packed structure (8, 9). Also, at low tem-

perature lithium undergoes a strain-induced transition from the body-centered cubic crystal to a face-centered cubic crystal (8). All three transitions show an increase in atomic volume for the lower temperature structure. At room temperature, three pressure-dependent transitions occur in cesium. As the pressure for each transition increases, there is an associated decrease in atomic volume for the higher pressure structure (13).

If enough francium is ever isolated to study its structure as a solid, the atomic volume found will probably be only slightly more than cesium's due to the lanthanide contraction.

The Alkaline Earth Metals, Group IIA

The alkaline earth metals are all solids at room temperature and atmospheric pressure. Under the above conditions three different crystal structures are found among the alkaline earth metals. Beryllium and magnesium are hexagonal close-packed crystals, calcium and strontium are face-centered cubic crystals, and barium and radium are body-centered cubic crystals. The periodic trend for the alkaline metals is similar to the trend in the alkali metals but the increase in atomic volume is not so great as in the alkali metals. Radium is affected by the lanthanide contraction, causing its atomic volume to be only slightly larger than barium's.

Beryllium, calcium and strontium all undergo temperature-dependent transitions to a body-centered cubic crystal. In beryllium this transition occurs with a decrease in atomic volume (3). An intermediate transition occurs in strontium before the body-centered cubic crystal is reached. From experience with calcium this hexagonal close-packed structure may be impurity-stabilized and therefore not a valid allotrope (3).

Barium may undergo up to four pressure-dependent transitions at room temperature (3, 12). The lowest pressure-dependent transition from the body-centered cubic crystal to a hexagonal structure is the only verified change.

Group IIIA

The members of Group IIIA all are solids at room temperature and atmospheric pressure. This paper will discuss only the allotropic highlights of the members of this group, because in this group there is no clear pattern of allotropy.

Boron's allotropy is both complicated and confusing. As many as sixteen distinct allotropes are reported; however, there is evidence that fourteen of these are actually boron-rich borohydride compounds (3, 66). Included on the graph are the four allotropes of boron most completely structurally identified. Two allotropes of aluminum normally exist, one of these is pressure-dependent. But as a thin film, aluminum has exhibited two other crystal structures (3, 24). There are five allotropes of gallium, only one of indium, and two of thallium. The periodic trend of increasing atomic volume as the atomic number increases is continued in Group IIIA. Boron has the smallest atomic volume of any element stable at room temperature and atmospheric pressure.

Group IVA

The members of Group IVA all are solids at room temperature and atmospheric pressure.

Seven (or possibly eight) allotropes of carbon exist (3). They can be divided into four groups: 1) graphites, 2) diamonds, 3) synthetic forms², and 4) metallic forms. Two types of diamonds exist; the most common form is the cubic variety, a second, so-called hexagonal type is found in some meteor craters (29). The next three members of this group, silicon, germanium, and tin, are isostructural with cubic diamond, at room temperature and atmospheric pressure. They each undergo a pressure-dependent transition to a crystal form that is metallic. Silicon and germanium each have two other pressure-dependent allotropes, while tin has only one other pressure-dependent allotrope. There are two allotropes of lead, one is stable only at high pressure (31).

The same periodic trend present in the last three groups is true within Group IV. Diamond, which is metastable at room temperature and atmospheric pressure, has the lowest atomic volume of any elemental allotrope.

From carbon's phase diagram and by analogy with the high-pressure behavior of silicon and germanium, a high-pressure metallic allotrope of carbon with an atomic volume 15-20% less than diamond has been postulated (3). In 1979 a new allotrope of carbon was formed that fits the postulated characteristic of lower atomic volume (27). This author was able to determine neither whether this is the postulated metallic allotrope or an entirely new allotrope nor under what conditions it is stable.

Many of the elements in Groups VA-VIIA are found as molecular species. Because of their multiatomic nature these elements crystallize differently from the monatomic elements. Instead of single atoms forming the structural basis of the element's crystal lattice, the molecular species of the element is substituted. This affects the molar volume calculated; for example, instead of a single atom's being in a crystal's unit cell, there are two or more atoms occupying the same site in the unit cell. So, to be consistent with the definition of a mole, all the molar volumes of these elements are reduced to atomic volumes for this paper. The molar volumes of these elements are presented parenthetically next to their atomic volume value on the table.

Group VA

Nitrogen is the only member of Group VA that is not a solid at room temperature and atmospheric pressure. All but one of the members of Group VA can exist as a polyatomic molecular species. Many of these molecules form the structural basis of the crystal allotropes of their elements. Nitrogen exists and crystallizes as diatomic molecules. Of the five molecular species of phosphorus P, P2, P4, P8, and P9, the molecule P2 is found only in the gas phase (35). The two so-called white phosphorus allotropes are composed of P4 molecules. The structure of Hittorf's phosphorus is based on a cagelike configuration of P_8 and P_9 molecules (3, 35). The remaining phosphorus allotropes are structurally based on a monatomic molecule. Tetratomic molecules of arsenic and antimony exist, but this molecular species has not been confirmed to be the structural basis of any of their allotropes though it is thought to be the structural basis of one uncharacterized arsenic solid (3, 39).

Three allotropes of nitrogen exist at low temperatures; two of them are stable at atmospheric pressure, and the third is found only at high pressure. The allotropy of phosphorus is too complex to be eovered adequately in this paper. Readers interested in the subject should consult Corbrige's book (36), which diagrams the known allotropes of phosphorus and the relationship among them. Mellor (35) provides an excellent review of the crystal structures of the phosphorus allotropes.

Arsenic, antimony, and bismuth all have the same type of rhombohedral crystal at room temperature and atmospheric pressure. In addition, arsenic has two or three other crystal allotropes. Two more allotropes of antimony and as many as six allotropes of bismuth exist at high pressure (12).

Group VA does not follow fully the established periodic trend, because nitrogen's atomic volume is greater than that of the most thermodynamically stable allotrope of phosphorus, a black phosphorus. Otherwise, from phosphorus to bismuth the periodic trend is followed.³

² By synthetic are meant those allotropes of carbon that are non-metallic, manmade, and that have not been found in nature.

 $^{^3}$ To change a monatomic atomic volume to the corresponding polyatomic value, multiply the monatomic atomic volume by the number of atoms in the element's molecule. Example: for α white phosphorus, which is structurally based on the P₄ molecule, polyatomic equivalent molar volume = $4 \times 17.02 = 68.08$.

Group VIA

At room temperature and atmospheric pressure, oxygen, a gas, is the only member of this group that is not a solid. With the exception of tellurium and polonium, all the members of this group have polyatomic species which form crystalline solids. There are two molecular species of oxygen, O_2 and O_3 . No crystal forms of O_3 have been identified; its molar volume presented here is based on density measurements (3). The observed molecular species of sulfur, are S_n where n=1,2,3,4,5,6,7,8,9,10,11,12,18, or <math>20(3,44). Those molecules of S_5 and higher are found in crystalline sulfur. The S_8 molecule, a ring, is the structural basis of the three common forms of sulfur. Selenium also forms crystals with this molecular species. Because the eight-membered ring allotropes of sulfur are the most common forms, only their atomic volumes are included on the graph.

Approximately 50 allotropes of sulfur are claimed. The two papers by Meyer (44, 45) do an excellent job of putting the allotropy of sulfur into proper perspective. Four allotropes of diatomic oxygen exist; the fourth was found recently and is stable only at room temperature and high pressure (41). There are possibly eight allotropes of selenium. Two Ses rings, one monotomic allotrope, and one thin-film allotrope have been confirmed, and two other thin-film and two pressure-dependent allotropes may exist (3, 12). Tellurium has three definite allotropes, a fourth has been claimed, and more may be present at very high pressures (3, 12). Only two allotropes of polonium are known.

As happened in group VA with nitrogen, the atomic volume of oxygen is greater than that of the next two members of its group, but from sulfur on, the periodic trend is consistent with the established trend. In terms of molar volume, the S_{20} aliotrope of sulfur has the largest molar volume of any elemental allotrope.

Group VIIA

Fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid at room temperature and atmospheric pressure. All are diatomic molecules. The low-temperature allotrope of fluorine is a monoclinic crystal, and the high temperature allotrope is a cubic crystal. An orthorhombic crystal is the only allotropic form of both chlorine and bromine. Iodine has this same structure, but there is evidence of a second high-pressure metallic allotrope (12). Astatine is so shortlived that its structure has not been studied yet. When this group's molar volumes are compared, no change is seen from the established periodic trend.

Group VIIIA

The noble elements all are gases at room temperature and atmospheric pressure. Both helium isutopes exist in the same three crystal forms. The major difference between them is that the temperature and pressure range for the existence of the body-centered cubic crystal is greater in ³He than in ⁴He (49). The lowest-pressure form is a body-centered cubic crystal; at higher pressures helium is a hexagonal close-packed crystal; and at very high pressures, its crystal structure is a cubic close-packed crystal (51).

Neon and argon each have two allotropes. For each, the first allotrope is a face-centered cubic crystal, stable at low temperatures, which at a higher temperature transforms to the second allotrope, a hexagonal crystal (3, 53). Krypton and xenon each have a single allotrope, a face-centered cubic crystal. Plenty of radon has been made, but as yet no one has determined its crystal structure.

Helium has a larger atomic volume than does neon. The cause for this anomaly is not clear but is probably related to helium's unusual properties. Otherwise, the established periodic trend holds true for Group VIIIA.

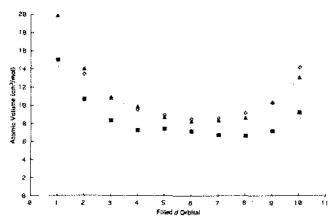


Figure 2. Atomic volumes of the transition elements

- Transition elements filling a 3d orbital.
- Transition elements filling a 4d orbital.
- Transition elements filling a 5d orbital.

The atomic volumes of the transition elements at room temperature and atmospheric pressure are graphically represented on a expanded scale.

The Transition Elements

Mercury, a liquid at room temperature and atmospheric pressure, is the only transition element not a solid under those conditions. Because the transition elements cover a number of groups, only their allotropic trends will be emphasized. With few exceptions, the same crystal structures exist at room temperature and atmospheric pressure for all the members of a given group (column)4 among the transition elements. Group VIIB, headed by manganese, and the two columns of Group VIIIB headed by iron and cobalt are the major exceptions to the trend. These three elements at room temperature and atmospheric pressure have a common crystal structure which is different from the crystal forms of the remaining members of their respective groups. Under different conditions, however, they will exhibit the crystal structure which is characteristic of their individual groups at room temperature and atmospheric pressure. At 237.25K and atmospheric pressure, mercury crystallizes into the same crystal system, hut not with the same lattice symmetry, as the other members of Group IIB. Actinium's allotrope is structurally different from allotropes of the rest of Group IIIB. It is believed that actinium has been studied only at room temperature. There are many instances in which transition elements in the same column undergo similar structural transformations.

The periodic trend for atomic volume among the transition elements is essentially the same as for the non-transition groups discussed above. There is still an increase down a transition column, but the atomic volume of the last two members of a transition column are nearly the same (4) (Fig. 2). This may be due to the affect of the lanthanide contraction on the third row of transition elements. It appears that hafnium and gold are more affected by the lanthanide contraction, which accounts for their decrease in atomic volume compared to the elements just above them.

In general, thin-film allotropes of transition elements have higher atomic volumes than do bulk amounts of these elements (3).

Many times when the elements are discussed there is an argument as to which element is the densest. Since atomic volume and density are mathematically related, such a discussion is appropriate. Using Donohue's method of averaging all reasonable lattice constants for a given crystal form of an element, osmium is the densest element (3). Iridium is only

⁴ Our use of the term "column" is appropriate for the discussion since Group VIIIB covers three columns of transition elements.

| | | Atomic | B | | of Allotropes | | |
|------------------------------|------------------|--|---|--------------------------|-----------------------|--------------|------------------------------|
| Eiërnent | Atomic Number | Volume V/cm³mol ^{−1} | Density ^a p/g cm ³ | Temperature Dependent | Pressure Depondent | Thin Film | Reference |
| | | ······································ | | | Coporidon | | |
| lydrogen (H ₂) | . 1 | 11.42 (22.85) ^d | 0.0882 | 1 | | | 2, 3, 6, 7 |
| euterium (D ₂) c | 1 | 9.87 (19.74) | 0.2040 | 1 | | | 2, 3, 6, 7 |
| ithlum | 3 | 13.02 | 0,53 | 1 | 1 | | 2, 3, 8, 9 |
| Bodium | 11 | 23.78 | 0.97 | 1 | | | 2, 3, 9, 10, 11 |
| otassium | 19 | 45,94 | 0.85 | | 1 | | 2, 3, 12 |
| tubidium | 37 | 55.76 | 1.53 | | 1(1) | | 2, 3, 12 |
| Cesium | 55 | 70.94 | 1.87 | | 3(1) | | 2, 3, 12, 13, 14 |
| rancium | 87 | * * * | | | | | |
| Berytlium 🗎 🗀 | 4 | 4.85 | 1.86 | 1 | (1) | | 2, 3, 12, 15 |
| dagnesium | 12 | 14.00 | 1,74 | | (1) | | 3, 12 |
| Calcium | 20 | 26.20 | 1.53 | 1 | (2) | | 2, 3, 12 |
| Strontium | 38 | 33.94 | 2.58 | 2 | | | 2, S |
| larium | 56 | 38.16 | 3,60 | | 1(3) | | 2, 3, 12 |
| tadium | 88 | 41.09 | 5.50 | | | | 3 |
| Poron | 5 | 4.39 | 2,46 | 3(12) | | | 2, 3, 16, 17, 18, 19, 20, 21 |
| lluminum | 13 | 10.00 | 2,70 | 1 | | 2 | 2, 3, 22, 23, 24 |
| ellum | 31 | 11.803 | 5.91 | 2 | 2 | | 2, 22, 14, 25 |
| nd i um | 49 | 15.78 | 7.29 | | | | 2, 3 |
| hallium | 81 | 17.22 | 11.87 | 1 | | | 2, 3 |
| Carbon e | 6 | 5.29 | 2.27 | 2 | 5 | í | 2, 3, 26, 27, 28 |
| Diamond | 6 | 3,42 | 3,51 | | 2 | | 2, 3, 28, 29 |
| Silicon | 14 | 12.06 | 2.33 | | 3 | | 2, 3, 30 |
| Germanium | 32 | 13.63 | 5.32 | | 2 | 1 | 2, 3 |
| in | 50 | 16.29 | 7.28 | 1 | ī | • | 2, 3 |
| ead | 82 | 18.26 | 11.34 | • | ń | | 2, 3, 31 |
| Nitrogen(N ₂) | 7 | 13.54 (27.07) | 1.03 | 2 | | | 2, 3, 32, 33, 34 |
| | , | 13.34 (21.01) | 1.03 | ٤ | | | 2, 0, 02, 00, 04 |
| White | 46 | 47 00 (60 00) | 1.00 | 3(?) | | | 2, 3, 35, 36, 37 |
| Phosphorus(P ₄) | 15 | 17.02 (68,08) | 1.82 | 3(:) | | | 2, 0, 00, 00, 07 |
| Black | 4 15 | 4 6 4 4 | 2 70 | | 3(?) | | |
| hosphorus | 15 | 11.44 | 2.70 | 1(1) | | | 2, 3, 12, 38, 39 |
| rsenic | 33 | 12.95 | 5.79 | 1(1) | (1) 2 | | 2, 3, 12, 36, 35 |
| atimony | 51 | 18.19 | 6.69 | | | | |
| ismuth | 83 | 21.31 | 9.80 | | 2(4) | | 2, 3, 12, 40 |
|)xygen(O ₂) | 8 | 17.36 (34.72) | 1.53 | 2 | (1) | | 2, 3, 41, 42, 43 |
| Zone(O ₃) | 8 - | 9.26 (27.78) | 1.73 | | | | 3 |
| Sulfur S ₈ | 16 | 15.53 (124.20) | 2,06 | (?) | (?) | | 2, 3, 44, 45 |
| Selenium | 34 | 16.42 | 4.80 | 2 | 2 | 1(2) | 2, 33 |
| ellurium | 52 | 20.46 | 6:24 | | 2(1+) | | 2, 3, 46, 47 |
| olonium | 84 | ~22.97 | ~9.1 | 1 | | | 2, 3 |
| luorine(F ₂) | 9 | 11,20 (22,39) | 1.70 | 1 | | | 2, 3, 34, 48 |
| hlorine(Cl ₂) | 17 | 17.39 (34.77) | 2.03 | | | | 2, 3 |
| romine(Br ₂) | 35 | 19.78 (39.56) | 4.05 | | | | 2, 3 |
| dine(l ₂) | 53 | 25.72 (51.43) | 4.93 | | (1) | | 3, 12 |
| statine | 85 | • • • | 1.4.4 | | · | | , |
| elium | 2 | 21.00 | | | | | 2, 3, 12, 49, 50, 51, 52 |
| eon | 10 | 13.23 | 1.52 | 1 | 2 | | 2, 3, 53 |
| eon rgon | 18 | 22.56 | 1.77 | 1 | - | | 2, 3, 38 |
| _ | 36 | 27.99 | 2,99 | , | | | 3 |
| rypton enon | 54 | 35.92 | 3.65 | | | | 3 |
| · . | 54 86 | 50.50 | | | | | 4 |
| adon | | | 2.00 | | | | |
| candium | 21 | 15.00 | 2.99 | | | | 2, 3 |
| ttrium | 39 | 19.88 | 4,472 | ^ | | | 2, 3 |
| anthanum' | 57 | 22,386 | 6.205 | 2 | | | 2, 3 |
| ctinium [*] | 89 | ~22.554 | 10.07 | | | | 2, 3 |
| utetium ^f | 71 | 17.78 | 9.84 | | (1) | | 2, 3, 12 |
| awrencium [#] | 103 | | | | | | |
| tenium | 22 | 10.64 | 4.50 | . 1 | 1 | | 2, 3 |
| rconium | 40 | 14.024 | 6.50 | 1 | 1 | 1 | 2, 3, 54 |
| afnium | 72 | 13.44 | 13,276 | 1 | (1) | 1 | 2, 3, 12, 54 |
| anadium | 23 | 8.32 | 8.12 | , | 3.77 | - | 2, 3 |
| anadium iobium | 41 | 10.83 | 8.58 | | | 1 | 2, 3, 55 |
| | 73 | 10.85 | 18.68 | | | 2 | 2, 3, 54, 58 |
| entalum | | | | | | | |
| hromium | 24 | 7.23 | 7.19 | | | 1 | 2, 3 |
| lolytidenum | 42 | 9.38 | 10.22 | 4 | | 1 | 2, 3, 54 2, 3, 54 |
| ungsten | 74 | 9.47 | 19.25 | 1 | | 1 | 2, 3, 54 |
| апдалезе | 25 | 7,35 | 7.47 | 3 | | | 2, 3 |
| echnetium | 43 | ~8.63 | 11.46 | | | | 2, 3, 57 |
| henlum | 75 | 8.86 | 20.56 | | | 1 | 2, 3, 54 |

Atomic Volumes and Densities of the Solid Elements at Atmospheric Pressure and Room Temperature, A.P.S

| | | Apornic | | Number | at Allatropes | | |
|--------------|--------|-----------------------|----------------------|-------------|---------------|------|--------------|
| | Atomic | Volume | Density* | Temperature | Pressure | Thin | |
| Element | Number | √/cm³mut [†] | $ ho/{ m g~cm^{-3}}$ | Dependent | Dependent | Film | Reference |
| Iron | 26 | 7.09 | 7.87 | 2 | t | | 2, 3, 12 |
| Ruthenium | 44 | 8.17 | 12.44 | | | | 2, 3 |
| Osmium | 76 | 8.42 | 22.58 | | | | 2, 3 |
| Cobalt | 27 | 6,67 | 8.83 | í | | | 2, 3 |
| Rhodium | 45 | 8.28 | 12.42 | • | | | 2, 3 |
| Iridium | 77 | 8.52 | 22.58 | | (1) | | 2, 3, 12 |
| Nickel | 28 | 6.59 | 8.91 | 1(2) | , , | | 2, 3 |
| Palladium | 46 | 8.56 | 12.00 | 1(2) | | | 2, 3 |
| Platinum | 78 | 9.09 | 21.46 | | | | 2, 3 |
| | | | 8.94 | | | ŧ | 2, 3 |
| Copper | 29 | 7.11 | | (1) | | 1 | 2, 3 |
| Silver | 47 | 10.27 | 10.51 | (1) | | 1 | 2, 3 |
| Gold | 79 | 10.21 | 19.28 | | | ı | |
| Zinc | 30 | 9,16 | 7.14 | | | | 2, 3 |
| Cadmium | 48 | 13.00 | 8.65 | | (1) | | 2, 3, 12 |
| Mercury | 80 | 14,09 | 14.24 | | 3(1) | | 2, 3, 58 |
| Cerium | 58 | 20.69 | 6.77 | 2 | 3(1) | | 2, 3, 12, 59 |
| Praseodymium | 59 | 20,60 | 6.77 | 2 | 1(2) | | 2, 8, 12 |
| Neodymium | 60 | 20.58 | 7.01 | 1 | 1 | | 3 |
| Promethium | 61 | 20,23 | 7.16 | (1) | 1 | (1) | 3 |
| Samarium | 62 | 19,98 | 7.50 | | (1) | | 2, 3, 12 |
| Europium | 63 | 28.97 | 5.25 | | | | 2, 3 |
| Gadolinium | 84 | 19.90 | 7.90 | 1 | 1 | | 3 |
| Terbium | 65 | 19,30 | 8.24 | ‡(1) | 7 | | 3, <i>60</i> |
| Dysproslum | 68 | 19,01 | 8.55 | 1 | 1 | | 3, 61 |
| Holmium | 67 | 18.74 | 8.80 | | 1 | | 3 |
| Erbium | 66 | 18.46 | 9.06 | | (1) | 1 | 3, 12, 62 |
| Thulium | 69 | 19.13 | 9.31 | | (1) | | 3, 12 |
| Ytterbium | 70 | 24.64 | 6.97 | 2 | (1) | | 3, 12 |
| Thorium | 90 | 19.80 | 11.72 | 4 | (1) | | 2, 3, 12 |
| Protactinium | 91 | 15.18 | 12.22 | 1 | 1 | | 3 |
| Uranium | 92 | 12.49 | 19,05 | 2 | | | 3 |
| Neptunium | 63 | 11.59 | 20,45 | 2 | | | 2, 3 |
| Plutonium | 94 | 12.29 | 19.86 | 5 | | | 2, 3 |
| Americium | 85 | 17.63 | 13.78 | ij | 1 | | 3, <i>63</i> |
| Curium | 96 | 18.05 | 13.68 | | | 1 | 3 |
| Berkelium | 97 | 16,84 | 14.67 | | | 1 | 3 |
| Californium | 98 | 16.50 | 15.10 | 1 | | | 64 |
| Einsteinium | 99 | 28.52 | 8.88 | | | | <i>65</i> |
| Fermium | 100 | | | | | | |
| Mendelevium | 101 | | | | | | |
| Nobeltum | 102 | | | | | | |

^{*} For elements that are gases and tiquids at room temperature the data are for the element's solid altotrope existing at the lowest temperature.

slightly less dense than osmium. These conclusions hold true for the average of the post-1955 measurements, as well as the pre-1955 measurements. The post-1955 measurements appear to be much more accurate than the pre-1955 values. The density calculated from Donohue's averaged lattice constants at 293K is ρ/g cm⁻³ = 22.58 for osmium and ρ/g cm⁻³ = 22.56 for iridium (3).⁵

Inner Transition Elements

All the lanthanides and actinides that have been studied are solids at room temperature and atmospheric pressure. A few lanthanides and actinides have unusual crystal structures. Cerium and praseodymium exhibit a collapsed, face-centered cubic crystal under high pressure (3, 12). This crystal is structurally identical to the normal face-centered crystal from which it was formed. It is considered a separate allotrope be-

cause the transition to the collapsed form is marked by a sudden decrease in atomic volume. Other unusual crystal structures among several inner transition elements are collapsed hexagonal close-packed and rhombohedral structures (3); these crystals retain the same space group as an uncollapsed crystal, but the number of atoms in the unit cell is double and triple the normal value, respectively. In some actinides and lanthanides these structures are stable at room temperature and atmospheric pressure. Lanthanum is the exception; it is the only transition element which exhibits such a structure only at high temperature.

The filling of an / suborbital has a very profound effect on

⁶ The atomic weights used in any calculations were taken from the IUPAC values of 1977 (5).

C Deuterium allotropes are not included on the graph.

[.] The polyatomic equivalent atomic (motar) volume was calculated for the polyatomic elements, and is presented perenthetically next to their atomic volume.

^{*} Synthetic allotropes of carbon have molar volumes similar to diamond.

Lantharum, actinium, tuteltum, and lawrencium are placed at this point in the table because their last added electron is thought to be a d'electron.

[®] Usually only the atomic volume and density on one allotrope of an element is reprosented in the table. However, additional values were included for elements that have two or more well-known allotropes. The discussion in the text is based on the numerical values listed in the table.

The number of other, confirmed temperature-dependent, pressure-dependent, and thin-film alliotropes is indicated in the table. The number in parentheses is the number of proposed allotropes of the element, it is suspected that a more detailed study of the proposed allotropes would show that many of them are one of the confirmed allotropes.

⁶ The calculated density published in Ref. (2) for iridium is 22.65 ρ/g cm⁻³. From the lattice constants given for this value, iridium's density is calculated to be 22.57 ρ/g cm⁻³. The cause for the difference is not known.

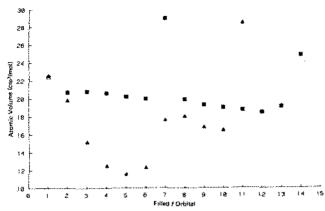


Figure 3. Atomic volumes of the inner transition elements.

- Inner transition elements filling a 4f orbital.
- ▲ Inner transition elements filling a 5f orbital.

The atomic volumes of the inner transition elements at room temperature and atmospheric pressure are graphically represented on a expanded scale.

the periodic trend in atomic volume. As was said earlier in the discussions of Group II and of the transition elements, the lanthanide contraction appears to be the cause for the small increase in atomic volume for an element which it affects, in comparison with a preceding unaffected element. The best example of this was the small increase in atomic volume for the third row of transition elements over the second row. The actinide elements are filling the second f suborbital, and with this, there occurs a second contraction of atomic radius, a so-called actinide contraction (67). This probably leads the actinide elements to have smaller atomic volumes than their corresponding lanthanides (Fig. 3). Einsteinium has a higher atomic volume than holmium, but so far its only allotrope has beeu found in thin films, it may well be that as with the transition elements, bulk amounts of einsteinium will have a smaller atomic volume.

In the progression across a lanthanide or actinide row, the stability afforded by filling the f^7 and f^{14} orbital is seen (4). Europium, vtterbium, and americium all show large increases in atomic volume over their surrounding elements. The four actinides following americium do not show a large decrease in atomic volume as expected. The reason for this is unclear. Nobelium may continue the trend since it fills the f14 orbital.

The last three actinides, fermium, mendelevium, and nobelium have not yet been structurally studied.

Conclusion

We have seen that, in the majority of groups (columns), as the atomic number increases, so does the atomic volume. Helium, which has a larger atomic volume than neon, is the only significant break from the periodic trend. The cause of this might have something to do with helium's other unusual physical properties. Two other important breaks from the periodic trend occur in the third row of the transition elements with hafnium and gold; the reason, it is believed, is that the lanthanide contraction strongly limits the expected increase in atomic volume because of its effect on an element's atomic radius (4). With the actinides filling the 5f orbital a second atomic radius contraction occurs (62). This accounts for the reversal of the periodic trend, with the actinides having smaller atomic volumes than their corresponding lanthanides. It will be interesting to see if the elements following the actinides will also show smaller atomic volumes than their next lower corresponding elements. Looking at where the lanthanide contraction has the most effect, it appears that the fourth row of transition elements will be the most affected by the actinide contraction. The instability of these elements may prevent their structural examination. The best hope for seeing if the reversal in atomic volume continues should be with the

elements that are to be found in the islands of stability (68).

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Some Opportunities for Reinforcement of Learning Among the Subdisciplines of Chemistry

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It is a common lament among physical chemists that students, even at the graduate level, are inadequately prepared in mathematics. The problem resides less in the lack of formal courses than in a failure to develop a "feel" for expressing chemical situations in mathematical language. A related problem is the tendency of students to compartmentalize their studies into quarter or semester packages; much of what was "learned" seems unavailable in later courses. Students frequently express resentment when asked to apply simple acid-base theory from the first-year course to estimation of the charge on a protein molecule in a biochemistry course. Much of this may be inevitable, but the faculty must not encourage it; we must search continually for ways to utilize material from an earlier course in a later one and to reward the students who are successful in carrying over material from one course to another.

There are many examples of topics taught in different contexts using different symbols but where the mathematical formalism is the same. One which has been frequently noted involves the Bouguer-Beer law in analytical chemistry and the first-order rate equation in physical (1). Presented here are some additional cases of equations of similar form which occur in quite different situations and which have been less widely discussed. Pointing out the similarity, which may not otherwise occur to the student, may assist in his effort to relate physical situations to mathematical form.

Hyperbolic Approach Toward Saturation

Michaelis-Menten Kinetics. For many enzymic reactions, the graph of initial velocity, v, versus substrate concentration [S], at constant enzyme level is a hyperbola as shown in Figure 1. This curve is the locus of the Michaelis-Menten equation, which is generally seen (2) in the form

$$v = \frac{V_{\text{max}}[S]}{K_{\text{M}} + [S]} \tag{1}$$

The asymptote, $V_{\rm max}$, is the limiting velocity when $[S] = \infty$, i.e., when all catalytic sites of the enzyme are occupied by substrate molecules. The Michaelis constant, $K_{\rm M}$, is equal to [S] when $v = V_{\rm max}/2$. To evaluate $V_{\rm max}$ and $K_{\rm M}$, a linear plot

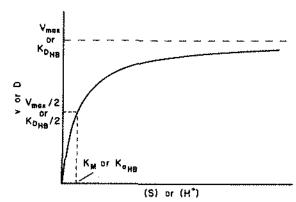


Figure 1. Graph of eqn. (1) for Michaells-Menten kinetics and eqn. (8) for the solvent extraction of a weak acid.

is preferable, of which the commonest (although not necessarily the best) is the Lineweaver-Burk version (3) shown in Figure 2. The equation of this graph is obtained by taking reciprocals of both sides of the Michaelis-Menten equation:

$$\frac{1}{v} = \frac{K_{\rm M} + [{\rm S}]}{V_{\rm max}[{\rm S}]} = \left(\frac{K_{\rm M}}{V_{\rm max}}\right) \frac{1}{[{\rm S}]} + \frac{1}{V_{\rm max}} \tag{2}$$

It is seen that the slope is $K_{\rm M}/V_{\rm max}$ and the intercept on the 1/v axis is $1/V_{\rm max}$.

Solving eqn. (1) for [S] and taking logarithms, one readily obtains

$$pS = pK_{M} - \log \frac{v}{V_{max} - v}$$
 (3)

The analogy both to the Henderson-Hasselbalch equation,

$$pH = pK_a - \log \frac{[acid]}{[conjugate base]}$$
 (4)

and, for that matter, to the Nernst equation for a redox couple $Ox + ne^- = Red$, is obvious

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]}$$
 (5)

Of course, where $v = V_{\rm max}/2$, $\rho S = \rho K_{\rm M}$, just as $\rho H = \rho K_{\rm A}$ when a weak acid has been half converted into the conjugate base. The mathematics when a base is half protonated or an oxidant half reduced is the same as when an enzyme has been half converted into enzyme-substrate complex. This has, in fact, been pointed out in a book (4) which few undergraduates are likely to encounter. On page 56 of the same book (4) is this statement regarding the hyperbolic curve: "Such a result is obtained whenever a process depends upon a simple dissociation; if, for a dissociation $XY \approx X + Y$, [Y] is held constant, plotting [XY] against [X] will give [a hyperbola]." The same writers note (p. 59) the similarity to Langmuir's isotherm.

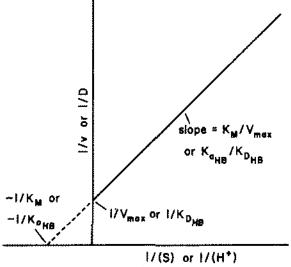


Figure 2, Graph of eqn. (2) for Michaelis-Menten kinetics and eqn. (9) for the solvent extraction of a weak acid.

Solvent Extraction of a Weak Acid

For a weak acid, HB, which partitions between an aqueous phase and an organic solvent, it is easily shown that

$$D = \frac{K_{DHB}}{1 + \frac{K_{AHB}}{[H^+]}} \tag{6}$$

where $K_{D\,\mathrm{HB}}$ is the distribution or partition coefficient for the species HB (i.e., $K_{D\,\mathrm{HB}} = [\mathrm{HB}_{\mathrm{org}}/[\mathrm{HB}]_{\mathrm{aq}})$ and D is a distribution ratio expressed using concentrations summed over all relevant species:

$$D = \frac{[HB]_{org}}{[HB]_{aq} + [B^{-}]_{aq}}$$
 (7)

Equation (6), found in treatises on solvent extraction (5) and in elementary quantitative analysis texts (6), is modified easily to accommodate other equilibria such as dimerization in the organic solvent. What has not, to our knowledge, been pointed out is that eqn. (6) can be written

$$D = \frac{K_{D_{\rm HB}}[H^+]_{\rm aq}}{K_{\rm ahB} + [H^+]_{\rm aq}}$$
 (8)

It is seen that eqn. (8) looks exactly like eqn. (1) and that Figure 1 can be labelled to represent either equation. Just as v approaches $V_{\rm max}$ when more and more enzyme molecules are working, so D approaches $K_{D\,{\rm HB}}$ as more and more B^- ions are protonated to form the extractable species HB. This is scarcely a scientific breakthrough, but it can be pointed out to undergraduates that the two equations both describe the approach to saturation for the simple case X+Y=XY, and that the approach is hyperbolic. It is seen that when $D=K_{D\,{\rm HB}}/2$, $[H^+]=K_{a\,{\rm HB}}$ analogous to the Michaelis-Menten case where $[S]=K_M$ when $v=V_{max}/2$. Because Lineweaver and Burk were biochemists, the double reciprocal plot has not appeared in analytical texts, but

$$\frac{1}{D} = \frac{K_{\text{aHB}} + [\text{H}^+]_{\text{aq}}}{K_{D_{\text{HB}}}[\text{H}^+]_{\text{aq}}} = \left(\frac{K_{\text{aHB}}}{K_{D_{\text{HB}}}}\right) \frac{1}{[\text{H}^+]} + \frac{1}{K_{D_{\text{HB}}}}$$
(9)

Thus a plot of 1/D versus $1/[H^+]$ yields a straight line of slope $K_{\rm eHB}/K_{D\rm HD}$ and intercept $1/K_{D\rm HB}$, as shown in Figure 2.

Protonation of a Base and the Oxygenation of Myoglobin

Sometimes traditional presentations obscure analogies and correlations that might be helpful to students. Since, albeit for good reasons, analytical chemists talk dissociation and pH rather than association and $[H^+]$, many students who are thoroughly familiar with sigmoidal titration curves have not the faintest notion that a graph showing the fraction, f, of a base protonated versus $[H^+]$ is a hyperbola, the equation for which is

$$f = \frac{K_{\rm b}[{\rm H}^+]}{K_{\rm w} + K_{\rm b}[{\rm H}^+]} \tag{10}$$

They then view the hyperbolic oxygenation curve for myoglobin (fraction saturated versus p_{O_2}) as something very special in biochemistry, whereas for the simple reaction Mb + O_2 = MbO₂, no other shape makes any more sense than for the reaction RNH₂ + H⁺ = RNH₃. If the hyperbolic curve is seen as unusual, how is the student then to experience the awe which the sigmoidal curves for hemoglobin and the allosteric enzymes deserve?

Langmuir Adsorption Isotherm

Most physical chemistry texts discuss adsorption (7), although the chapter on surface chemistry is frequently omitted from the courses where these books are used. Langmuir's model for monolayer adsorption on an idealized surface leads to an equation of the form

$$v = \frac{cp}{1 + bp} \tag{II}$$

for the volume of a gas under standard conditions adsorbed by a unit mass of solid as a function of the pressure, p, at constant temperature. A graph of v versus p is, of course, hyperbolic. Further, $c = v_{\text{max}}b$, where v_{max} is the limiting value of v corresponding to complete surface coverage. The assumptions in Langmuir's derivation, although probably invalid for most real surfaces, are approximately correct for the binding of protons to a base in solution, of substrate molecules to many enzymes, of oxygen to myoglobin, etc.: binding at definite sites, all sites equivalent, no interactions between sites or between bound ligands. Langmuir sounds like a protein chemist! On page 339 of reference (7) is found the following: "To test whether [the Langmuir isotherm] fits a given set of data, we take the reciprocal of each side to give 1/v = 1/v $(v_{\text{max}}bp) + 1/v_{\text{max}}$. A plot of 1/v versus 1/p ought to give a straight line if the Langmuir isotherm is obeyed." Historically, the Michaelis-Menten equation (8) slightly predates Langmuir's (9).

Successive Formation Constants

We close with an equation which is well-known in two different areas and which was derived, apparently independently, by two workers who probably never heard of each other. The second derivation rings true, with not the slightest hint of plagiarism. The teachers who use the equation seem not to talk to each other, nor do students carry it from one course to another.

The hemoglobin molecule, Hb, can bind four molecules of oxygen. For each step, a macroscopic equilibrium constant may be written:

$$H_b + O_2 = H_bO_2$$
 $K_1 = \frac{[H_bO_2]}{[H_b] p_{O_2}}$ (12)

$$HbO_2 + O_2 = Hb(O_2)_2$$
 $K_2 = \frac{[Hb(O_2)_2]}{[HbO_2]p_{O_2}}$ (13)

$$Hb(O_2)_2 + O_2 = Hb(O_2)_3$$
 $K_3 = \frac{[Hb(O_2)_3]}{[Hb(O_2)_2]p_{O_2}}$ (14)

$$Hb(O_2)_3 + O_2 = Hb(O_2)_4$$
 $K_4 = \frac{[Hb(O_2)_4]}{[Hb(O_2)_3]p_{O_2}}$ (15)

The p_{O_2} is tantamount to an oxygen concentration via Henry's law, and the equations above are written in the customary form.

Now, Hb can be titrated with O_2 , but the K-values cannot be obtained by simple inspection of a graph of the titration data as students do in elementary courses. However, these values can, at least in principle, be extracted from the data. Knowing the initial [Hb] and the quantity of added O_2 , then by measuring the partial pressure of free O_2 one can calculate for that point in the titration the average number of O_2 molecules bound per Hb molecule, designated $\overline{\nu}$. The equation for obtaining K-values from successive determinations of $\overline{\nu}$ was given in 1925 (10) and is known in biochemistry as the Adair equation, which may be written as follows:

$$\overline{p} = \frac{K_{1}p_{0_{2}} + 2K_{1}K_{2}p^{2}_{O_{2}} + 3K_{1}K_{2}K_{3}p^{3}_{O_{2}} + 4K_{1}K_{2}K_{3}K_{4}p^{4}_{O_{2}}}{1 + K_{1}p_{0_{2}} + K_{1}K_{2}p^{2}_{O_{2}} + K_{1}K_{2}K_{3}p^{3}_{O_{2}} + K_{1}K_{2}K_{3}K_{4}p^{4}_{O_{2}}}$$
(16)

A discussion of eqn. (16) may be found in a modern book (11).

Few chemistry teachers outside the biological area have ever heard of the Adair equation, but inorganic and analytical chemists who deal with complex ions are familiar with Bjerrum's formation function. This is used to calculate successive formation constants for the binding of a ligand such as NH₃ to, say, Cu(II) ions. As presented independently in 1941 (12), the formation function, \bar{n} , which is the average number of ligands (A) bound to a metal ion, is

$$\overline{\mathbf{n}} = \frac{k_1[\mathbf{A}] + 2 \, k_1 k_2 [\mathbf{A}]^2 + \dots N \, k_1 k_2 \dots k_N [\mathbf{A}]^N}{1 + k_1 [\mathbf{A}] + k_1 k_2 [\mathbf{A}]^2 + \dots + k_1 k_2 \dots k_N [\mathbf{A}]^N}$$
(17)

Bierrum applied eqn. (17) to the stepwise addition of ammonia to metal ions, determining [NH₃] by utilizing the glass electrode. Numerous adaptations have been "derived," sometimes overlooking fair acknowledgment of Bjerrum and never mentioning Adair, for obtaining successive constants by polarography, solvent extraction, spectrophotometry, and other techniques. The same sort of equation could obviously be written for the protonation of a polyfunctional base, although students may not realize this simply because acid-base chemistry is usually treated in terms of dissociation.

Summary

The examples presented above could be embellished with activity coefficients and other refinements, but this would only obscure the major theme. Sometimes a simple model, stripped of frills, captures the essence of a real situation in chemistry, and sometimes, mutatis mutandis, a model with the same features approximates the truth in an entirely different chemical situation. A few students will see the basic similarities even if the two situations arise in different courses, but those who really need our help will not. Showing less gifted students how models of the same form lead to equations of the same form takes very little extra time. Alert teachers will recognize that the examples given here barely scratch the surface.

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A New Approach to Overhead Projection



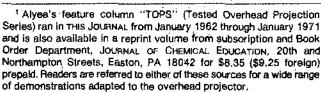
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Recently I had the pleasure of attending a seminar in La-Salie, Illinois, presented by Hubert Alyea, the master of the overhead projector (among other things).1 This rekindled memories of yearly visits which Alyea had made to Northern Illinois University in my undergraduate days. I was reminded how impressive it is to see an experiment projected to fill completely an 8 ft × 8 ft screen. I feel that the only obstacle to the widespread use of this technique has been the need to construct a special projector, so I would like to suggest a simple

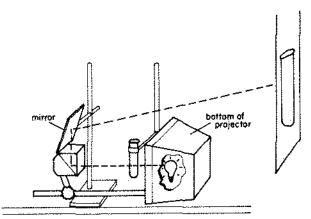
modification that can be made to an ordinary overhead projector.

Turn the overhead projector onto its back2 and affix an ordinary mirror to the projector as shown in the figure. Use a clamp and ringstand to hold the mirror in place. By holding or otherwise securing an Alyea cell or ordinary test tube between the light source and the mirror, one can carry out demonstrations that can be seen by everyone in the room.3



² Teachers should be aware, however, that some brands of overhead. projectors may have safety switches which automatically turn off the projector if it is tipped over. Also, when placing the projector on its side, be sure not to cover up the ventilation slots which are used for

³ Unless the projector image is very high up on the screen, the projector itself may block the light from the lower third of the image. This problem can be overcome by propping up the edge of the projector nearest the mirror on a block.



Schematic of the projection apparatus. The mirror is adjusted to reflect from the projection head.

provocative opinion

Trends and Issues in International Chemical Education

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As problems become apparent in the teaching of chemistry, committed instructors attempt to find solutions. Thus issues are identified and trends developed. This is a continuing and evolutionary process. Some issues appear to be cyclic; they wax and wane during fairly distinct time periods (e.g., the theory versus application debate). Some appear to be continuous; they have existed for decades and seem to defy solution (e.g., how to integrate effectively, or at least relate, the theoretical and practical work). From time to time, truly new problems emerge (e.g., how to utilize fully microelectronics in instruction); these require trail-blazing in chemical education.

Although a number of trends can be identified, let us focus attention on eight of the current trends. Each grows out of a clearly identifiable need. Although there may be differences in degree, each transcends all educational levels (primary, secondary, tertiary and adult/continuing education), and each has relevance for countries in all stages of development. The directions of these trends are toward:

(1) designing courses and curricula for general education, (2) increasing the interdisciplinary content, (3) lowering the costs of lahoratory and field work, (4) coping with aud utilizing the microelectronics revolution, (5) developing more versatile examination and evaluation systems, (6) improving the education and status of teachers, (7) promoting research and advanced degree programs in chemical education, and (8) facilitating national, regional, and international communication and cooperation.

Designing Courses and Curricula for General Education

Once the primary purpose of chemical education was to prepare a limited number of secondary school students for admission to the universities and a limited number of university students for careers in chemistry. Thus, we catered to no more than 15% of the students and ignored the large majority. This is no longer possible. All of our people enjoy the benefits and/or suffer the negative consequences of chemistry in everyday life. All have a need for and a right to some understanding of chemistry and of scientific processes, a right to an operational everyday literacy in science. There are at least three groups, in addition to those who will become chemists, who require some education in chemistry. Together, they overlap to form the entire population. One group is comprised of those who will draw on a knowledge of chemistry in their professional work (e.g., health scientists, engineers, agriculturalists). Another consists of all those who will be the managers, the decision-makers in the society (e.g., the prime ministers, legislators, industrial managers, university administrators). The third includes citizens in every walk of life who must make decisions and manage their lives with respect to foods, additives and substitutes, medications, sources of energy, protection of the environment, shelter, transportation, communication, and a myriad of other factors based on chemistry that determine the quality of life and of the culture. Existing courses do not meet these needs: they cannot be adapted successfully since they were designed for entirely different purposes. New courses and approaches to teaching, perhaps modular in design, that are motivational and sufficiently relevant and articulate to promote public understanding of chemistry, of the potentials and limitations of science, and of cost/benefit tradeoff is essential. In this trend, we are moving toward the teaching of science to everyone, every year, from primary school through at least the first two years of higher education with the public at large as the ultimate target audience.

Increasing the Interdisciplinary Content

Chemistry is increasingly viewed as the most interdisciplinary science, the central science, with ties to every critical area of human endeavor. For example, the health scientists turn to chemistry for new pharmaceuticals, better nutrition, or correction of chemical imbalances caused by organ transplants or those reflected in mental illnesses. Chemotherapy is effectively used in the treatment of cancer. The biochemicotechnological revolution in agriculture provides other examples. The fertilizers, the pesticides and the chemically based irrigation and food processing systems are all examples of chemistry in action to help feed the world's growing population. Artificial nitrogen fixation and man-enhanced photosynthesis are active areas of research that hold promise for the future.

Many more examples could be cited; the list is almost endiess. Just let your mind roam through the images conjured by areas of our discipline such as geochemistry, atmospheric chemistry, chemical oceanography, environmental chemistry, industrial chemistry, cosmochemistry, hiochemistry, etc.

How do we bring these interdisciplinary aspects of chemistry into our classrooms and laboratories? In fact, how do we take our students out into the natural world where chemistry reactions abound? Good interdisciplinary courses and curricula require very demanding and sophisticated development, implementation, and evaluation efforts. Teachers must be retrained and examinations altered. Leadership must be provided by the chemists with help from the educators. Productive research and effective decision-making both require a broadening of chemistry content for the future scientist and for the citizen.

Lowering the Costs of Laboratory and Field Work

Austerity has struck chemistry departments in every region of the world, yet chemists remain convinced that practical work is of central importance in the learning of chemistry. Therefore, it is essential to keep costs at current levels or to lower them if possible without sacrificing quality. In addition, the expansion of chemistry teaching into interdisciplinary areas such as geochemistry and environmental chemistry brings with it an increase in experimental work.

Developing effective equipment for the laboratory is com-

This paper was presented as a plenary lecture in the International Workshop on Locally Produced Laboratory Equipment for Chemical Education at the Royal Danish School of Educational Studies, Copenhagen, Denmark, August 11–17, 1983.

manding most of the attention at present. Related questions should include the following: What new experiments that teach the important principles of chemistry at lower cost can be designed? Can the cost of chemicals be cut by using substitutes, lower-grade reagents or semi-micro quantities? What new equipment is needed as field work increases? How can we manage storage for the extended experiments required in the new interdisciplinary areas (e.g., environmental chemistry)? Could and should computer simulations replace some of the laboratory work?

Coping with and Effectively Utilizing Microelectronics

A relatively new but rapidly advancing influence on instruction in chemistry is the use of microelectronic devices such as microcomputer and electronic balances and pH meters. The high technology revolution is here to stay. Computers and robotics are changing the world of work and the daily lives of millions of people, and they most assuredly are changing the world of chemical education.

In chemistry, computers are already used extensively in the more developed countries and are beginning to be used in developing nations as well. In instruction they are used for interfacing with laboratory apparatus, to promote comprehension of the three-dimensional geometry of molecules and of dynamic systems and reaction mechanisms through graphics, to simulate experiments, analyze data, manage complex calculations, for drill and practice, to manage assessment, and to handle the interminable record-keeping. The hardware is increasing in versatility and decreasing in cost. Software is the limiting factor. Creative chemical educators are needed as never before to generate effective instructional software.

Developing More Versatile Examination and Evaluation Systems

Wherever external examinations that determine a young person's future exist, teachers are under pressure to prepare students for the examinations. If the examinations require "pure" chemistry and the recall of facts, the teaching will be tailored to these goals. With the growing convictions of the importance of interdisciplinary content, of social relevancy, and of the development of such intellectual skills as problem-solving, application, interpretation, and decision-making, the examinations must be dramatically altered in content and in style to reflect the new learning goals. The teaching will change quickly if new knowledge and thinking is expected from students in order to score well on these examinations. But how can these changes be implemented? Who will provide the leadership for change? Who will supply the ideas and shape the questions? This type of effort draws few professional rewards.

Other changes in the evaluation system are needed, and innovators are at work. Examples can be found in continuous evaluation/assessment systems, Keller-type mastery teaching, and the use of the computerized question banks that promote flexibility, individualization, and varied, yet balanced, assessment instruments.

improving Teacher Education and Status

The youth of a nation is its most valuable resource. How then can concern for the quality of teaching and for the care and encouragement of competent teachers have such a low priority in so many nations around the world? New modes of teacher training are desperately needed and are being explored in some instances. Incentives to enter the teaching profession and ways of rewarding excellence are being tested. Recognition that a nation's future is at risk when the quality of its teaching is declining is finally dawning on national leaders and the public at large. To be a competent teacher at the secondary or tertiary level requires as many years of higher education as the much higher paying professions of medicine, engineering, or law. The monetary and social rewards of teaching must be similar to those of the other professions in order to keep good teachers in the classrooms and to attract a strong new generation of teachers. Although this will require social change, revamping of budgets, new methods and materials for teacher training, and a host of other actions, it must be done, and it must move from the very small beginnings now evident to large scale programs within this decade.

Promoting Research and Advanced Degrees in Chemical Education

A strong hase of research in chemical education is needed; a comparatively weak one exists now, but chemical education is growing in recognition as a research area. This can be further facilitated by the development of stronger master's and doctoral degree programs in chemical education. More funding is urgently needed for research. There is evidence now of growth in sophistication of research design and techniques. More centers where chemical education is recognized as a sub-discipline of chemistry are developing, and the international exchange of research results and ideas is occurring through the literature and in seminars, conferences, study tours, and student exchange programs. This is happening, for example, in Israel, Australia, Yugoslavia, Thailand, the United Kingdom, and the United States. Let there be no apologies for the developmental base for much of our research and advauced degree thesis work. Advances in chemical education are heavily dependent on research and development work. Instead, let this groundswell grow, and help it to thrive.

Faciliteting National, Regional, and International Communication and Cooperation

During the past decade, there has been steady growth in chemical education programs in such established organizations as the American Chemical Society (ACS) and the International Union of Pure and Applied Chemistry (IUPAC) and through the United Nations Education Scientific and Cultural Organization (UNESCO). New organizations with chemical education interests are emerging. Examples are the International Organization for Chemical Sciences in Development (IOCD) and Chemical Research Applied to World Needs (CHEMRAWN). The programs of these and other organizations are growing in strength and variety (e.g., newsletters, seminars, workshops, conferences, the publishing of monographs and source books, the exchange of curricula and teaching materials as sources of ideas and experiments). This workshop provides a prime example through the exchange of ideas and materials from both the developing and developed world, and in the cooperation of national and international organizations such as the Danish Chemical Society, IUPAC, and UNESCO.

These eight trends are global. Each is apparent in most nations regardless of stage of development. They differ in degree of urgency, of course. For example, the trend of "Lowering the Costs of Instruction" is a high priority in many developing countries, but it is of importance, too, in the more developed countries. "Coping with and utilizing microelectronics" is strongly affecting chemical education in many of the industrialized nations, but other countries are also experiencing the initial vibrations of this change. It will be interesting to compare these trends with those apparent five years hence. How many will continue to develop? Will some have disappeared? Is real progress evident? It should be interesting to monitor change and to determine what the future holds for chemical education.

chemical bonds

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The Role of the Humanities in the Teaching of Chemistry

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When I first faced the task of teaching chemistry to nonscience majors in 1972. I thought that the assignment would not be very exacting--certainly less exacting than teaching chemistry to majors. I soon realized that this type of teaching assignment is quite difficult and that the main difficulty is the subject itself: chemistry simply intimidates many nonscience majors. These students usually view chemistry as an alien world that is insensitive to their needs and that cannot possibly be relevant to their academic experiences. They would opt not to be in the chemistry classroom if they had anything to say about the matter.

Unfortunately, another factor that contributes to the barrier between nonscience majors and chemistry is a lack of commitment on the part of some of the chemistry teachers who teach these students. Obviously, the barrier is not limited to chemistry but applies to all the sciences. In this regard, a salient point has been made in a recent report of a National Research Council committee (1): "... teaching the nonscience majors remains the science department's unwanted chore too often."

Yet the chemistry course for nonscience majors is likely to become more, rather than less, firmly entrenched in the requirements of higher education. In a world where chemical developments have impact on almost every aspect of society, the absence of such a requirement would significantly limit the general education of nonscience majors and would thus contribute to a citizenry that is not as well informed as it should be, since, (2): "... there are students who while not scientists will have to deal specifically with scientific and technical issues in their professions, the National Research Council committee [referred to previously] observed, pointing for examples to journalism, law, and the ministry.

How, then, can we as teachers of chemistry make what is, perhaps, the only chemistry course that our nonscience majors will take an experience that is simultaneously challenging, meaningful, and pleasant? My response is based on a nontraditional concept, namely the integration of chemistry with the humanities. This approach has worked well for me for ten years and employs as its fundamental premise the fact that the humanities are a rich source of material that can exemplify

Editor's Note: Dominick Labianca, whose work has been published in this feature before (THIS JOURNAL 59, 843 (1982)), here explores in a more general way the methods of using the humanities to teach chemistry, especially to those students who see science as alien to them. Since these students are usually more comfortable with novels and magazines, why not use these to "hook" them into chemistry? Lablanca describes a variety of ways it can be done; those of us who like this approach will find plenty to choose from here.

This paper is a modified version of an invited paper presented at the Seventy-Seventh Two-Year College Chemistry Conference, New York City Technical College of The City University of New York, Brooklyn. NY, October 22-23, 1982.

chemical principles, stimulate critical thinking along scientific lines, and demonstrate to nonscience majors that chemistry is indeed relevant to their academic experiences. In addition, making these connections serves to remind us that (3): "... science is not an arrogant dictator in the whole arena of life but rather a democratic companion of philosophy, of art, of religion, and of other valid alternative approaches to reality." The following comments of James M. Banner, Jr., Chairman of the American Association for the Advancement of the Humanities, are appropriate for chemical educators at both the two-year and four-year college levels (4):

Sharing so much, the sciences and the humanities must...now conclude a new partnership on behalf of all knowledge and understanding. The communities of both ... should become more closely involved at all levels and in all pursuits. For without joint efforts-intellectual, institutional, and civic-both will suffer and, along with them, American culture will suffer, too.

Banner makes another point (similar to Weaver's, quoted earlier) that may be relevant to chemistry/humanities integration: "To be a good scientist," he says, "one must be more than a scientific specialist." To be successful at teaching chemistry within the context of the humanities, chemistry teachers must be willing to expand their expertise beyond the confines of their discipline, and they must be willing to establish meaningful dialogue with teachers in other disciplines—such as literature, history, and the arts—and to draw upon the expertise of such teachers in designing courses that effectively integrate chemistry with the humanities.

Chemistry/Humanities Integration: A Design

Organization

I will now describe in some detail one of several examples of courses that can employ chemistry/humanities integration. The course has a weekly three-hour lecture component and a three-hour laboratory component, and the length of a semester is fourteen weeks. The theme of the course is pollution-of the human body and of the environment. I have selected this theme because the humanities provide a great deal of supporting material—so much, actually, that the course can be periodically modified so that it can vary from semester to semester and can, therefore, never become stagnant. Two examinations are given during the semester, and, in terms of the total time required for these, one week is allotted. Thus, actual teaching occurs during thirteen weeks of the semester, and a final examination is given during a regularly scheduled final examination period at the conclusion of the semester. The formal delineation of these thirteen weeks is then as follows: five weeks for basic concepts involving atomic structure, chemical bonding, reactions, and organic chemistry; four weeks for environmental pollution; and four weeks for drugs and poisons (i.e., pharmacology and toxicology).

Basic Concepts

The first five weeks of the course are probably the most difficult for both teacher and student because the emphasis is on theory, and the more theoretical aspects of basic chemistry can, at times, be boring for some students and, consequently, a source of frustration for the teacher as well. A good text often makes the task considerably less formidable than it would otherwise be. John W. Hill's "Chemistry for Changing Times" (5) has served me well, A student study guide accompanies the book, and the combination can be used effectively to cover the requisite material in the time allotted. The text also uses a historical approach in the presentation of significant chemical developments. The teacher can expand on this aspect of the book hy drawing from other sources and can thus effectively employ chemical history to humanize and thereby arouse interest in what otherwise might turn out to be a not-so-exciting part of the course.

The laboratory component of the course is a 50–50 blend of the traditional and the nontraditional. The first seven weeks, which focus on the former, involve experiments that not only reinforce the lecture material of the first five weeks but also afford the students the opportunity to experience the "hands-on" nature of chemistry. The experiments can be of the teacher's own design or can be some of those appearing in manuals such as "Chemical Investigations for Changing Times" (6). Based on the very positive reactions of my students to experiments concerned with topics such as physical and chemical properties of matter, qualitative analysis for ions, molecular model building, and synthesis, I would suggest that at least some of the experiments concentrate on these topics.

Environmental Pollution and Drugs and Poisons

During the remaining eight weeks of the course the students are still participating in traditional laboratory experiments. The apparent lack of lecture/lahoratory coordination is deliberate: the students are given time to begin to learn the material that then becomes the basis for their nontraditional laboratory experience. In each of the last seven laboratory sessions of the course, discussion and critical analysis of material from the humanities constitute the laboratory exercises, which become the focus of the course. Particular emphasis is placed on the connections between this material and the information learned in the lectures. Student participation is essential; the class is divided into seven groups, and at each laboratory meeting, one group—relying on input from the teacher whenever necessary—leads the class for that session. The entire class is not required to read all the works associated with the sessions to be described below. Therefore, the group responsible for a session must inform the class about each reading so that there can be meaningful discussion. The lahoratory report, too, differs from the norm. It is a summary of the discussion, critical analysis, and "chemical connections" referred to above and does not exceed 500 words. (Not enough writing takes place in chemistry courses, and assignment of this type of laboratory report is one way of rectifying that condition.)

The chemistry of air and water pollution is dealt with in detail in the lectures on environmental pollution. In each of three laboratory classes, the emphasis, respectively, is on the following:

- Charles Dickens' novels "Hard Times" and "Onr Mutnal Friend" and William Blake's poem, "London;"
- Dickens' novel "Oliver Twist" and Blake's two poems, both entitled "The Chimney Sweeper;"
- three National Geographic articles that depict the devastating effects of air and water pollution on works of art.

Both Dickens and Blake were social crusaders, and their writings offer many examples of the damaging effects of environmental pollution on both the living and nonliving.

Dickens' "Hard Times," for example, makes the reader aware of the damage wreaked by pollution on an 1850's Lancashire manufacturing town (7):

It was a town of red brick, or of brick that would have been red if the smoke and ashes had allowed it; but as matters stood it was a town of unnatural red and black like the painted face of a savage. It was a town of machinery and tall chimneys, out of which interminable serpents of smoke trailed themselves for ever and ever, and never got uncoiled.

In "Our Mutual Friend" (8), Dickens wrote that "Animate London, with smarting eyes and irritated lungs, was blinking, wheezing, and choking; inanimate London was a sooty spectre. . . ." This description of the repulsive aspect of a polluted city is reinforced in Blake's poem, "London."

The danger of being a part of "animate London" is further portrayed in "Oliver Twist," where Dickens describes the plight of the chimney sweep. Many orphan boys—some as young as six—were chimney sweeps. As a consequence of their repeated exposure to coal combustion by-products—most notably, benzo(a) pyrene, which is known to be responsible for modifications in the structures of DNA and RNA that cause cancer—they contracted scrotal cancer and thus were among the earliest diagnosed victims of chemical carcinogenesis. The lot of the chimney sweep is also poignantly depicted in Blake's two poems, "The Chimney Sweeper" (one from his "Songs of Innocence" collection and the other from his "Songs of Experience").

The National Geographic articles shift the emphasis to the twentieth century. The first article (9) describes how the city of Florence, "an incomparable treasure house of art, had been engulfed in a roaring tide of silt-laden water and fuel oil" when "the Arno River had risen from its banks" in 1966. The second (10) details how sulfur oxide "pollution eats away at (Venice's) marble sculpture." The third (11) serves to reinforce the message of the second: acid rain, stemming from sulfur oxide pollution, and from nitrogen oxide pollution as well, is destroying both natural and man-made beauty. From forests and croplands to Athens' Parthenon, Rome's Colosseum, India's Taj Mahal, and our own Statue of Liberty, acid rain is insidiously inflicting its destruction. These articles also contain numerous photographs that can be used for discussion and analysis.

The course concludes with the segment on drugs and poisons. Hill's text provides an overview of these two topics, and particular emphasis is placed on the central nervous system (CNS) stimulant cocaine, on such CNS depressants as the opium-derived drugs morphine and heroin, on cyanide poisoning, and on heavy metal poisons. The four remaining laboratory sessions concentrate, respectively, on the following:

- 1) the book "Cocaine Papers" by Sigmund Freud;
- either of the films, "The Seven-Per-Cent Solution" or "The French Connection;"
- the book "Drugs in America: A Social History, 1800-1980" by H. Wayne Morgan;
- 4) the detective novels "The Pale Horse" by Agatha Christie, "A Whiff of Death" by Isaac Asimov, and "The Documents in the Case" by Dorothy L. Sayers and Robert Eustace.

Freud's "Cocaine Papers" provides considerable insight into what a recent *Time* cover story called the substance that "is becoming the all-American drug" (12). According to a comprehensive introduction by Robert Byck, the book "is a complete chronicle of Freud's involvement with cocaine and ... a history of ... cocaine, since its first isolation from the coca leaf in 1855 to the end of the 19th Century" (13). The cocaine theme is further reinforced in the film "The Seven-Per-Cent Solution," which was released in 1976, with a screenplay written by Nicholas Meyer, the author of the best-selling novel of the same title. The title refers to the the "seven-per-cent solution" of cocaine that the famed fictional detective Sherlock Holmes injects at the beginning of "The Sign of the

Four," one of Arthur Conan Doyle's Holmes stories. Both the novel and the film bring Holmes and Freud together "through the all-important link of cocaine" (14).

"The French Connection," the 1971 film based on the book of the same title by Robin Moore, is of particular interest in terms of depicting the extensive and sophisticated network that exists for the illegal distribution of heroin; of showing how a standard spot plate test for heroin is used to identify the drug; and of describing how the extent of purity of the drug can be established by means of a melting point determination employing a Thiele tube. The depiction of the melting point determination also serves as a connection to the experiment on the physical properties of matter that is conducted earlier in the course.

"Drugs in America: A Social History, 1800–1980," which is written by a historian, is an insightful analysis that effectively complements the biochemistry of the various drugs discussed in class. Morgan stresses the importance of history in understanding drug problems (15):

The stody of history can develop perspective or a sense of irony. Throughout my research I have tried to recall the implications in the observation of an anonymous morphine addict written in 1876; "This is an inquisitive, an experimenting, and a daring age—an age that has a lively contempt for the constraints and timorous inactivity of ages past. Its quick-thinking and restless humanity are prying into everything. Opium will not pass by untampered with." This same observation is as true today as then and doubtless will merit quoting in generations to come. Every enduring social problem is rooted in some basic debate over inherited values and can neither be comprehended nor affected without an understanding of its history.

The rationale for the selection of detective novels has been aptly stated by Daniel L. Weiss, a pathologist and executive secretary of the Medical Sciences Division of the National Academy of Sciences (16):

The pleasure of science is accessible to anyone who makes the effort to look at it—superficially or in depth. There is a special beauty in the order and universality of scientific exposition. The well-constructed detective story provides one of the easiest windows through which to enjoy that beauty. Dear reader, you might even be entrapped by science's seductive charm.

"The Pale Horse" is a novel in which the instrument of death is a heavy metal poison; thallium. The plot centers around the thallium-induced deaths of several victims of a carefully disguised and very well-organized murder-for-hire scheme. The literary-chemical analysis of this intriguing piece of detective fiction can be expanded to include two news articles that relate the novel to authentic situations. One article (17) deals with the accidental thallium poisoning of a 19month-old girl whose life is, quite literally, saved by an alert nurse who had been reading "The Pale Horse" while attending the semiconscious girl. The nurse suggested to doctors—who had been unable to diagnose the girl's condition—that she might be a victim of thallium poisoning, apparently because her symptoms were similar to those of the victims of thallium poisoning described in the novel. The second article (18) concerns a killer who was not only sentenced to life imprisonment for using thallium to murder two of his fellow workers at a British factory but who was also consulted by physicians who treated the girl referred to previously.

Asimov's novel "A Whiff of Death" is used in conjunction with the presentation on cyanide, which is the murder "weapon" used in the novel. Additional aspects of the novel that others have used for discussion with nonscience majors (19) are listed below:

- Lahoratory safety. This can be related to the murder of the student and the subsequent attempted murder.
- 2. Honesty. The necessity for the accurate reporting of data.
- 3. The value of research at a university. What are its roles and functions? How does it benefit the university, the faculty

- member, the graduate student, the undergraduate nonscience student?
- 4. Does "publish or perish" exist? What does it mean? Has it any merits?
- 5. Is there any relationship between teaching and research? Can one be a good teacher without being involved in research?

"The Documents in the Case" was written by Dorothy Sayers in collaboration with Robert Eustace, who was actually a physician named Eustace Robert Barton. The death that occurs in the novel involves muscarine poisoning, and stereochemistry plays a crucial role in resolving the mystery. Of significance, and quite pertinent to the message of this paper, is the extensive background possessed by Sayers, a writer whose penchant for science is clearly displayed in her novel. That background was summarized in a recent article appearing in The New York Times (20):

Dorothy Sayers was a Latin scholar; a student of Medieval history; an expert translator of Dante; a poet; a playwright; a feminist before most people knew about feminism; an authority on Christian philosophy; one of the first women to ever receive a degree from Oxford, and, when the demands of scholarship permitted, a sophisticated writer with an formidable knack of writing novels and short stories about absolutely horrid people who go around plotting morder.

Conclusion

I would like to conclude this paper by making a couple of points. The first is that a course of the type described here requires periodic evaluation by the students. They should be asked to provide written input—anonymous if preferred—each semester, so that the teacher can be made aware of the degree of effectiveness of the teaching approach that is utilized. The second point is a repetition of one that I made earlier: the course should never be allowed to become stagnant. A number of other examples that stress chemistry/humanities integration can be utilized:

- synergistic drug interaction and Wilkie Collins' famous Victorian detective novel, "The Moonstone" (21);
- the chemistry of "London Smog" and Charles Dickens' "Bieak House" and Friedrich Engels' "The Condition of the working Class in England" (22);
- chemical warfare and Erich Maria Remarque's "All Quiet on the Western Front" (23);
- 4) anesthesia and Walt Whitman's poem "A March in the Ranks Hard-Prest, and the Road Unknown," T. S. Eliot's poem "The Luve Song of J. Alfred Prufrock," George Bernard Shaw's play "The Ductor's Dilemma," Remarque's "All Quiet on the Western Front," and Stewart Brook's "Civil War Medicine" (24).
- water poliution and Henrik Ibsen's play "An Enemy of the People" (25);
- 6) nuclear chemistry and warfare, the 1959 film "Hiroshima Mon Amour," John Hersey's "Hiroshima," and historical treatment of the effects of the devastation of Hiroshima and Nagasaki.

The nontraditional laboratory component of the course can also be modified to include invited lectures by teachers in the humanities who can speak on topics relevant to those covered in the course. If chemistry and humanities teachers are really willing to extend themselves, I see no reason why a course that focuses entirely on chemistry cannot be coordinated with supporting courses in literature, history, and the arts.

Acknowledgment

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view from my dastroom

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"The Fundamental Things Apply As Time Goes By"

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Kansas Lies Outside My Door . . .

There are two very different views from my classroom. It depends upon whether the door is open or closed. The view with the door open is disheartening. I see a nation sorely in need of an Educational Renaissance, a country that spends more on alcohol and tobacco than upon public secondary education. I see too many schools out of control, disciplinary standards so eroded that the purposes to which education should aspire become long-forgotten goals as teachers struggle to survive each day. I see insensitive, bureaurocratic systems that frustrate dedicated people until they quit in disgust or adapt and adjust and begin to accept the insanity around them as the natural order of things. I am not an educational philosopher nor a student of the social and cultural ills that beset our nation and our school system. I can do little to ameliorate the large-scale problems that confront us. I am only a chemistry teacher, so I close my door, face my class, try to make my "little corner" as excellent as it can be, and leave the larger problems to those better equipped to deal with them. It would seem, however, less than honest to write a "view" article without at least including a reference to these deeper problems. They are so much a part of all our lives.

... But I Teach in the Land of Oz

With the door to my classroom closed, the view brightens considerably.

Teaching is a strange endeavor, After practicing it for over 20 years, I have found very few absolutes. The program at Niles North has been recognized as "excellent" by those who judge such things. That's very gratifying, but also frightening. It's gratifying because I often wonder how others who see many classrooms might judge what goes on in mine. It's frightening because at any given moment I am not always certain exactly why I am doing what I am doing, despite years of pondering the topic. Teaching seems to be more art than science. We do what seems right at the moment, hoping that we inspire more often than we frustrate, enlighten more often than we confuse, and bring joy more often than we hring pain. We never know for certain what effect we are having on our students. I know what I do, and hope it is more right than wrong for most of my students. Many people have told me,

some in praise, others in implied or direct criticism, that what I do is not what most teachers do. Perhaps that's true, perhaps not. At any rate, here is how I see things.

"The square of the hypoteneuse seldom comes up in real life" 1

I have become convinced over the years that many of the accepted methods of teaching introductory chemistry are, at best, virtually useless, and at worst, downright harmful. That is a very strong statement, and certainly demands elaboration and justification. Let's begin by clarifying what I see as the ultimate value in taking a course in chemistry. Too often, especially in this era of the "behavioral objective," we focus our attention and efforts on getting the student to be able to achieve the right answer to a problem, e.g., "The student will be able to transform the weight of a chemical into the number of moles of the chemical." Since many of our students have a lot of difficulty trying to solve typical introductory chemistry problems, we valiantly search for "techniques" and "gimmicks" to assist them, the most popular of which is the factor-label approach to solving problems. Somehow or other, this philosophy has never made much intuitive sense to me. It would seem that there should be a larger purpose in having our students spend so much time studying our discipline than simply learning how to work stoichiometry problems, or write electron configurations, or calculate free energy changes for reactions, or any of the other multitudinous tasks to which our students apply themselves. Certainly students emerging from a year of study should be able to do these things, but to do them mechanically and without understanding is to do little of real value. Unfortunately, it appears that we too often establish as our goal the performance of these tasks. We should be striving to develop in the student an understanding of the concepts underlying the calculations and an insight into the incredibly simple mathematical relationships that are involved in the vast majority of problems that we ask our stu-

¹ Rooney, Andy, "Sixty Minutes," Nov. 14, 1982.

dents to solve. Once this viewpoint is accepted, the entire methodology changes.

First, let's consider the method by which many, if not most, of the quantitative concepts we teach are presented. I refer to the all too common practice of allowing a mathematical equation and its algebraic manipulation to substitute for an intuitive understanding of the concept which we desire the student to understand. Just about any concept can be used for illustration. Let's take a simple one-density. Try this experiment. Ask your students who have studied density in junior high or an earlier course what density is. Most of those who "remember" will answer that density is mass over volume, D = m/V. Now that's well and good. Their answer is "correct". The deeper question, however, is whether or not they really understand the concept of density. If your students are like mine, the answer is that some of them do, but an amazingly large percentage of those who have learned the formula for density and can even solve elementary problems involving the computation of densities have either a vague, inaccurate, or in some cases, no idea at all of what density really is.

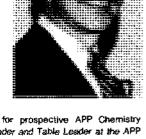
But how can you ascertain that they do not understand a concept when they can manipulate the equation? Try questions without numbers, so there is nothing to manipulate algebraically. Suppose you have two substances, let's say lead and Styrofoam®. Lead is denser than Styrofoam. Which weighs more for one cubic centimeter? (Apologies to the physicists for using the term weight here.) It may seem improhable, but many students who can solve density problems will still say that Styrofoam weighs more for one cubic centimeter. Ask which weighs more, 3.00 g of lead, or 3.00 g of Styrofoam. Many will answer that 3.00 g of lead weighs more "because it's denser." Ask which occupies a larger volume, 3.00 g of lead, or 14.00 g of Styrofoam, and then turn it around, and say 14.00 g of lead or 3.00 g of Styrofoam. In my opinion, only those students who understand what they are dealing with will quickly recognize that the first question can be answered with the qualitative information given, while the second cannot.

No Concept Is So Simple that It Can't be Misunderstood

Let's take an even simpler example, one for which I am indehted to Dr. Arons of the University of Washington. Dr. Arons is foud of asking his students, "What is area?" The

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conducted numerous workshops for prospective APP Chemistry teachers, and has served as a Reader and Table Leader at the APP Reading for the past seven years. He tias also served on the ACS-NSTA Subcommittee It since 1978, cheired the committees which prepared the 1982 ADV and 1984 ADV examinations, and recently was appointed vice-chairman for the high school level examinations.

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typical answer is $A = l \times w$. He then draws a figure such as this on the blackboard



and asks, "Does this figure have an area?" An incredible number of students will answer, "NO!!!" Since they know no way of computing the area, it must not have one. They have little if any idea of what area is, but they could solve certain types of area problems if called upon.

I am not suggesting that we should hide mathematical relationships from our students, but I am suggesting that to begin the introduction of a concept with the equation that relates to the concept hinders understanding. Too many of our students can manipulate these equations algebraically, get most of the problems correct, and yet have virtually no real understanding of what they are doing. The equations they memorize are often quickly forgotten, whereas if we can teach them the concept, this will be retained. It becomes part of the way they view the world, and these intuitive understandings seem to be remarkably resistant to loss with time.

To thoroughly understand a concept such as density, two things are necessary on the part of the student. First, he must completely understand, on a gut level, each of the quantities involved in the concept. Secondly, he must also understand, again on a gut level, what is really meant by the mathematical relationships involved. At first, this may appear to be a rather difficult task, but think about it for a moment. There really aren't that many individual concepts in a typical chemistry course-mass, weight, volume, length, temperature, time, charge, energy (kinetic and potential), the mole, force, area, perhaps a few others. Most other concepts are simply combinations of these. Density is mass per unit volume, concentration is moles per liter, the rate of a chemical reaction is molar per second, or moles per liter per second. How many mathematical relationships are there? With some exceptions, the vast majority are either direct or inverse proportions. If we concentrate our time and effort towards leading the student to fully understand the quantities with which he is dealing, and to thoroughly comprehend what is really meant by the mathematical relationships, chemistry becomes, instead of a never ending series of new things to be learned, just

High school chemistry teachers from around the country open their classroom, through this feature, for all to see. Teachers are invited to share their techniques, methods, ideologies and alternative views. Contributions should be sent to the feature editor.

Gery Dunkleberger, the new editor of View From My Classroom, is the Supervisor of Science for the Carroll County Public Schools and holds en adjunct appointment at Western Maryland College. He taught chemistry, physics, and general science for eight years and was an assistant principal for three years.

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Dunkleberger has actively participated in the Maryland Association of Science Teachers of the NSTA. In 1975, he was awarded the Gustev Chaus-NSTA Award for innovations in science teaching at the secondary

new combinations of a very few things in just a couple of mathematical relationships.

If at First You don't Succeed . . .

Trying to teach concepts can be very difficult and frustrating. It's often a slow, repetitious, tedious process when the student doesn't catch on right away. It's one thing to define a gram; it's another to understand what it is. It's one thing to write down the equation for density; it's another to understand what it is. There is a tremendous temptation to simply present the equations, show how they are manipulated, and have the student learn to manipulate the equations in the same manner. Its much easier to use the factor-label method. Now the student can convert grams of CO2 into molecules of CO2 without having to understand what a mole really is. He just cancels units. That's very efficient, but what has the student really learned? More importantly, perhaps, where is the excitement? Where is the joy? I think there is joy in understanding. There is little joy in algebraic manipulation and canceling units.

There are many techniques for trying to teach concepts. We all use them. Translate the abstract into the concrete whenever possible and necessary (after all, one of our goals is to improve our students' ability to think abstractly). Draw analogies, but draw them carefully. Choose your analogies for their teaching value, not just for their humor or cleverness. Most importantly, constantly ask why. Continually quiz the student so he must demonstrate understanding, not just fluency. When the philosophy changes, the techniques will spontaneously develop.

They Laughed when I Sat Down at My Calculator . . .

Perhaps the greatest misconception regarding introductory chemistry is that it is a mathematically demanding discipline. Indeed that is what appears to frighten many students away from our classes. How terribly unfortunate this is. After all, what "math" do we do, anyway? Mostly, we add, subtract, multiply, and divide. We do use exponential notation, and some students need work on that, but electronic calculators have even done away with most of that difficulty. When students say they "just can't do the math," what they mean is that they cannot take the data in a problem and manipulate it properly. They multiply when they should be dividing, divide with the wrong number on top, and continually make errors that no functioning human mind, it would appear, should ever make. To us, they seem incredibly stupid, even though we know this isn't true. The student is convinced that chemistry involves some sort of mental processes that only the inteliectually elite are capable of engaging in. I really don't think that's true.

The first problem we ever work in class is by far the most important of the year. I ask my students, "A school has 3000 students in it. There are 30 students per room. How many rooms are there in the school?" No student in my 20 years of teaching has ever missed this problem because he didn't know how to combine the numbers, and this includes a recent class of six "special education" students. "One hundred rooms," they immediately shout out. We literally spend an entire hour analyzing how we worked this problem. Why did we divide 3000 by 30? Why didn't we multiply them to get 90,000 rooms? Students literally laugh at this suggestion. That would be ridiculous, outrageous, stupid, they agree. Well then, why not divide the other way, to get 0.01 rooms? Equally ridiculous! But why? I pretend that I worked the problem incorrectly and have them try to explain their thinking. They have great difficulty in doing so. They just knew how to work the problem. That's the point, and the bottom line is that the vast majority of problems we work in chemistry involve exactly the same thinking process. How many moles in 3.45 g of Fe(NO₃)₃? Same problem. How many grams in 3.4×10^{-3} mole of H₂SO₄? Same type of problem, only now we are calculating the number of students from the number of rooms

and the number of students per room. How many liters of a gas at STP are occupied by 4.3×10^{22} molecules? Same thought process, only we use the process twice. Amazingly, almost all students quickly realize that the thought processes are indeed the same. Then, they ask, why do I have so much trouble working the problems when they are expressed in grams, or liters, or moles, or moles/liter, or grams/mole, or whatever, but no problem when working with students and rooms? There are two answers to that question. First, you don't really know what is meant by a gram, or a mole, or the phrases gram/mole, or kilojoule/mole, or mole/liter. You may think you do, but you do not. Secondly, the numbers aren't "nice," like 3000 and 30, and you let the numbers interfere with the logic. That's what we have to work on, and work on it we do, all year long, at every opportunity. It's hard work, for both the student and the teacher. It's not easy to explain "why" you divided the numbers like you did. You go over it literally hundreds of times.

Most of the students eventually get the idea, and to see the joy on their faces when they realize that chemistry is easy is very gratifying. By the middle of the course we can really zoom along. Chemistry isn't a thousand different problems. It's just a few different problems using different quantities. Once we understand the quantities and the relationships involved, it's really only one basic type of problem, done over and over and over.

"I got the right answer, and you expect me to think, too?"

We avoid "gimmicks." Students want to use proportions. I don't allow that. Did you calculate the number of rooms in the school this way?

$$\frac{x \text{ rooms}}{3000 \text{ students}} = \frac{1 \text{ room}}{30 \text{ students}}$$
$$30 x = 3000$$
$$x = 100 \text{ rooms}$$

No? Why not? It's because you understood about students, and students/room, so proportions weren't "necessary." They ask if they can use proportions anyway, because, after all, it's correct, and they can solve the problems this way. Absolutely not! You haven't understood anything. You've just learned an arrangement in space. What about the factor-label method? I strongly advise against it. It's artificial. You can solve the problem and not understand anything about the quantities with which you are working.

I know this is a radical approach in the view of many teachers. They have told me so. Some think it's foolish not to allow students to utilize such an "efficient" approach. Yes, it is efficient if all you want is the answer. Yes, it's much easier to teach. Unfortunately, I don't think the students have learned what really is important to know.

Is this approach workable? The answer is obviously yes, since my students have been very successful by any objective measure one might apply. Can this approach be utilized with "below average" students? Every indication I have ever received says yes. Indeed, my recent experience in teaching a special education class seemed to suggest that, given enough time and concrete references, even students classified as "below basic" can learn to reason quantitatively, and enjoy doing so.

Is this approach "better" than the traditional methods utilizing proportions, factor-label, equations, etc.? This I do not know, since I have never taught by any other approach, even on day one. Obviously, good chemistry students are produced by a number of approaches. As Mark Twain once wrote, "You pays your money, you takes your choice."

If it's Tuesday, This Must be Laboratory

Laboratory work in introductory chemistry is critically important for most students, but unfortunately it is often

elevated to a position just short of a diety. What is important is that in the laboratory, students get concrete references to things which we take for granted. They see precipitates form, substances dissolve, temperatures of solutions rise as exothermic processes occur, etc. We have seen these things many times, so we tend to assume that our discussions of these phenomena are meaningful to students. Sometimes they are, but sometimes they are not. One thing that does appear to be fairly consistently true is that students need to be continually shown the relationship between what is done in the laboratory and what is discussed in class. They seem to treat the two aspects of the course as separate entities. They can go into the lab and precipitate AgCl, but when you ask them the next day to name one insoluble ionic solid, they can't think of any. They can become fairly expert at applying Le Chatelier's Principle, but fail to understand how you can precipitate a little BaCrO4 when you add barium nitrate solution to a solution of potassium dichromate. Like East and West, lab is lab, and lecture is lecture, and never the twain shall meet. Of course they do meet: they are all part of the same subject, and one complements the other. It just cannot be assumed that the student sees the relationship. Students need to be trained to relate one aspect of the course to the other.

Teaching Descriptive Chemistry is Like Memorizing the Prime Numbers

Descriptive chemistry seems to be much in vogue now. That is probably unfortunate. Considering the limited time we have to teach our subject, I see little of intrinsic value in teaching descriptive chemistry for its own sake. Descriptive chemistry is valuable because it provides the real examples with which to illustrate and clarify the ideas and principles which we want our students to learn. The Periodic Table is important, and relating chemical and physical properties to the Periodic Table and similarities among family members is very useful. It allows students to systematize a lot of factual information. although extrapolation from the known to the unknown must be done cautiously, especially when using the first period elements as the "examples." Certainly students should learn the properties and formulas of common laboratory reagents, if only for efficiency and safety. Efficiency also causes me to require my students to memorize the formulas and charges of common cations and anions, although philosophically it is uncomfortable to mandate such a task. It is to be hoped that descriptive chemistry will be learned not in isolation, but as an adjunct to more fundamentally important concepts. We may find knowing the properties of hundreds of substances

fascinating, but that does not mean that our students need to know these things. Furthermore, even if they learn them, these facts will be quickly forgotten if learned in isolation. Learned in conjunction with principles, they will be remembered much longer and much more accurately.

Much has been made over the past several years of the incident involving the graduate student who thought AgCl was a "pale green gas," and this example has perhaps even spurred the movement back to descriptive chemistry. Yet it seems to me that this example argues strongly against the teaching of descriptive chemistry. I suspect that the student involved did learn the properties of AgCl at one time. However, he also learned the properties of Cl₂, and probably learned both facts in isolation. He simply mixed them up. I would argue that a student with a good understanding of the fundamental nature of bonding in ionic solids and nonpolar gases would be very unlikely ever to say that AgCl was a gas. That just wouldn't make any sense.

A Few Closing Comments

It may be unfortunate, but it seems that one of the most important aspects of teaching is "style," a flair for the dramatic, the unexpected, the unusual way of presenting things. What we say should be the most important thing, but how we say it in fact seems to be equally if not more important in motivating students and maintaining their interest. Dramatic gestures, voice inflections, stories, etc., should be developed by every teacher until they become part of his or her repertoire. For some reason, it is these seemingly superfluous things which are passed from one class of students to the upcoming class and often causes them to elect to take our course. It shouldn't be this way, but it is.

Learn as much as you can about every one of your students, especially those that do not excal in your course. All students have value, and knowing their talents outside of our discipline makes it easier for us to respect them, and this respect will shine through. Every student we teach is better than we are at something, be it music, art, athletics, acting, computers, tinkering with cars, or bobbing for apples. Knowing what they are better at than we puts things in perspective.

Teach by example, not by decree. Show what you value by your actions, not by your words, and be grateful that they do not accept all that we deem worthwhile. That's what makes them all unique individuals.

Pre-Test Volunteers Needed for ACS/NSTA Test in High School Chemistry

The examination committee needs volunteers to give a pre-test for the Form 1985 examination. The test will provide statistical data for the selection of items to be used on the 1985 test.

The pre-test will be ready by May 1, 1984. Teachers may administer the test at any time. However, it is imperative that the answer sheets be returned before June 15, 1984. Also, in order for the data to be statistically valid, it is important that all students attempt all questions given to them. Therefore, sufficient time needs to be provided for the administration of the test. It is not necessary, however, that the total test be given at one sitting. The test may be separated and administered in two parts.

From volunteers responding, a sample representative of high school chemistry will be selected. All will be notified when the sample us been selected.

Chemistry teachers interested in pre-testing the Form 1985 test should respond by February 15, 1984 to: William Arnold, 1328 Bellbrook Avenue, Xenia, OH 45385. Phone: (513)372-7385.

² Davenport, D., J. CHEM. EDUC. 47, 271, (1970).

cooperative education

Development of a Cooperative Education Program at the University of Victoria

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In 1976/77, following discnssion as to possible changes in curricula and in teaching methods, the Chemistry Department in conjunction with the Department of Physics proposed the introduction of a cooperative education model at the undergraduate level. Following approval by the University Senate, the two-department model began, with 48 students undertaking work terms in the summer of 1977. Other departments quickly joined and there are now established co-op programs in chemistry, physics, mathematics, geography, public administration, computer science, and other areas:

The university's philosophy has been to give the respective departments as much of the control of the programs as possible, although there is a central director's office which maintains uniformity in record keeping and serves as a liaison between departments and various governing councils within the university.

As the operation has enlarged to its current total of about 80 students, the infrastructure within the department has developed considerably. We currently place 20–30 students in the fall and spring terms, with usually about 40 students in employment over the summer. Work terms are based on a 13-week model, although students often complete 16 weeks of paid employment. The department seeks to provide students with professionally oriented positions in all aspects of chemistry in all parts of Canada during their work terms. Most of the responsibility for the day-to-day organization is assumed by a Chemistry Co-op Director (a faculty member) and a Chemistry Co-op Coordinator (also a continuing member of staff). They are assisted by a departmental Co-op Committee of six faculty members who assist in reading reports, work site visits and, to a lesser extent, negotiations for positions.

Students attend the university for five years. On completion of their honors or major co-op program, they have fulfilled all the requirements of the university degree and have completed 24 months of work experience as well (see table). The faculty are responsible for developing positions in industry or government, and representatives of companies and government departments are invited to the campus to discuss ongoing student work commitments and to interview prospective

Cooperative Program in Chemistry at the University of Victoria

| YEAR | Fall (SepDec) | Spring (Jan—Apr) | Summer (May—Aug) |
|------|------------------|---------------------|---------------------|
| 1 | 1st year | 1st year | "1st year" |
| | campus term | campus term | work term |
| | | | (Optional) |
| 2 | 2nd year | "2nd year" | 2nd year |
| | campus term | work term | campus term |
| 3 | "3rd year" | 3rd year | "3rd year" |
| | work term | campus term | work term |
| 4 | 3rd year | "4th year" | 4th year |
| | campus term | work term | campus term |
| 5 | "4th year" | 4th year | • |
| | work term | campus term | |

students for the following work term. Students on work terms are visited either by faculty members or by the Co-op Coordinator at the work site, where continuing discussions of the quality of the job and the level of student work required are carried out. Further aspects of job development are also discussed.

On completion of a work term, students are required to write a report describing in detail the work completed. This report is then assessed both by the department and by a representative of the employing agency. Satisfactory completion of such a report is required for continuation in the program, and an amendment is also made to the student's transcript indicating the satisfactory completion of the work term, although no formal academic credit is given. Students are required to complete successfully at least five work terms in order for the co-op annotation to be added to their diplomas.

Experience has shown that work-term positions divide into two classes, (1) those of a more routine technical nature involving first or second year students who are beginning to acquire familiarity with instrumentation and techniques, and (2) positions for third and fourth year students who generally find themselves in research and development laboratories carrying out either small projects, or participating in ongoing research. In this way students mature in their chemical experience, and all Chem. Co-op graduates have quickly found employment. Our students are sought after, since many employers recognize that the training time required is much less for students who already have extensive experience in a variety of locations.

Currently we have students participating in work programs in every major area of chemistry. We encourage our students to experience a variety of locations, both geographically and in chemical challenge, in order to provide a better background for their own career selection. Most employers take their position as coeducators very seriously, and we have found it to be very rewarding to be able to work so well with enthusiastic members of the industrial community. The number of graduates to date is small (somewhat over 30), but about half of the students who complete the co-op program enter graduate school.

The cooperative program requires much of the time of the faculty members actively involved in it. They have an obligation to place students in jobs which involves traveling for job development and on-site work visits. The costs associated with an operation of this type are high, and the institution must be prepared to make a full commitment in a venture such as this. There is, however, much to be gained by both the student and the university. Not only have we identified motivated students who will pursue careers in chemistry, but we have also begun a dialogue with many companies. This dialogue takes forms which range from informal consultation to the opportunity for industrialists to comment and advise on course content. Links have also been made between industry and research groups within the department.

On the negative side, however, faculty members have less time to devote to their research duties, and departments must make assessments of this aspect in defining the administrative duties of faculty members. Our goal is to admit 25 students a year to our Co-op Program. This, for a department with a faculty and professional administrative staff of 24, is about the maximum consistent with an efficient operation. Currently we are graduating about 10 co-op students a year. We

are delighted with the success of our venture, since our entry into the co-op model was the first of any department in western Canada and, although surprising to many companies due to our geographical location, it has certainly enhanced the profile of our department. Although we have had some experience with a graduate cooperative work program, our emphasis will remain at the undergraduate level.



Delaware Science Olympiad

John C. Cairns, State Supervisor

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This past spring, Delaware held its seventh Science Olympiad; over 600 students from grades 9 through 12 from nearly all the public and many private high schools met on the campus of Delaware State College in Dover for a day of competitive events. We have found these Science Olympiads to be both exciting and beneficial to the students, teachers, and school officials, and we recommend their consideration by anyone looking for an alternative to the science fair. The positive results of these events, which are held on the last Saturday of April each year, include an increase in student enrollment in science classes, an opportunity for students to compete on a team and learn about team spirit, an increased attitude on the part of students that science can be fun and exciting as well as rigorous, and a chance to make young people feel good about being bright. For those interested in such results, we report here on the organizational details and content of our last Olympiad in the hope it will serve as a guide for getting similar activities started in other states.

Organization and Funding

Delaware is not unique in the development of the Olympiad concept. St. Andrews Presbyterian College in North Carolina (1) and Indiana University of Pennsylvania are two other schools that have held an Olympiad. Delaware is unique in that the Olympiad has been running continuously seven years, it is statewide in its operation and structure, and it covers all fields of science and many areas of mathematics and engineering. In its most recent edition, it consisted of over 25 different contests or competitive events.

Delaware State College was selected as the site for the Olympiad because of its strong science department and its central location. Officials there were eager to become involved. They use the Olympiad as a part of their recruiting program

Initially, funding was provided through corporate contributions, but since 1979 all fiscal support has been provided by its sponsors, the Delaware Department of Public Instruction and the Delaware State College. A small registration fee of about one dollar per student is collected to help pay for a catered "fast food" lunch. None of the 50 public school teachers nor the faculty of Delaware State College receives payment for this effort. Game development, monitoring, and score keeping are done by these groups because they enjoy doing it. There is a large investment in time and talent in the Olympiad by teachers from Delaware and from the college.

No rents are charged for facilities. Custodial costs are borne by the recruiting office of the college. However, expenses are incurred for certificates for all students and for medals and trophies for young people taking first, second, and third place in each event. About 375 trophics and medals are awarded to the participants at the awards ceremony at the end of the day.

Competitive Events

Some competitive events were modeled after old television programs such as "Password," "GE College Bowl," and "Almost Anything Goes." Others are formatted like an old-fashioned spelling bee. Some events require knowledge of facts while other events concentrate on application of laboratory skills.

Another group of events requires a student to construct a device and bring it with him/her to the Olympiad. Some were "fun events" with only a flavor of science.

Competitive Events Involving Chemistry

- 1) Science Bowl. This event is patterned after the television program "GE College Bowl." All questions are taken from high school science textbooks. This event is most rigorous; schools typically practice so that each youngster will know the rules and questioning format. Each team competes in three rounds against two different teams each round. The highest total scores qualify the top three teams for the final round prior to the awards assembly in the afternoon (3).
- Qualitative Analysis. Each two-member team is asked to identify certain positive ions in a solution, using an unknown solution, flow chart, and necessary chemicals and equipment. Speed and accuracy count (4).
- 3) Password. Password is modeled after the television program of the same name and involves three opposing two-person teams. A team member attempts to guess an unknown science word. One-word clues are given by the teammate who knows what the word is. The opportunity to give clues and respond to these clues passea from one team to the other in a regular fashion.
- Periodic Table Quiz. This is an oral quiz in which answers are the names of the elements. It is conducted like a spelling hee.
- Calculator Contest. Students are given problems to solve, using a hand-held calculator. The problems are typical word problems taken from science textbooks. Speed and accuracy count.
- Titration Race. Each participant has three tries at titrating a standard solution (phenolphthalein indicator). Speed and accuracy count.
- Naming Compounds. A written "test." This event tests the ability of the student to write and name common compounds typically found in a high school laboratory.
- Balancing Equations. A written test of a student's ability to balance a variety of equations.
- 9) What Is It? A series of 20 close-up 35-mm slide shots were

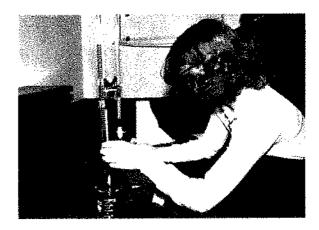


taken of everyday laboratory equipment and then shown at the orientation assembly. All students were asked to identify these items.

- 10) Who Is It? Over 80 pictures of well-known "scientists" in all scientific fields from about 1650 to the present are placed on poster board. Students simply pick up a quiz sheet and attempt to identify as many of these scientists as possible.
- 11) Reading Scales. Students must correctly measure more than 20 different objects using a variety of laboratory equipment.
- 12) Categories. Students are given five categories and six letters for each of the categories. They are to fill in a grid with examples of each category. The examples must begin with the chosen six letters. This contest requires about one hour to comnlete.

Other Competitions

- 1) Scavenger Hunt. This is an outdoor event in which contestants are sent out to find ubjects from a search list of biulogical terms.
- 2) Rocks to Riches. Participants must identify as many minerals and rocks as possible in 40 min.
- Estimating. Participants are asked to estimate lengths, masses, and volumes in metric units. The best estimates win.
- 4) Name that Organism. Students are asked to identify a variety of plants and animals that are native to Delaware.
- Tea-making Contest. This is a solar energy event. Youngsters are given certain parameters and asked to construct a device to heat water—using the solar concept. Theoretically, the hot water could then be used to make tea and thus the title of this event.
- 6) Obstacle Course. Another four-member team event; the team traverses an obstacle course much in the manner of the old television program "Almost Anything Goes." The event is given a scientific flavor. At different spots along the physical obstacle course, mental obstacles are met.
- 7) Computer Programming. Students are given a variety of problems to solve.
- Paper Airplane Flying Contest. Given certain parameters, students are to design and construct a paper airplane. At the Olympiad, airplanes are flown out-of-doors. The scoring is hased upon distance, accuracy, and time of flight (5).
- Fermi Questions. A Fermi Question is a question in physics which seeks a fast, rough estimate of quantity which is either difficult or impossible to measure directly. For example, "How many drops of water are there in Lake Michigan?" The solution requires an estimate of the volume of a drop and the volume of Lake Michigan. Another example, "How many ping pong balls are needed to fill a sphere the size of Venus?
- 10) Bridge Building. Given certain parameters of length, width, height, and material, each youngster is to design and build a



- bridge to carry the greatest possible load. Scoring is done by placing weights on the bridge until it breaks (7).
- 11) Biotrivia. Played as an old-fashioned spelling bee, this event consists of a series of oral questions about biology, medicine, ecology, etc. (8).
- 12) Egg Drop. Given certain parameters, a youngster is to design and build an apparatus to safely drop an egg from the telescope observation tower at the college. Scoring is based upon successfully landing the egg in the shortest period of time.
- Trajectory. A student is given certain parameters and is asked to design and build an apparatus to launch a projectile through a certain range. The mass of the projectile is given, but the range is unknown until the day of the event. The range of the projectile is randomly assigned just prior to the competition. The range could be from 1 m up to 30 m. One shot only is permitted. Thus, much practice must be done at home to calibrate the instrument.

Tea-Making, Paper Airplane Flight, Bridge Building, Egg Drop, and Trajectory are the events which we use in place of a statewide science fair.

Not every youngster can enter every event; however, many youngsters enter as many as four or five contests during this grueling, tough, tiring, fun, fantastic, frustrating day!

In order to encourage advance registration, a game was developed. The first 10 schools to properly solve a tough mathematical expression with 45 different variables were awarded olympic-style medals on a blue ribbon. Correct solutions to the problem had to accompany the advance registration form. Clues were given for each variable. Some clues dealt with science, while others concerned Delaware or the Olympiad.

Since the winners of this event were known prior to the Olympiad, awarding of these ribbons was the first order of business at the awards assembly near the end of the day. This gave teachers who ran games late in the day a little more time to grade papers and turn in their results.

The Olympiad has grown both in the number of events and the number of young people participating, but more importantly, the success of the Olympiad is measured by the number of students that have attended and left feeling good about themselves.

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Models to Depict Hybridization of Atomic Orbitals

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The elements of symmetry of the regular octahedron have been used effectively in models constructed for the purpose of demonstrating the hybridization of atomic orbits. The octahedron served as a cage to contain the representations of both the old s, p, and d orbitals, and the new hybrid orbitals which resulted from the hybridization.

Whereas the old orbitals were represented wholly within the octahedral cage, the new orbitals extended beyond the confines of the cage at appropriate equivalent positions. The s orbital consisted of a ball at the center of the cage, while all the remaining orbitals, old and new alike, were represented by sticks.

In each model, care was taken to show the proper orientation of all the original directional orbitals with respect to each other. The p_x , p_y , p_z , $d_{x^2-y^2}$ and d_{z^2} orbitals were all displayed along the 4-fold axes of the octahedron, while the old d_{xy} , d_{yz} , and d_{zx} , if involved in hybridization, were shown along the 2-fold axes of the octahedron.

The old s, p, and d representations were painted the following bright colors: red for s; orange for p; and yellow for d. This is the order of increasing energy in the visible spectrum. (Green was reserved for f orbitals.) White was used for all the new hybrid orbitals, a move which appropriately suggested "mixing" of orbitals, or colors.

The positive or negative character of each lobe of a p or d orbital, as given by the sign of the wave function, was designated by a red or black band, respectively. The negative collar of the $d_z z$ orbital was shown as two black polar caps on the surface of the red ball representing the s orbital, and perpendicular to the z axis.

Figures 1 to 6 are photographs of six models of hybridization: linear, sp; trigonal, sp^2 ; tetrahedral, sp^3 ; planar, dsp^2 ; trigonal bipyramidal, dsp^3 ; and octahedral, d^2sp^3 .

These models were found to be useful in the teaching of topics in symmetry, hybridization, covalent and coordinate bonding, and complexes.

Models suitable for individual study were constructed from the following materials: 6.5 cm, round toothpicks; glue; water putty¹; and water paint.

Eighteen toothpicks were used to construct the octahedral cage: twelve for formation of the 6.5 cm edges of the octahedron; and the remaining six toothpicks for construction of the three mutually-perpendicular, 4-fold axes of the octahedron, each axis being projected about 2 cm from opposite cor-

At this stage of construction, the foundation had been laid for representation of all old and new directional orbitals which lay along the x, y, z axes. Any other directional orbit could be represented by additional toothpick segments placed along other appropriate octahedral axes of symmetry.

Each hybrid orbital was always shown as a full-length toothpick, which originated at the center of the cage, and protruded out from the cage along the proper axis of symmetry.

After all the directional orbits had been displayed, a ball of water putty (about 15 g dry powder to 5 ml water) was molded about the center of the cage. This ball represented the s orbital. Further stabilization of the model was effected by hardening of the putty.

The original s, p, and d designations, all of which lay wholly

The resultant hybrid designations, which were equal in number to the original oribitals were partly inside and partly outside the cage. That part of the hybrid orbital outside the ocathedron was painted white; the internal part was painted white only if it was not coincident with a p or d orbital.

All remaining unpainted parts of the model were made "flat" black in order to draw attention away from the cage.

The photograph of the model of octahedral hybridization, Figure 6, illustrates the coincidences of the s, p, and d original orbitals with the 4-fold axes of the cage. In Figure 6 the d^2sp^3 hybrids are also shown along these axes.

In the construction of larger models, which were more suitable for group instruction, the long stems of fireplace matches replaced the toothpicks. Each linear dimension was doubled.

Acknowledgment

The author is indebted to his colleague John Sapp for the photographs.

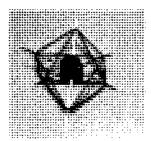


Figure 1, Linear, sp.

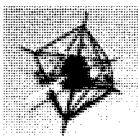


Figure 2. Trigonal, sp2.

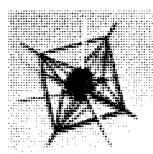


Figure 3, Tetrahedral, sp3.

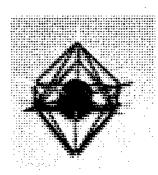


Figure 4. Planer, (d_{x2-y2})sp2.

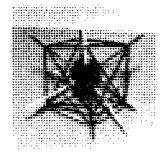


Figure 5. Trigonal bipyramidal, $(d_{z^2})sp^3$.

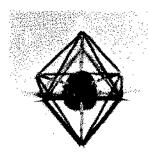


Figure 6. Octahedrai, $(d_{z^2})(d_{x^2-y^2})sp^3$.

within the octahedral cage were painted red, orange, and yellow, respectively.

^{1 &}quot;Rock Hard Putty," Donald Durham Co., Des Moines, IA 50304.

real world of industrial chemistry

edited by

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A Private Corporation as Part of a Chemistry Department

An Eleven-Year Synergism

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Background and History

Academic institutions constantly strive to meet the challenges of the future. Nobody has a complete list of ideas and programs that spell success for the next decade, but some obvious concerns which need attention should be on everyone's list and would include the following. In order to keep an academic institution strong and relevant, the educational experience must match the needs of the students. Certain educational experiences must be related directly to real-world concerns to give the stamp of reality to those experiences. A caring institution must find ways in which dollars can be produced to assist students in paying for their educational experiences. Finally, a beneficent institution cannot operate isolated from its surroundings but must provide answers to problems within the local community and serve the needs of people in every way possible. This serves not only to enhance the quality of life in that community, but also to develop friends, the number and quality of whom help determine the strength of an academic institution.

During the late 1960's several National Science Foundation programs such as the Student Originated Studies program provided the opportunity for student teams to work on projects that provided real-world experiences and helped to solve problems for people in the local community. Unfortunately the guidelines for eligible projects changed frequently, sometimes annually, and it became difficult to anticipate the direction of these federal programs. As a result, it became impossible to plan for more than one year in advance and therefore to incorporate these very positive programs into the curriculum. Thus, they never became an integral part of the

on-going educational experience,

By 1970 the future directions and needs for Carroll College had been described and some experience had been gained with programs involving students, work projects, research, and independent study. The list of community and private problems and concerns that required some technical expertise for resolution was ever increasing, and many of our science students were capable of providing such expertise. These factors appeared to call for something new to be formed that (1) did not involve government support, (2) was long lasting, (3) could become an integral part of the curriculum, (4) could provide students with a research/work experience, (5) could provide reasonable salaries for students, and (6) could provide a service to people. The answer came on a July evening in 1970 during a very productive student research seminar. I decided that a new venture should be launched to provide students with a unique learning experience on a continuous basis. The

idea was discussed with Roy Christoph, then chairman of the Biology Department, and we agreed to continue discussion with a mutual friend who was a chemical engineer and vice president of a large Milwaukee industry. Shortly, the three of us agreed to form a private, for-profit, corporation. We sought legal assistance and were advised to draw up an agreement with the College which would provide legal protection for both parties. It was also important for the private corporation to pay taxes, have our own insurance, and not participate in the tax-exempt status of the academic institution. Incorporation of the company, named Bionomics Corporation, was fairly simple, because our business partner was aware of statutory regulations and had friends who could answer questions and provide advice. We hired an accountant, selected an insurance agent, and obtained some help in advertising. Each of the three officers invested \$500 in the company and received 500 shares of stock. This initial capital was used to pay incorporation fees and advertising costs, buy stationary and office forms, purchase a telephone answering device, and install a private business telephone. No additional capital has been needed to date.

The formal agreement with Carroll was approved by the Board of Trustees, but initially the College administration wondered how things would operate, and whether every department on campus would begin a similar operation. The fact that the two faculty involved had more than fifty years association with the College helped to allay initial administration concerns. The administration could assume from this long association with the College and past performance of the people involved that the best interests of the College were

being considered.

The original agreement between the College and Bionomics Corporation was not very complex and has never been changed or modified. It included the ideas that every attempt would be made to hire Carroll students as employees, and the company would take care of its uwn financial and business matters and have its own insurance program. The company would be permitted to use instruments, laboratory space, and equipment located in the Carroll Chemistry and Biology Departments and pay the institution a percentage of the gross income. If the College wished to terminate its association with Bionomics Corporation, it was required to provide a one-year termination notice. The corporation also agreed to make additional contributions to the academic institution as financial circumstances allowed.

Following a year of operation we recognized that most laboratories were providing specific services (specific analytical tests, analysis of samples, evaluation of products) but few were interested in accepting general problems that required an understanding of fundamental laws of science and expertise in many areas. This, therefore, became our "area" of work, and we have had little or no competition. Our clients include consultants with no direct laboratory affiliation who require laboratory data to substantiate their proposals, other laboratories not interested in working on non-routine problems, and industries having problems but lacking in-house expertise.

Examples of Problems and Projects

Over the last eleven years, Bionomics Corporation has worked with more than 60 different clients. The following examples indicate the challenging work that is involved and the great diversity of projects.

- Research was done to develop a process for the addition of sodium silicate to public water supplies to control high iron concentrations. The process had advantages over the more common sodium phosphate addition process. Bionomics Corporation now monitors and solves community water problems in several states.
- 2) An attorney asked if it were possible for an analytical chemist to "analyze" a spent ampoule from a police breathalyzer test and answer some questions regarding the validity of the test. Research on the reaction of alcohol and other organic compounds with K₂Cr₂O₇ with respect to rate, completeness of reactiou, temperature dependence, and micro methods analyses produced sufficient answers to win a court case. This was followed by many other cases, and eventually a new Wisconsin law was enacted which required all police departments in Wisconsin to save all spent breathalyzer vials until after the court trials.
- 3) A company was interested in manufacturing artificial cheddar cheese and asked that several components of the cheese be identified. A technique involving headspace sampling was developed that was able to determine micro quantities of several cheese components in biological media.
- 4) A California-based company was interested in determining the amount of pectin lost from lemon rinds when the rinds were exposed to storage in the sun. A series of reactions involving several parameters with analyses of products was required in the study.
- 5) A gear manufacturing company had a recurring problem of oversized gears after heat treatment of the product. A special chemical reduction technique has been developed to economically remove a few thousandths of an inch of metal from finished gears.
- 6) Bionomics Corporation performed the analytical testing ou several cosmetic products (hair grooming, facial lotions) that are distributed nationally. This work, lasting three years, was done for a company with headquarters in England.
- An assay was developed for a component in a product used in conjunction with vaporizers. Regular testing continues for this company which is located in Michigan.
- 8) Bionomics Corporation worked with an engineering consultant to describe the feasibilty of converting carbohydrate-containing waste into ethanol. Companies producing materials such as waste barley, corn, spaghetti, and tapioca required a detailed description of how their materials could be converted to ethanol.
- 9) A small community was situated next to two very large and deep stone quarries, and the owners of the quarries were asking the city council for permission to dig deeper by 50 feet. The people were asking questions such as, "What effect will these quarries bave on our water wells?" and "What effect does blasting have on the quality of water?". Bionomics Corporation had to design experimental work to answer these questions and then to describe options available, possible concerns for the future, and economic implications.

The process by which students became involved is fairly simple. Students interested in working on projects inform the corporation officers and describe their skills and approximate available time. As projects became available students are hired for the job. Initial discussions describe the experimental work possibilities and as work begins, the student is required to make decisions for and modifications of the experimental

design. All work is done within a time framework, and students can feel the tensions that emerge when designed experiments do not work. At times, critical experiments must be completed during exam week, and students quickly learn to accept responsibilities.

Evaluation

As we look back on work done over the past decade, Bionomics Corporation has accomplished most of its goals. Every year Bionomics Corporation employs twelve to fifteen students and provides for them an experience beyond the regular science curriculum. Some students graduate with more than twice the usual laboratory experience. Students, as employees of Bionomics, earn a reasonable wage, and several students are able to earn several thousands of dollars each year. Upon graduation the list of Corporation projects is clearly described on the students' resumés.

The time involved in running Bionomics is difficult to assess, and, at times, the pace is fairly intense. Carroll faculty have never received a reduction in teaching hours or committee work to direct this work. The hours would approximate the effort associated with an active undergraduate research program. Much valuable time was gained when we stopped writing yearly grant proposals for research funds, student stipends, and faculty summer salaries, although our grant activities have continued in other areas. The average gross income for Bionomics Corporation has been about \$20,000 per year over the last ten years, and we are able to give a substantial check to the college administration every year.

The problems we have solved have become excellent student laboratory experiments in chemistry courses and practical examples of chemical concepts and theories in lectures. This decade of industrial experience has provided a deeper understanding of the operational parameters that guide the business world and we can relay this information to our students. Business contacts, job vacancies, and new needs in technical expertise have been valuable in improving career counseling services.

The College administration has appreciated Bionomics Corporation because of its academic and financial contributions and because it required no institution funds to get started. The College admissions and development offices are aware of Bionomics and its contributions. They believe that this venture has strengthened the academic program and produced many friends for the College.

Ingredients for Success

Several ideas and suggestions are listed to help describe and characterize the people and operational conditions that are useful in forming a successful corporation.

- Start a private corporation for the right reasons. Bionomics Corporation was designed as a for-profit operation, but it has always maintained its primary goal of helping students in their educational experiences. Many times during the last decade people have suggested and described in detail plans that would multiply work activities by a factor of twenty or more. These plans would have increased profits but they also had the potential of distorting the other major objectives of the program. Therefore, one should be absolutely certain of his priorities before beginning.
- The concept of a corporation must fit into the goals and objectives
 of a science department. There must be individual, departmental,
 and administrative support.
- It is very useful for faculty to attract the best available talent from
 the industrial world as partners. This special expertise is very
 useful in solving prublems and answering questions. The concept
 of a private corporation is a great incentive for industrial leaders
 to become interested in a new venture.
- The name of an academic institution is extremely important, and it must be prutected at all times. A corporation may do useful work in many areas including the courtroom, and it is therefore recommended to form a private corporation that is separate from the academic institution.

- It is advantageous to form a company with no permanent employees. One of the most frustrating problems in husiness arises when promises are made which cannot be fulfilled because there is no work. It is important that faculty feel no unusual pressures to seek work. When there is work to be done, competent people (students) are hired for the job, and the academic institution receives its share of the income. Other than telephone, telephone listings, and bookkeeping costs, there are no fees, rents, etc., that must be paid on a regular basis.
- Recommended characteristics of principal corporation ufficers: It is important to develop a rapport with people working in industry, to listen to problems, and to define questions. It is important to communicate with people in many different technical areas, to build a network of friends, and to become an "expert" in many areas in a relatively short period of time. It is useful to be able to be involved in many things at once, to be able to make estimates of work time, to relate to economic pressures, and to be able to make important decisions based on minimal technical data. Above all, it is important to have good credentials as a laboratory scientist and to have confidence that a problem can be solved.

Conclusion

The formation of Bionomics Corporation eleven years ago in unique association with Carroll College has been very useful to many students. From its first day, the company moved in positive directions, providing relevant experiences to students and helping them pay their college bills, sharing profits with the College, attracting science students to Carroll, and being a service to many people. The corporation did not involve College dollars to get started, it is integrated into the curriculum, it does not depend on government support, and its limits are bounded only by the creativity of its officers. The Corporation has never forced the College or the department into an unwelcome situation or direction.

It is difficult to project how an arrangement of this kind would work at other academic institutions. There is potential of course, for twisting the goals of such an enterprise and using it for self gain. If deep trust and integrity exists among all those involved, the possibility for success is great.

report of the polymer core course committee

Polymer Samples for College Classrooms

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University of Southern Mississippi, Hattlesburg, MS 39406

Gerald S. Kirshenbaum

Celanese Engineering Resins, Summit, NJ 07901

Laboratory experiments aid the student in gaining some practical information on polymers, and this knowledge can be enhanced by the use of available samples of commercial polymers. Many firms producing polymers are aware of the educational value of commercial samples but have not been able to establish liaison with the professors, and vice versa.

Accordingly, Charles E. Carraher, Co-chairman of the Pulymer Education Committee of the American Chemical Society, appointed the authors of this report as members of a subcommittee to compile a list of sources of commercial plastic samples and to make this list available to chemistry professors seeking such samples.

Fortunately, the Education Committee of the American Society of Metals had already published a list with the names of 22 companies and Vern DeCorte of ARCO Chemical Co. and Charles R. Morin of Packer Engineering Associates have granted permission for the ACS Polymer Education Committee to incorporate their list into the accompanying comprehensive list.

It is our sincere hope that this will not only aid chemistry professors in securing polymer samples but that it will encourage other firms to add their names to this important list. The members of the subcommittee will continue to accept new names of suppliers with the object of publishing an addendum to this initial list.

Sources of Polymer Materials

This list provides sources of polymers and technical information whom professors can contact directly. The companies listed are usually willing to provide gratis small quantities of their standard commercial products to universities for teaching or research purposes. It should be understood, however, that special requests for noncommercial materials might necessitate some minimum charge. The following tables indicate the type of polymer and forms (resin, fiber, film, molded parts, etc.) that are available. In addition, all companies have offered technical brochures and other descriptive information. The companies and key contacts are also provided.

Special thanks go to the Society of Metals which has included polymers in its directory of samples and allowed us to use its listings in this report.

1. B. F. Goodrich C. A. Daniels Elastomers P.O. Box 122 Avon Lake, OH 44012 (216) 933-6181

Mark Dannis 9921 Brecksville Rd. Brecksville, OH 44141 (216) 447-5000

2. Ethyl Corp.

A. J. Haefner P.O. Box 341 Baton Rouge, LA 70821 (504) 359-2226

3. General Electric Corp. Daniel W. Fox Plastic Tech. Dept. One Plastic Avenue Pittsfield, MA 01201 (413) 494-4911

4. Stauffer Chemical Co. S. Altscher Eestern Research Ctr. Dobbs Ferry, NY 10522 (914) 693-1200

5. Bordon Chemical

Arthur J. Yu Thermoplastic Div. 511 Lancaster St. Leominster, MA 01453 (617) 537-1711

6. Hoechst Fiber Industries W. S. Wagner Box 5887 Spartanburg, SC 29304

(803) 579-5238

7. Borg Warner Chemical G. A. Momeau Technical Center Washington, WV 26181 (304) 863-7054

8. Hooker Chemical Corp. A: H. Colwell

> **Durez Division** Walck Rd. N. Tonawanda, NY 14120

(716) 696-6320

9. Ciba-Geigy Corp.

J. Saunders 444 Saw Mill River Rd. Ardsley, NY 10502 (914) 478-3131

10. Ashland Chemical Co.

William L. Tordoff Foundry Products P.O. Box 2219 Columbus, OH 43216 (614) 889-4689

11. Allied Chemical Corp.

G. J. Schmidt Box 1021 A Morristown, NJ 07960 (201) 455-3335

12. Air Products & Chemicals

J. T. Wharton Trexlertown Labs #1 P.O. Box 538 Allentown, PA 18105 (215) 398-6703

13. ICI Americas inc.

H, J. L. Schuurmans P.O. Box 411 Hopewell, VA 23860 (804) 541-9395

14. Phillips Fibers Corp.

J. G. Scruggs P.O. Box 66 Greenville, SC 29602 (803) 242-6600

15. General Electric Co.

H. P. Thomas Laminated & Insulating Materials Business Dept. 1350 S. Second St. Coshocton, OH 43812 (614) 622-5310

16. PPG Industries

R. Dowbenko P.O. Box 9 Allison Park, PA 15101 (412) 487-4500

17. Dow Chemical

J. N. Schramm Quality Assurance 2030 Dow Center Midfand, MI 48640 (517) 636-4590

18. Arco Chemicals

G. Alan Osan (Styrenics) 1500 Market Street Philadelphia, PA 19101 (215) 557-2832 LaVern J. DeCorte (others) 3801 West Chester Pike Newtown Square, PA 19073 (215) 359-2518

19. Tennessee Eastman Co.

W. C. Wooten Kingsport, TN 37662 (615) 246-2111, Ext. 2776

20. Goodyear Tire & Rubber Co.

W. Perkins, Polyesters (216) 794-7639 R. E. Fruzzetti, Polyurethanes (216) 794-3974

J. Lal, Polybutadiene & SBR Rubbers (218) 794-3196 R. A. Marshall, Polyvinyl Chloride (216) 794-7119

Elastomer & Chemical Research 142 Goodyear Blvd. Akron, OH 44316

21. Monsanto Plastics & Resins Co.

Customer InquiryCenter 800 N. Lindbergh Blvd. St. Louis, MO 63166 (314) 694-1000

22. Sherwin-Williams Co.

J. L. Gordon Chemical Coatings Division 11541 S. Champlain Ave. Chicago, IL 60628 (312) 821-3000

23. Celanese Plastics & Speciattles Co.

E. Mulligan Desk 300 Box 1000 Summit, NJ 07901 (201) 522-7500

24. Hercules, Inc.

L. M. Landoil Wilmington, DE 19899 (302) 995-3000

25. Phillips Chemical Co.

R. E. Benefield Plastics Tech. Ctr. Bartlesville, OK 74004 (918) 66 t-9420

26. Mobay Chemical Corp.

H. S. Byroe. Penn Lincoln Pkwy. West Pittsburgh, PA 15205 (412) 777-2000

27. Firestone Corp.

J. F. Cornellus 1200 Firestone Pkwy. Akron, OH 44317

28. Bell Laboratories

L. Thompson 600 Mountain Ave. Murray Hill, NJ 07974 (201) 582-3000

29. Malaysian Rubber Bureau 15 Atterbury Blvd. Hudson, OH 44236 (216) 653-8282

30. Albany International

Ernest Kaswell Route 128 at U.S. 1 Dedham, MA 02026 (617) 326-5500

31. Wilson-Fiberfil

V. DuPont P.O. Box 3333 Evansville, IN 47732 (812) 424-3831

32. Calgon Corp.

R. G. Smith Box 1346 Pittsburgh, PA 15230 (412) 777-8000

33. Custom Reshis

W. M. Warner P.O. Box 933 Henderson, KY 42420 (502) 826-7641

34. Curwood, Inc.

G. Shudy 718 High St. New London, WI 54961 (414) 982-5110

35. Celanese Fibers Company Henry Taskler P.O. Box 1000

Summit; NJ 07901 (201) 522-7500 36. Drew Chemical Corp.

Edward Antonucci One Drew Chemical Plaza Boonton, NJ 07005 (201) 263-2789

37. Johnson Wax

Sally Aiello 1525 Howe St. Racine, WI 53403 (414) 554-2000

38. Molded Dimensions Inc.

B. P. Barry 701 Sunset Road Port Washington, WI 54074 (414) 284-9455

39. A. D. Smith-inland inc.

Kenneth J. Oswald 2700 W. 65th Street Little Rock, AR 72209 (501) 568-4010

40. Norplex

Kim Evenson 1300 Norplex Drive La Cross, WI 54601 (608) 784-6070

41. Square D Company

Tim Early P.O. Box 3107 Asheville, NC 28802 (704) 252-0300

42. Menasha Corp.

Stephen McSweeney Molded Products Group 426 Montgomery St. Watertown, Wi 53094 (414) 261-3162

43. Rexham Corp.

Michael Finnegan Flexible Packaging Div. U.S. 31 North Edinburgh, IN 46124 (812) 526-5511

44. The West Company

E. J. Smith Phoenixville, PA 19460 (215) 935-4500

45. Kenrich Petrochemicals

Salvatore J. Monte E. 22nd St. P.O. Box 32 Bayonne, NJ 07002 (201) 436-5610

46. Organometallics, Inc.

Route 111

East Hampstead, NY 03282

47. The Society of the Plastics Industry Inc.

355 Lexington Avenue New York, NY 10017 Write for SPI Literature Catalog and teaching aids.

48. Society of Plastics Engineers

14 Fairfield Dr. Brookfield Center, CT 06805 43 controlled samples of commonly used plastics are available at nominal cost.

49. Polysciences Inc.

B. D. Halpern Paul Valley Industrial Park Warrington, PA 18976 Catalog of Monomers and Polymers

50. Owens-Corning Fiberglas Corp.

Ann Bucher Marketing Communications Fiberglas Tower Toledo, OH 43659

51. Helvoet Pharma Inc.

John T. Cronin 9012 Pennsauken Highway Pennsauken, NJ 08110

52. McWhorter Inc.

R. R. Harris Cottage Place Carpenterville, IL 60110

53. Kontron inc.

Barry Asher 9 Plymouth St. Everett, MA 02149

54. Deertield Scientific Co.

S. Sherr, Mor. P.O. Box 284 Randalistown, MD 21133

55. AMP Inc.

B, H. Olmstead P.O. Box 3608 Harrisburgh, PA 17105

A variety of polymer samples from their analytical laboratory are availabie.

Materials Available Keyed to Sources

| · Materials | Sources |
|-------------------------------------|---|
| ABS | 7, 17, 26, 31 |
| Acetates | 5, ‡2, 18, 30 |
| Acrylics | 16, 28, 30, 52 |
| Afkyd | 10, 16 |
| Dellulosics | 19, 24, 30 |
| Chlorinated Polyethylenes | 17, 24 |
| Chlorinated PVC | 1 |
| Eastomers | i, 20, 44, 51 |
| • | 24 |
| Epichlorohydrin Elastomers | |
| роху | 9, 15, 17, 40 |
| thyl Cellulose | 17, 24 |
| fluoropatymers | 11, 30, 37 |
| urfural Alcohol | 10 |
| (evlar | 30 |
| lelamine | 40 |
| latural Rubber | 27, 29 |
| łomex | 30 |
| lylons 6 | 11, 31, 33 |
| 6, 6 | 23, 30, 31, 34, 41, 43 |
| Others | 31 |
| | 3, 8, 10, 15, 40, 41 |
| Phenolic | |
| olyacetal | 23, 31, 41 |
| olybenzamidazole | 30 |
| olybutadiene | 1, 20 |
| olycarbonate | 3, 26, 31, 42 |
| olyesters Thermoset | 16, 37, 41, 42, 50 |
| PET | 6, 13, 19, 20, 26, 30, 34, 41 |
| PBT | 3, 23, 31, 41 |
| Others | 19 |
| olyother Urethano | 37 |
| olyethylene | 11, 17, 18, 19, 25, 28, 31, 34, 42, 43, 44 |
| • | 30, 40 |
| olyimkle | · |
| olyphenylene Oxide | 3, 42 |
| olyphenylene Sulfide | 25, 41 |
| olypropylene | 14, 18, 19, 23, 24, 25, 29, 34, 35, 42, 43 |
| olystyrene | 17, 18, 28, 31, 42 |
| olysulfone | 28, 30, 41 |
| olyurethane | 1, 10, 16, 20, 53 |
| olyvinyl Chłoride | 1, 2, 4, 5, 12, 20 |
| BR Rubbers | 20, 51 |
| tyrene-Acrylonitrile | 17 |
| lyrene-Butadiene | 17, 20, 25 |
| ityrene Maleic Anhydride | 18 |
| · · | |
| inyl Ester | 17 |
| inylidene Chloride | 17, 34 |
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| astics and Resins (unspecified) | 21 |
| eactive Coatings (unspecified) | 22 |
| olyelectrolytes | 32 |
| olymers as Flocculants, Dispersants | 3 6 |
| ater Soluble Polymers | 24 |
| later Borne Emulsion Products | 37 |
| tanate Coupling Agents | • |
| Imping Rubber Kit | |
| iphatic tsocyanates | 26 |
| | 28 |
| ire and Cable Materials | |
| ot Melt Adhesives | 19 |
| SHAPE/FORM | |
| olymer Sample | 1-12, 16-21, 23-26, 28, 29, 31-34, 36-38, 41-43, 48, 55 |
| ber | 6, 11, 14, 19, 20, 24, 30 |
| lm | 13, 17, 24, 34, 35, 43 |
| reet | 3, 11, 15, 18, 20, 43 |
| ompounds (filled) | 3, 7, 25, 26, 31, 38 |
| mulsion | 5, 12, 37 |
| tex | 5, 17, 27, 29 |
| am | 17 |
| | |
| aminate (Cu-clad) | 15, 40 |
| aminates (unclad) | 23, 34, 40, 43, 52 |
| pating | 10 |
| bric (non-woven) | 14, 30 |
| olded Parts | 25, 38, 41, 42, 44, 48, 55 |
| pamed Molded Parts | 42 |
| Ire and Cable Materials | 28 |
| pe and Fittings | 39 |
| | |

Bits and Pieces, 19

Most authors of Bits and Pieces will make available listings and/or machine-readable versions of their programs. Please ead each description carefully to determine compatibility with your own computing environment before requesting materials from any of the authors. Revised Guidelines for Authors of Bits and Pieces appeared in the December 1982 and December 1983 issues of the JOURNAL.

This month's Bits and Pieces begins with another tested review of a noncommercial teaching program.

POLYMERLAB

Fred D. Williams, Michigan Technological University, Houghton, Mi 49931

Hardware: Apple II+, 48K, 1 disk drive

Software: OOS 3.3, Applesoft

Level and subject: Senior or graduate polymer lab

Available from: Project SERAPHIM, Apple Disk #5; cost \$4 for disk and documentation

The adventure game "Polymerlab" is designed for senior and graduate-level students in polymer science. There is no question that students will need a basic understanding of polymer science to complete the game. The player explores a research laboratory, has seven tests run on an unknown polymer (IR, DSC, elemental analysis, viscometry, asmometry, light scattering, electron microscopy, and NMR) and performs experiments in a chemistry lab by typing in two-word commands to the computer (i.e., go north, take viscometer, do experiments, etc.). There are many problems that must be solved and items found before certain activities, experiments, and tests can be accomplished. One example is: to work in the lab you must have safety glasses, which the thin librarian will only give you if you give her a sandwich (which you must find!).

Documentation for adventure games is always (unfortunately?) brief and ambiguous. Polymerlab is nu exception. I assume the feeling is that half the fun is finding out how to play the game. There is a letter to the instructor that hriefly explains what is needed to perform the tests on the unknown polymer. When the game is started the introduction gives general directions on how to play the game. As players become familiar with adventure game playing they realize the options available to them. Early on, however, adventures can seem very con-

fusing.

One very nice feature is that the game can be saved while in progress and then continued at a later time. This worked out very well for the students who had only a short amount of time to play at any given session. Also, when completely stumped a student could save the game and go get help. A cheat program (for the instructor to check the students' results) is available. This program must be removed from the student disk!

We did not find any "bugs" in the program, although the procedure for seeing the test results was somewhat awkward.

The documentation indicates that the game should take 4–6 hr to play. We found that to be very unreasonable; it generally took our students 10-20 hr to play (I hope this is not a reflection on our studeuts). I feel that it is too long to use in a classroom or laboratory situation. To use the game as part of a lab course in the future I will give the students additional information about what must be done

to complete the game rather than having them figure it out for themselves.

The subject matter is well covered and very accurate except, however, for the IR spectra which leave a little to be desired and are difficult to interpret.

The students' reactions to the game were mixed. In general all of the students enjoyed playing the game and applying their polymer science knowledge to complete the game. However, the students that were not previous adventure game players were often lost and needed help to continue the game. Even the accomplished adventure players spent over 10 hr completing the game. The general feeling of the students was that the game should include information about what was needed to complete each experiment (for example, when one tries to run the NMR the program could say "to run an NMR you need solvent aud NMR tubes"). This would still have the same value as a polymer science game and would cut down the playing time to a more reasonable 4-6 hr, making the game faster moving and much more fun for the students who are not adventure game fanatics.

While watching the students play the game, I could see that they were very involved and completely enjoying themselves except when they got to a point where they did not know what to do next. At this point they needed help to continue not because of their lack of knowledge of polymer science but because of their lack of adventure

game knowledge.

Overall, I think the game is very good. I plan to write up an additional instruction sheet for the students in my polymer science laboratory course that want it. This will include a map and indicate what is needed to complete each experiment. I feel this will not hurt the game and will allow all of the students to complete the game. I will also make the game available to all of our undergraduate and graduate polymer science students to play on the computer. I like seeing the students playing this game instead of the games (Pac-Man®, etc.) that they generally play.

BERNARD GORDON III

Materials Science & Engineering Polymers Pennsylvania State University 325 Steidle Building University Park, PA 16802

Review II

Throughout the course of this review, I, as one who has not greatly utilized computer materials as an integral part of my instructional effort, am forced to contemplate this "wave of the future." I am forced to think what this new method of education means to us old educators who did not use floppy disks in our school days. I used a circular slide rule in school, but was able to adjust to the calculator revolution, but here we are talking about greater magnitudes of difference. Does utilization of this new technique mean that an actual hands-on laboratory experience for the student will disappear? With

| Summary Ratings | | |
|------------------------|------------|----------------|
| Category | Reviewer I | Reviewer if |
| Ease of use | Good | Average |
| Subject matter content | Excellent | Good-excellent |
| Pedagogic velue | Good | Good-excellent |
| Student reaction | Good | Average |

disappearing equipment budgets for expensive specialized laboratory instrumentation such as laser-light scattering or membrane osmometers, one can still "teach" these topics for the cheap price of an Apple IIe. It is also a lot easier since one doesn't have to make up solutions for the osmometer or seek a dust-free environment in which to do light scattering but, instead, only locate an electrical outlet and the necessary software package.

The necessary software package in this case was Fred Williams' "Polymerlab." This is an "education adventure game" that has as its purpose the identification of an unknown polymer. One could easily extend this concept to a qualitative or quantitative analysis laboratory and even to a qualitative organic laboratory with its heavy emphasis on spectroscopy.

The adventure game idea used here is significantly different from "refresher course" or lecture review/supplement packages such as Stanley Smith's "Introduction to Organic Chemistry" [reviewed by Hutchcroft and Susskind, J. CHEM. EDUC., 60, A179 (1983)]. Here, certain data require a library search, simulated laboratory equipment must be accumulated, one must decide how to enter the facility, safety glasses must be located before an experiment can be started, and successful completion of the unknown identification comes about only after the students take the research director's quiz on the unknown. Some students must try to find a lost notebook in order to verify their results. All essential ingredients of a laboratory experience are utilized and blended together very creatively to produce an introduction to analytical polymer chemistry.

This program is not really intended for the novice but assumes some course work or other experience in polymer chemistry. It was particularly useful in the situation where I first used it, which was with a group of students in my polymer synthesis advanced undergraduate laboratory. The analytical content of this program makes it a perfect complement to a course that has a heavy organic polymer synthesis emphasis. The students all had had a one-semester introductory lecture course and some were enrolled in a coatings technology degree program. About half way through the course, after the students had successfully carried out step-growth and chaingrowth synthesis reactions, they were charged with the task of using this program to find out the identity of an unknown polymer on their own time over a two-week period. They could sign out the disk at their convenience. Planned dilute solution viscosity and DSC experiments (which appear in Polymerlah) were dropped from my laboratory schedule in favor of an epoxy synthesis.

Four of the better students wrote their observations and feelings on the experience of using the computer in lieu of a "hands on laboratory" experience. One of these four was successful in identifying the unknown and took the quiz in the research director's office. This quiz even incorporated a little of the history of polymer chemistry in it. This student said she spent 10 hr solving the unknown and had to make a map of each of the rooms for positioning of where everything was. Some experiments couldn't be carried out because of difficulty in finding solvents, NMR tubes, or other necessary equipment. In general, the students didn't like having to spend time trying: (1) to figure out how to get into the building; (2) to find where the safety glasses were; (3) to find the viscometer and light-scattering tubes and other "adventure-like" preliminaries before the experiments could be carried out. But, generally, all students seemed to like and enjoy interpreting the data in order to deduce the unknown structure. One student was able to complete only five out of eight experiments, became frustrated in trying to locate equipment, and commented that more printed information such as a list of input statements should accompany the all-too-brief instructions. Such an experience in frustration realistically simulates the difficulties one often encounters in trying to locate some

chemical or piece of equipment in order to do an experiment, and for this reason the lesson in patience is well taught here.

The average time the students spent on the program was 7 hr—the lowest 4.5 hr. I intentionally gave them no assistance in running the program or in interpreting the directions. One of my goals was to explore the feasibility of utilizing this experience in the future as a truly independent study project. One student admitted great difficulty in using the 120 or so commands possible and was able to progress only by discussing with the others how they accomplished their success. I noticed there was some spirited discussion between the individuals on various parts of the adventure and only one student thought to "climb a ladder to find a solvent on top of the file cabinet." (Safe chemical storage practices are certainly not taught here.) The students did request that I make some polymer texts available to them while they were using the program, which I did,

In retrospect, I think I didn't allow the students sufficient time to investigate their unknowns at their own pace, and I would modify my handling of this assignment in the future. I would carry out the "hands on" lab synthesis experiments as planned, and at the beginning of the course give each student an individual copy of the disk with instructions to solve the identity of the unknown polymer by the end of the course. The degree of success each of the students had in identifying the unknown, or in doing the experiments necessary to identify it, parallels the amount of time the students spent with the program. The experiments in the program that replaced the ones I had planned were IR, DSC, viscosity, osmometry, and NMR. We didn't have equipment and I had not planned elemental analysis, light scattering, Raman or electron microscopy. The advantage to me in using this program was to have additional real laboratory time for polymer synthesis experiments. But at the same time I was able, with this CAI project, to incorporate polymer analysis into my course. For this reason, I found the program very useful,

Could this program be used as a complete substitute for a laboratory experience in polymer chemistry? All students answered "no" to this question; they all seem to enjoy the laboratory experience and learning new techniques. Almost all felt that it is a very valuable supplemental experience and should be available to future students taking the synthesis lab. They commented that it was an excellent problem-solving experience. Given the importance of polymer chemistry and the equipment limitations that many schools will have in bringing this subject into the mainstream of the traditional chemistry professional program, I would tend to answer "yes" to the question above. A good polymer lecture course followed by a tutorial or independent study semester using this program would be an excellent way to introduce this muchneeded subject area to an undergraduate chemistry major. If a school is not equipped to do these experiments, I would recommend by all means that this program be used. It lacks the stimulus of having a "live" instructor but it does teach self-reliance and independence, and for these reasons CAI does have its place in the total education effort that we make in chemistry.

In addition to this program one should consider the ACS computer course "Introduction to Polymer Chemistry" also usable on the Apple II. A trial disk as a test is available from ACS headquarters in Washington and a review of the course will appear in the "Reviews" section of THIS JOURNAL in April. In combination Polymerlab and the ACS course represent a total package for those wishing to hring polymer chemistry into their programs without additional teaching staff.

JERRY R. WILLIAMSON Eastern Michigan University Ypsilanti, Mi 48197 Editor's Note: The following comments on the reviews of GASLAWS published in the December 1983 issue indicate changes made in Project SERAPHIM materials in response to reviewer suggestions. They also indicate a common problem faced by authors who try to write microcomputer-based drills that involve numeric problems.

Comments on Reviews of GASLAWS

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GASLAWS is an adaptation of a mainframe program we have used for a number of years as part of an extensive CAI package. For each unit in the lecture course, e.g., ideal gases, there is a program the students use as a first problem set to cover mechanical-type exercises upon conclusion of the unit. Students work the problems at a terminal and a summary of their scores goes to the instructor. As a result of this philosophy individual programs do not contain expository material, discussion of the program's scope, or an indication of the scoring system. These are provided in a single handout at the beginning of the semester.

In-program directions are intended to be terse but complete, as a reminder of any forgotten feature of the package. The program is designed to be modifiable, and it may be necessary to tailor the directions to a local situation. Examples noted by the reviewers where this would appear desirable are: (1) numeric expressions like 3*5/4 can be entered as problem answers, as stated in the introduction, at the end of each problem, and in the SCRATCH PAD directions; (2) the hierarchy of arithmetic operations and the need for parentheses is stated in the SCRATCH PAD directions; (3) answers calculated by SCRATCH PAD can be submitted directly as problem responses without rekeying, by using the #-key feature, but this feature was only implicit in the instructions. It has been made explicit in the updated version so that future users will not miss this important feature.

The current program prints all numeric values to three significant figures (four in SCRATCH PAD), and checks accuracy of responses to 1%. These two parameters can be varied easily by the instructor. The problems with significant figures, noted by the reviewers are inherent in Microsoft BASIC and not unique to GASLAWS or the IBM PC. BASIC will not print trailing zeros to the right of the decimal point, i.e., 13.0 and .210 are printed as 13 and .21; therefore occasional discrepancies in significant figures are bound to occur. A similar problem that occurs only occasionally and was not noted by the reviewers is printing of some numbers with repeating nines, e.g. 49.9999 when 50 is intended, despite the programmer's best efforts. This problem seems to occur less frequently with the IBM BASIC compiler and can be circumvented completely by printing only double precision numbers, but that doesn't help when significant figures are important.

Computer-Simulated Distributions of Molecular Speeds

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Computer-aided instruction has many uses, important among which is the simulation of experiments that would be too costly or too complicated for a student laboratory. One such experiment concerns the study of kinetic theory and molecular velocity distributions as they develop on a microcosmic scale. Physically, such experiments are difficult and are often replaced by studies of indirectly related macro phenomena such as the transport properties of gases, the complexity of which often obscures the important aspects of the theories which are being emphasized.

We have developed a computer-assisted package that not only simulates the experimentally accessible three-dimensional problem of the unfolding of velocity distributions, but also allows study of one- and two-dimensional cases. Experimentally, the simulation relates directly to kinematic descriptions of shock waves, explosive modeling, and distributions in supersonic nozzle beams where relaxation from an initial energy input is important. Pedagogically, the package allows the instructor to help students obtain a strong intuitive understanding of velocity distributions and their development by proceeding from conceptually simple to conceptually complex situations while retaining a direct tie to physical reality. Thus, the student can be led through an increasingly complex set of simulated situations that finally result in an understandable, usable model of three-dimensional physical reality.

This group of simulated experiments has several objectives in addition to the primary goal of providing data useful in studying kinetic theory and velocity distributions. Among these are

- 1) Teaching computer programming.
- 2) Teaching statistical data analysis.
- 3) Teaching the usefulness and limitations of models.

The package is appropriate for use in physical chemistry laboratory and can be easily modified for use in advanced freshman laboratories.

A common approach to the development of the kinetic theory of gases found in many physical chemistry texts (1) consists of an ab initio treatment making use of a velocity space approach to yield a two-dimensional form. Actually, using such a model, the one-, two-, and three-dimensional forms can be derived. All three differential functions are shown in Table 1 along with the mean, most prohable, and root-mean-square speed associated with each one. Graphical representations of the distribution functions are shown in Figure 1.

Table 1. Distribution Functions and Related Equations

| I DAGE IV. DISCONDING I AMPLICATION AND INCIDENCE PARTICIPATION | | | | | |
|---|--|---|--|--|--|
| | 1 Dimension | 2 Dimensions | 3 Dimensions | | |
| Distribution Functions | $dn_o = N \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{m}{kT}\right)^{1/2} e^{-mc^2/2kT} dc$ | $dn_c = N \left(\frac{m}{kT} \right) c e^{-mc^2/2kT} dc$ | $dn_c = N \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{m}{kT}\right)^{3/2} c^2 e^{-mc^2/2kT} dc$ | | |
| Most Probable Speed | O | $\left(\frac{kT}{m}\right)^{1/2}$ | $\left(\frac{2kT}{m}\right)^{1/2}$ | | |
| Average Speed | $\left(\frac{2kT}{\pi m}\right)^{1/2}$ | $\left(\frac{\pi k \vec{1}}{2m}\right)^{1/2}$ | $\left(\frac{8kT}{\pi m}\right)^{1/2}$ | | |
| Root Mean Square Speed | $\left(\frac{kT}{m}\right)^{1/2}$ | $\left(\frac{2kT}{m}\right)^{1/2}$ | $\left(\frac{3k\hbar}{m}\right)^{1/2}$ | | |

 $dn_c = number of particles having speeds between c and <math>c + dc$

N = number of particles in the system

dc = incremental speed

a ≖ speed

m = particle mass

7 = Kelvin temperature

k = Boltzmann constant

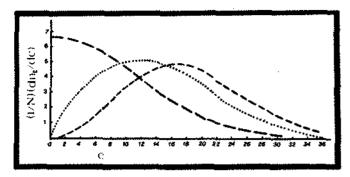


Figure 1. Theoretical distributions. Speed/10⁴ cm s⁻¹ versus $(1/M)(dn_c/dc)/10^{-6}$ s cm⁻¹. One dimension ---; two dimensions ·---; three dimensions ----, T = 300K, m = 2.0 armu.

While the final form of the three-dimensional distribution function is shown in most texts, it is uncommon to see the final one-or two-dimensional distribution function presented. Also, it is interesting to note that the most probable speed for a one-dimensional system is zero.

Programs were written to simulate one-, two-, and three-dimensional distributions. In all cases, up to 100 particles comprise the system under study. Particle direction of motion and position are chosen randomly. However, for each particle, the following parameters can be specified: mass, radius, and speed. In the simplest situation, one begins with particles having the same mass, radius, and speed, although any combination of parameters is possible. Finally, for the system the overall dimensions of the particle container (line, square, or cube) can be chosen as a function of the space occupied by the particles (length, area, or volume).

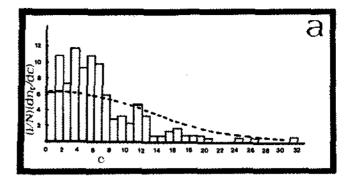
After initial parameters are determined, the particles are allowed to move and collide. All collisions in the two- and three-dimensional systems are assumed to be elastic including those with the walls. In the one-dimensional system, however, insufficient degrees of freedom exist for the distribution to develop, so it is necessary that collisions with the walls be inelastic. That is, the particle closest to each wall can lose or gain energy randomly on collision with the wall in quantities up to the energy possessed by the particle.

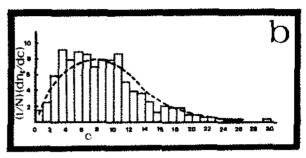
As the distribution unfolds, the speed, position, and direction of motion of each particle can be monitored at chosen intervals. A histogram of number of particles versus speed can be printed at any time along with an overlay of the theoretical normal curve as calculated from the differential forms shown in Table 1. Termination of the program results in a printout of final data as listed above in graphical and tabular form.

The programs were written in extended BASIC for use on a Hewlett-Packard 9845B (56K), and can be modified for most other systems of similar size. Explanations, directions, and appropriate documentation are also a part of the package. Depending on the speeds, system size, number of particles, and size of particles, elapsed real time to randomization varies.

Students can be asked to perform individual experiments on systems up to 100 particles; however, the speed distribution develops only after a relatively long real-time interval. If computation time is critical, each student can be asked to work with systems of 50 particles or fewer observed over short, specified time intervals and data can be combined for final analysis. System dimensions can also be altered to insure more collisions per time interval.

In typical experiments, a student is asked to run a simulation of 50 identical particles beginning at identical speeds. Then, there are several data accumulation and analysis tasks which the student is asked to perform, given the raw data for 50 particle simulations for each class member. Figure 2 shows typical data sets for one-, two-, and three-dimensional cases.





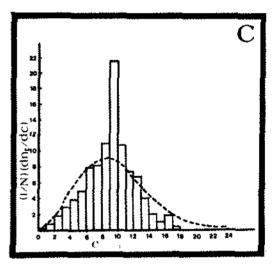


Figure 2. Experimental (bars) and theoretical (dashed lines) distributions. Speed/ 10^4 cm s⁻¹ versus (1/M)($d_c/d_c/10^{-6}$ s cm⁻¹. Part a, one dimension; part b, two dimensions; part c, three dimensions. m=2.0 amu; initial speed = 1.0×10^5 cm/s.

Data shown are ten composites of 50 particles each. Superimposed on each graph is a theoretical distribution curve. Analysis and development is accomplished as follows.

- The student confirms that collision elasticity is maintained in the two- and three-dimensional systems by writing a program that calculates system energy at beginning and end of the simulation. The student also determines the final inelastic contribution of wall collisions in the one-dimensional case.
- 2) The student compares, quantitatively and qualitatively, the one-, two-, and three-dimensional results from the simulation to the theoretical curves. In order to accomplish this, each student must write a program that will accumulate and plot a histogram of class data and plot a normalized theoretical curve. Quantitative comparison of simulated data with theoretical prediction is accomplished using a chi-square goodness-of-fit calculation (2) comparing simulation results to each theoretically predicted curve. The comparison program is written as part of the histogram program and is used for both individual student data sets as well as whole class results.

- 3) The student derives and compares values for $C_{\rm aver}$ $C_{\rm mpr}$ and $C_{\rm rms}$ for all systems for both theoretical and simulated results.
- 4) The student discusses all aspects of the data and results in essay form, explaining statistical fluctuations, curve shapes, and curve comparisons.

More complicated experiments can also be derived, using non-identical particle sizes and/or masses and non-identical initial particle speeds. Data analysis is, of course, much more complex in these situations.

Interfacing Microcomputers through Jaystick inputs

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In today's world, video games touch the lives of millions of people and yet few of these people understand the connection between the manipulations of the joysticks and the subsequent events on the video screen. This article describes how this rather common device can be revised to allow the recording of data from an experiment. The computer used for this investigation is the TRS-80 Color Computer, and the charging and discharging of a capacitor in an R-C circuit (a simulated first-order kinetics reaction) is used as an application example.

Joysticks are used in video games to interface the player with the microcomputer. Normally one does not use the term interfacing to describe this interaction, but, in fact, real time interfacing is the proper term. Figure 3 is a schematic of a joystick connection found on the TRS-80 Color Computer. Pin 5 supplies a 5-V DC voltage. Pin 3 is the ground pin. The 5-V DC potential from pin 5 is connected to pin 3 through a 100-K-ohm potentiometer. The wiper of the potentiometer is connected to pin 1. Another wiper from a similar potentiometer is connected to pin 2. Pin 4 is used for "firing". Moving the joystick from extreme left to right allows the input voltage at pin 1 to vary from 0-5 V while moving the joystick from extreme up to extreme down causes the voltage on pin 2 to vary in a similar manner. Because each joystick uses two potentiometers, and two joystick inputs are available, a total of four analog inputs are available for connecting 0-5-V analog signals to the microcomputer. The voltage at pins 1 and 2 are then sampled by the microcomputer and converted to a 6-bit binary number. A 5-V input signal corresponds to a bit pattern of 63 (all 1's-in a 6-hit register) while a 0-V input signal corresponds to a bit pattern of 0 (all zeroes in the 6-bit register). A 2.5-V input signal corresponds to a bit pattern of 32 (bit 5 is 1 while bits 4 through 0 are 0). A hit pattern may be converted to a voltage by dividing it by 63 and multiplying this ratio by 5.

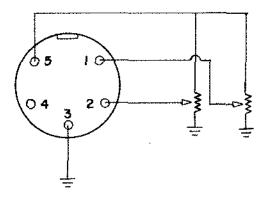


Figure 3. Joystick schematic; Radio Shack TRS-80.

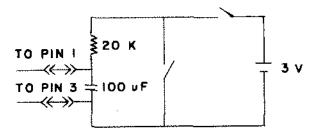


Figure 4. R-C circuit interfaced to joystick input: Radio Shack TRS-80.

Figure 4 shows the schematic for an example application: graphing voltage across a capacitor in an R-C circuit. Shielded leads from pins 1 and 3 of the right-hand joystick input are connected across a $100 \cdot \mu F$ capacitor in series with a $20 \cdot K$ -ohm resistor. The R-C circuit is connected in series with a switch and a 3-V DC battery. The software for graphically recording the voltage across the capacitor is the following:

10 PCLS; 20 SCREEN 1,1; 30 PMODE 4; 40 FOR B = 0 TO 255; 50 A = JOYSTK(0); 60 LINE (B, 180 - 3.5+A) - (B, 180 - 3.5+A), PSET; 70 NEXT B; 80 GO TO 10.

Closing the switch and simultaneously entering RUN allows one to record the data graphically on the video monitor. The discharging curve is recorded by opening the switch and shorting the capacitor through the resistor. The switch in series with the R-C circuit is closed to charge the capacitor, while the switch in parallel with the R-C circuit is closed to discharge the capacitor.

Precautions such as using shielded cable and polarity and not exceeding an input voltage of 5 V should be observed. Shielded cable is necessary for the connection between the microcomputer and the experiment because it minimizes extraneous voltages induced by electromagnetic fields. Voltages greater than 5 V could damage the microcomputer. Polarity reversal could cause the microcomputer to malfunction and possibly even damage it.

Through proper input voltage management (such as using op-amps to condition the input voltage to a value between 0 and 5 V), one may use this simple interface scheme to record data from laboratory instruments. This allows one to use the computer-video monitor as a relatively inexpensive recorder. Four different events may simultaneously be monitored.

Readers who desire to use this interfacing technique are invited to write to me for further information.

Measuring and Calculating Energetics of an Electrochemical Cell

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We describe here a physical chemistry experiment in which the Gibbs free energy, entropy, and enthalpy of the cell are determined from cell potential as a function of temperature. A very inexpensive personal computer is used to acquire, record, and analyze the data. The entire cost of computerizing the experiment is well under \$500, including the cost of a

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television set and a cassette tape recorder, thus making the

system affordable to even small institutions.

The Timex/Sinclair TS1000 is currently the least expensive personal computer on the market and is available at many retail stores for under \$50. The TS1000 is a potentially powerful scientific tool. For example, the Sinclair ZX81 (the forerunner to the TS1000) has been used as an instrument controller (3) and to replace a chart recorder (4). The TS1000 employs the same microprocessor, the Zilog Z80A, found in many other microcomputers costing over ten times as much.

The physically small package of the TS1000 (4 \times 17 \times 17 cm) includes a 2K programmable memory. Tape input and output connections are provided. The operating system is a BASIC interpreter that supports 9-digit floating-point numbers and intrinsic functions used in scientific calculations such as LOG, SIN, COS, etc. The POKE command and USR function provide a means of entering and executing the computer's native Z80 machine code. A line editor is also provided. Its convenience is somewhat offset by the inconvenience of a very small non-standard flat-membrane keyboard. However, standard size keyboards are available as well as a host of other peripheral devices, including printers and memory modules.

The VOTEM analog interface module, available from Down East Computers, 2 is used to convert an analog voltage into a digital frequency for presentation to the TS1000 computer. The module includes a semiconductor temperature probe and a means of electrical connection for measuring voltages between 0 and +1 V DC. The temperature probe allows measurement of temperatures between +25 and +125°C. Resolution of less than 1 part in 20,000 is claimed for a typical VOTEM/TS1000 system, which translates to about 0.00005 V for voltage measurements and 0.04°C for temperature measurements. Absolute accuracy depends on the choice of the calibration coefficients used in the program. These are predetermined from a calibration procedure supplied with the module. Accuracies within ±0.002 V and ±0.5°C are obtainable. The high input resistance of the interface (greater than 200 megohms) allows direct connection to the electrochemical cell and obviates an input buffer circuit.

The VOTEM module incorporates a voltage-to-frequency conversion technique. This technique works well in our application because it offers high resolution and inherent noise immunity (5). The output signal of the VOTEM module is a square wave that swings between 0 V and +5 V and can drive TTL-level inputs. The tape input of the TS1000 computer is coupled to a TTL gate that forms one bit of an input port to the Z80 microprocessor. A Z80 machine language routine is called from BASIC and returns a value proportional to the frequency of transitions at the tape input. Sampling period is determined by the software. Since the data are slowly varying signals, a relatively long conversion period of about one second is used. Any noise appearing at the input is effectively integrated, or averaged, over the sample period.

The apparatus consists of a galvanic cell and constant-temperature bath, a TS1000 with a 16K memory module, a VOTEM analog interface, a black-and-white television set, and a portable audio cassette tape recorder (Fig. 5). A thermal printer that retails for about \$100 is also incorporated into the hardware and the software. The printer provides a convenient form of permanent copy but is not essential. This computer system constitutes a complete and very inexpensive data acquisition system. The cost, excluding the printer, was approximately \$340.

The cell used for testing was

|Ag (Hg)|AgC||CdSO₄ (0.02M)|Cd(Hg)|

Another suitable cell would be

{Cd(s)}CdSO₄ sat'd[Cd(Hg)]

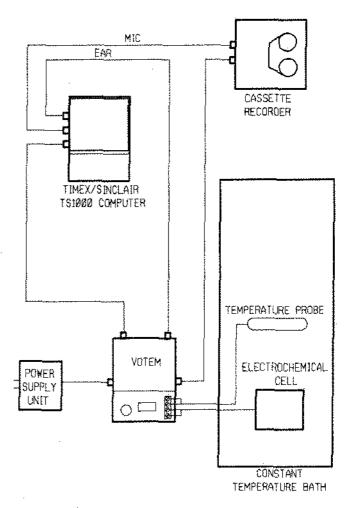


Figure 5. Block diagram of the computerized measurement system.

The TS1000 and the VOTEM module here serve as a potentiometer and thermometer (see Fig. 5). The procedure for collecting data is:

- 1) Adjust water bath to initial temperature.
- Instruct the TS1000 to collect data.
- Collect 6 temperature values, then 6 voltage values, then 6 temperature values. Display and store the mean and standard deviation.
- 4) Bring the bath to the next temperature and repeat the measurement process. (Here a water bath with a programmed temperature ramp would be useful.)

After all data are collected, calculations, including propagation of errors, are performed by the computer. The students are not divorced from the calculations because they are instructed to duplicate the values manually. $\Delta G(T)$, $\Delta H(T)$, and $\Delta S(T)$ are displayed and/or printed. These quantities are calculated by

$$\Delta G = -nFE$$

$$\Delta S = -(\delta \Delta G/\delta T)_{p}$$

$$\Delta H = -[\delta(\Delta G/T)/\delta(1/T)_{p}]$$

 ΔS and ΔH are calculated at the mean temperatures and mean reciprocal temperatures. In other words, the mean derivative is calculated over a small temperature interval.

Data collection is semiautomatic; intervention by the operator is required to manually switch between the voltage and temperature modes. However, additional simple hardware

² Down East Computers, PO Box 3096, Greenville, NC 27834,

Table 2. Data and Calculated Results, Ag-Hg Amalgam Cell

| Temperature (K) | EME (V) | ∆G (kcal/mole) |
|-----------------|--------------------|-----------------|
| 284.42 (±0.03) | 0.84426 (±0.00005) | 81.460 (±0,005) |
| 290.08 (±0.03) | 0.84091 (±0.00005) | 81.716 (±0.005) |
| 295.39 (±0.03) | 0.84833 (±0.00005) | 81.853 (±0.005) |
| 301.35 (±0.03) | 0.84980 (±0.00006) | 81.995 (±0.005) |
| Temperature (K) | | ΔH (kçal/mole) |
| 289.80 | | 71.278 (±0.378) |
| 295.61 | 74.539 (±0.328) | |
| Temperature (K) | Δ | S (cal/K-mole) |
| 289.91 | : | 35.8 (±0.7) |
| 295.72 | | 24.8 (土0.7) |

could be incorporated to realize a fully automatic data collection system.

Some data and results obtained from our cell are presented in Table 2. Deviation from standard values is due mainly to the non-unity activity coefficients of the solid phase components. Our cell was prepared with approximately 2% and 5% silver-mercury and cadmium-mercury amalgams, respectively. The emphasis of this experiment is to insure that the student can perform the calculations on real data, rather than reproducing textbook data.

In an experiment such as the determination of the activity coefficients from cell measurements, the emphasis will be shifted towards the accuracy reproducibility of the data. The measurement system described above will, of course, work equally well in the latter experiment. The system can be adapted to a variety of other experiments in a variety of environments. For example, in one of the many standard undergraduate acid-base related experiments the only additional necessary components are a pH electrode and a high impedance buffer amplifier, or pH meter with chart recorder output.

A BASIC listing of the program used in the experiment is available from the authors upon request. Please include \$1 to cover costs of copy and postage. The program is also available in TS1000 machine readable form on cassette tape for \$10.

One-Semester Microcomputer/Instrument interfacing Course

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We describe here a one-semester graduate course in microcomputer interfacing currently being taught in the Chemistry Department of Rutgers University. Our objective was to teach hardware and software aspects to students having some proficiency in programming and a good background in chemical instrumentation. The course differs from others reported in the literature (6-10) by attempting, in one semester (42 hr), to bring students to a level of competency which would enable them to interface most common laboratory devices. This highly compressed course was designed to quickly give our graduate population the expertise to computerize the data collection procedures required in their thesis research or in their work in the chemical industry. The main thrust of the course was to teach enough of the programming languages (BASIC and assembly), electronics, and interfacing to complete a project within the semester.

Since the Chemistry Department did not have microcomputers before this course was developed, a fully-equipped

Table 3. Interfacing Course Syllabus

| Topic | Time Required (wk) |
|------------------------------------|-----------------------|
| I. Introduction | 1 |
| A. Background Evaluation | · |
| B. Course Description | |
| C. Introduction to Microcomputers | |
| D. Project Orientation | |
| II. Flow Charting | 1 |
| III. Introduction to BASIC | 1 |
| tV. Electronics | 2 |
| A. DC Circuits | |
| B. Integrated Circuits | |
| C. OP-AMPS | |
| V. Number Systems | 1 |
| A. Binary Numbers | |
| B. BCD | |
| C. Hexadecimal | |
| D. Boolean Algebra | |
| VI. AIM-65 | 1 |
| A. Memory Map | |
| B. Versatile Interface Adapter | |
| C. Machine Commands | |
| D. Microprocessor Architecture | |
| VII. Introduction to Assembly | 1 |
| A. 6502 Registers | |
| B. Instruction Set | |
| C. Open and Addressing Modes | _ |
| VIII. Analog to Digital Convertors | 2 |
| A. Programming in Assembly | |
| Programming in BASIC | |
| C. Digital-to-Analog Convertors | _ |
| X. Assembly | 2 |
| A. Text Editer | |
| B. Assembler | |
| C. Subroutines | |
| D. Jump Commands | |
| E. Interrupts | |
| X. Project Demonstrations | 2 |

microcomputer room was established. Initially, three Rockwell AIM-65's were purchased³ and installed in a room which was converted into a computer laboratory. Also, analog/digital (A/D) and digital/analog (D/A) converters were necessary for many of the projects. A unit, available from Excert, Inc.,⁴ contains an 8-channel, 8-bit A/D converter and two 8-bit D/A converters. Three of these units were purchased for student use. In addition, three peripheral boards were built for laboratory exercises. Each board contained 8 LED's which were connected to Port A of the 6522 VIA (Versatile Interface Adapter). Eight dip switches were connected to Port B. By the proper manipulation of machine codes or PEEK or POKE commands, the students could present digital data on the LED's or read the digital data represented by the switch positions.

Several texts were used to cover BASIC programming, assembler programming, and an overview of the field of microcomputers (11-14). A course syllabus is shown in Table 3. Flow charting and a review of BASIC were presented first so that programming assignments could begin immediately. A flow chart was required with every program, and programs and/or circuit problems were assigned every week.

The main objective of the course was to get each student to complete an interfacing project. Each project was chosen to solve a prohlem that the student might have solved using traditional methods. A list of suggested projects are in Table 4.

³ Rockwell International, Anaheim, CA.

⁴ I/O 802, Excert Inc., White Bear Lake, MN.

Projects that do not require an A/D or D/A convertor:

- 1. Counting or measuring with a photocell
- 2. Control of a stepper motor
- 3. Digital piotter
- 4. Parallel printer
- 5. Control of LED's
- 6. Read digital data from switches
- 7. Time of day digital clock
- 8. Event timer
- 9. Morse code send/receive
- 10. Frequency counter
- 11. Games paddles, joysticks
- *12. BCD input from an instrument with BCD output
- 113. Digital thermometer
- 14. Light pen
- 15. Connect two VIA's (versatile interface adapters)
- 16. CRT terminal (or other RS-232C device)
- 17. Bit pad or digitizer
- 18. Speech synthesizer
- 19 Hall effect switches
- *20. Optically coupled switches

Projects that require an A/D convertor:

- * 1. Build an A/D convertor
- * 2. Any instrument with an analog signal (i.e., HPLC detector, A.A., etc.)
- 3. PM tube in a single beam spectrophetometer
- 4. Thermocouple

Projects that require a D/A converter:

- 1. Digital voltmeter
- 2. X Y plotter
- 3. Strip chart recorder

These projects required a considerable amount of effort, and this was taken into account in several ways. There was no final for the course, but every project had to be demonstrated in class. The grade earned on the project counted for 50% of the course grade (25% of the course grade was based on a mid-term and 25% on homework). Since there were many types of projects and each was different in difficulty, a project scoring system was set up. A complexity rating, "C", was assigned to each project depending on the amount of work required. "C" ranged from values of 0.7 to 1.3, depending on how complex the tasks were. At the end of the semester, after the demonstration, a success factor, "S, was awarded based on how much of the project was completed. This factor ranged from 0 to 100%. The project grade was calculated from the product, $C \times S$. Using this system, some students were motivated to take on highly complex tasks with the hope that their project grade would make up for deficiencies in other grades.

Providing the students with an appropriate electronics background proved to be challenging. It was difficult to decide how much and what topics to cover so that all students could complete their projects. However, an especially successful

technique was a one-period laboratory demonstration on the fundamentals of soldering, wire wrapping, bread-boarding, and the use of test equipment such as oscilloscopes and multimeters. This provided students with the expertise to determine the analog characteristics of their own circuits. Operational amplifiers or voltage divider circuits were constructed by the students to match the dynamic range of the D/A-A/D converters. The circuit designs were obtained from various reference books (15-17) or by consultation with the instructors and the departmental electronics technician. Fabrication was entirely the student's responsibility

Any programming course can take from one to four semesters to bring a student up to a high level of proficiency. In this course, only half a semester was left when assembly programming was introduced. The topic was covered to the limit that the class could write and debug simple routines that would interact with more complex BASIC programs. The assembler routines were restricted to data transfer or acquisition through the 6522 VIA. In this way, the students could use a simple assembly routine to complete their project while the lectures covered more advanced concepts in theory.

Our experience was that, given additional help by the instructors, graduate students and upper level undergraduates could attain adequate interfacing facility in a one-semester course. Out of an initial enrollment of 17 students, 12 successfully completed their projects. The major conceptual difficulties were in the use of machine language, and in conditioning analog signals to be compatible with the A/D converter. Consequently, the course has been restructured to spend less lecture time on the BASIC language and more on electronics and the use of assembly language in interfacing.

A more thorough description of the course (which includes details on the individual projects) and a circuit diagram of the peripheral hourd are available through Project SERAPHIM at a cost of \$4. (Make checks payable to Project SERAPHIM, Account 20350.)

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Projects successfully completed by a student.

tested demonstrations

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The Rainbow Connection

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This demonstration illustrates rather dramatically how the color of certain organic acids or bases (acid-base indicators) can be influenced in a reversible manner by changes in pH. It is based on a "magic trick" described by Wilson, et al. Although it has obvious applications as a pedagogical tool, it is described here in the context of a routine which we have employed as part of chemistry demonstrations shows the Iowa State University Society for Chemistry Undergraduate Majors and ACS Student Affiliates has been presenting for a number of years.

The demonstration employs three indicators which are completely colorless in acidic solution but form the three primary colors in basic solution.

Reagents Needed

Indicators

The following combination of indicators give the "rainbow colors" indicated.

RED
 g phenolphthalein plus 3.0 g mnitrophenol
 ORANGE
 g phenolphthalein plus 6.0 g m-nitrophenol

3) YELLOW 6.0 gm-nitrophenol

4) GREEN 0.6 g thymolphthalein plus 6.0 g m-nitrophenol

5) BLUE 1.5 g thymolphthalein

6) VIOLET 0.9 g phenolphthalein plus 0.4 g thymolphthalein

Each of these indicator combinations is dissolved in 30 ml of 95% ethanol and stored in 30-ml dropping bottles labeled with the "color" indicated.

Acid-Alcohol Solution

Mix 250 ml of 0.05 M aqueous sulfuric acid with 250 ml of 95% ethanol. Transfer this liquid to a bottle (capacity 10 oz or more) equipped with an automatic "shot dispenser" as commonly used for alcoholic drinks, delivers 1.5 oz per "shot." (We use a 25.4-oz liquor bottle.)²

NaOH Solutions

Transfer 1200 ml of a 0.012 M NaOH solution to a clear glass pitcher. (The standard 2.5-pt "pitcher" commonly used in beer halls serves very well.³)

¹ Wilson, J. W., Wilson, Jr., J. W., and Gardner, T. F., "Chemical Magic," Chemical Magic, Box 331, Los Atamitos, CA 90720.

 2 A good quality shot dispenser should be used, and the dispenser should be thoroughly cleaned immediately after use. An alternative method, which does not require the use of a shot dispenser is to use a 50-mi graduated pipet, which has appropriate intervals of 5 mi heavily marked so they are more visible, and add 5-ml aliquots to each tumbler. If this procedure is followed, the acid-alcohol solution concentration should be increased. Equal volumes of ethanol and $0.4\ \rm M\,H_2SO_4$ works well.

3 A small mark should be made on the pitcher at a point corresponding to slightly more than the total volume needed to fill the 6 tumblers to be used in the demonstration. The pitcher should contain at least this volume of the base solution.

Prepare a dropper bottle containing 100 ml of a 0.2 M aqueous NaOH solution.

H₂SO₄-Glycerin Solution

Dissolve 10 ml of 18 M H₂SO₄ in 20 ml of glycerol, and transfer the solution to a dropper bottle.

"Doctored" Glass Tumblers

Clean six glass tumblers (approx. 12 oz). Arrange these in a single row extending from left to right along the demonstration table. Place 2 drops of the red indicator in the center of the first tumbler; do not allow any to splash on the sides. In a like fashion, place 2 drops of the orange indicator in the second tumbler, and continue adding 2 drops of each of the appropriately colored indicator solutions in a glass in the proper "rainbow" sequence—red to violet. Allow the solutions to dry. There is no hurry about this. The tumblers can be prepared a week ahead of time, or they can be allowed to stand at room temperature just long enough for the solutions to evaporate to dryness—about 1 br or so. If a heat lamp or heat gun is used to expedite the drying, care must be exercised not to decompose the indicators thermally.

The result should be six tumblers each with a dry film of a different indicator deposited on the bottom; this film should be practically unnoticeable to the audience.

Needed "On Stage" to Present the Demonstration

The six "doctored tumblers" should be arranged in sequence (red, orange, yellow, green, blue, and violet) before a white background. (We have found the added visibility provided by a light box, which illuminates the glasses from below and behind, makes the demonstration especially colorful.) In addition, have on hand

The bottle of acid-alcohol solution
The pitcher of 0.012 M NaOH solution
The dropper hottle of 0.2 M NaOH solution
The dropper bottle of H₂SO₄-glycerin
Stirring rod and towel

The Demonstration Routine

Step 1. Each tumbler is picked up in succession, the inside wiped "clean" with the towel, and the tumbler returned to its proper place in the row. Of course, the indicator film on the bottom must not be disturbed in this operation. (Note: From this point on, various solutions will be added to the tumblers. These additions should always be made in the same sequence, e.g., left to right.)

Step 2. Equal volumes (1 'shot,' 1.5 oz) of the acid-alcohol solution are poured from the bottle into each tumbler using the shot dispenser. In doing this, try to direct the stream of liquid so it does not fall directly on the indicator residue; the less the residue is disturbed and the less the indicator disperses in the solution by the time the next operation is completed, the better the effect.

Step 3. Using the pitcher, add to each tumbler enough of the 0.012 M NaOH solution to fill the tumbler approximately halfway. Pour the liquid slowly, directing the liquid towards the sides. If the base solution comes in contact with the indicator, a momentary "flash" of color may be observed, and one wishes to avoid this as much as possible. At this time, the added NaOH should not be sufficient to render the solution basic.

Step 4. The demonstrator looks at the six tumblers, half-filled with what appears to be a water-clear solution,

apparently observes there is enough liquid remaining in the pitcher to add more to the tumblers, and proceeds to do so, beginning with the first tumbler in the sequence. This time, the solution is poured rapidly from the pitcher and the tumbler filled to approximately ¾-in, from the top. As the liquid is added, each solution is observed to change instantly to one of the "rainbow colors." (The rapid addition of the excess base to the still-acidic solution, which by this time has solubilized the indicator, should mix them adequately and result in an almost instantaneous formation of the base-form of the indicator throughout each solution.)

Step 5. From the dropping bottle, add enough of the H₂SO₄-glycerin solution to each tumbler to return the solutions to their original acidic condition. The same amount of this glycerin-acid mixture should be added drop-wise to the center of each tumbler. Three drops should be adequate, but one should determine the exact amount by experiment before the performance. When the last tumbler is filled, squirt about two droppersful of the acid-glycerin into the pitcher in as inobtrusive a way as possible. If carried out correctly, the very dense acid-glycerin solution will sink to the bottom of the tumbler without dissolving, and the indicator should remain in its hasic form. To insure this, we prefer using the very viscous acid-glycerin solution. The same effect may be achieved with practice using a more dilute mixture (up to a 50:50, v/v, 18 M H₂SO₄-glycerin).

Step 6. The solutions in the tumblers are then stirred rapidly, starting with the first tumbler, and as each solution is stirred, the color disappears. (NOTE: One must not wait too long before starting to mix the solutions, else the colors begin to fade prematurely.)

Step 7. Using the dropper bottle containing the 0.2 M NaOH solution and a stirring rod, rapidly "titrate" the contents of each tumbler back to its original color.⁴

Step 8. The tumblers of solution are then poured, one at a time, in succession, back into the pitcher. The result is a colorless solution, much like the original.

Safety Precautions

Once prepared, the solutions are so dilute that there is virtually no safety hazard with the experiment.

Discussion

We have used this demonstration extensively in chemistry "magic" shows, where the explanation of the phenomena is left to the audience. In a classroom situation, we have concluded the demonstration by asking the students how it was done. The presentation is always given concurrent with a lecture on acid-base indicators. Once the students are informed that only acids or bases are used in the demonstration, and they conclude that there are indicators, other than phenolphtalein, which are colorless in acid solution and turn color in base, they generally deduce what is taking place. This deduction is arrived at only after some rather interesting class discussion and a better understanding of such things as how indicators work and how universal indicators or pH papers are prepared.

⁴ A variation we have used is to pour only enough of the NaOH from the pitcher to obtain the desired color changes in step 4. (About the same volume of solution should be in the tumblers at this point.) Perform step 5, but do not add any of the glycerin-H₂SO₄ acid solution to the pitcher. Instead of performing step 7, restore the colors by filling each glass with NaOH solution which remains in the pitcher. At this point, in as inobtrusive manner as possible the two dropperfuls of the glycerin-H₂SO₄ solution are squirted into the now empty pitcher. The demonstration is concluded as described in step 8. This routine does not require the 0.2 M NaOH, but it does require a bit more skill on the part of the demonstrator to perform it effectively.

Error in the Minimum Free Energy Curve

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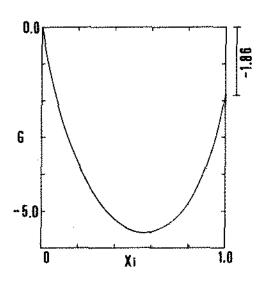
In order to show graphically how a homogeneous chemical reaction occurring at constant temperature and pressure tends toward a minimum of free energy, a curve such as that shown in the figure is often presented. However, some general chemistry texts label the quantity at the right side of this figure incorrectly. They call it ΔG^0 , the standard free energy change of the reaction, $2 G^0(BrCl) - G^0(Br_2) - G^0(Cl_2)$, where the G^{0} 's refer to the standard molar quantities.

The Br₂ and the Cl₂ (considered ideal gases) each start out $(\xi=0)$ at 1 atm partial pressure, which is their standard state. However, since the reaction occurs at a constant pressure of 2 atm, the BrCi ends up $(\xi=1)$ at two atmospheres, not its standard state. Therefore, the quantity referred to as ΔG^0 is actually ΔG^0 plus the change in free energy for increasing the pressure of two moles of BrCl from one atmosphere to two atmospheres, $\Delta G^0 + 2$ RT in 2.

The equation for the figure is

$$\begin{split} G &= (1-\xi)(G^0_{\text{Br}_2} + RT \ln P_{\text{Br}_2}) \\ &+ (1-\xi)(G^0_{\text{Cl}_2} + RT \ln P_{\text{Cl}_2}) + 2\xi(G^0_{\text{BrCl}} + RT \ln P_{\text{BrCl}}). \end{split}$$

Details of the derivation as well as a general discussion of the type of error under discussion here may be found in the paper by Spencer.¹



Chemical reaction:

$$Br_2(g) + Cl_2(g) \xrightarrow{400 \text{ K}} 2 BrCl(g)$$

initial condition: 1 mol Br₂(1 atm) + 1 mol Cl₂(1 atm) $\xi = \text{mol BrCl}/2$, $K_p = 7$, $\Delta G^p = -6.47$ kJ, ξ (at equilibrium) = 0.57

¹ Spencer, J. N., J. CHEM. EDUC., **51**, 577 (1974).

chemical of the month

The Culver Academies Culver, Indiana 46511

Nitric Acid

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Old Names:

Latin: Aqua Fortis, Acidum Nitri, Aqua Dissolutiva

French: Eau de Depart, Acide Nitrique German: Starkwasser, Salt Petersaure

Alchemist's Symbol:



History

The earliest reference to nitric acid is in the writing of the eighth century Arab scholar Geber, who prepared nitric acid by "distilling a pound of cyprus vitriol, a pound and half of saltpeter and a quarter of a pound of alum." In 1658 Glauber obtained concentrated fuming nitric acid by distilling niter with oil of vitriol (sulfuric acid). In 1776 Lavoisier proved that nitric acid contained oxygen. The complete chemical composition was established in 1816 by Gay-Lussac and Bertholet.

Occurrence

A considerable amount of nitric acid is produced by lightning and in the combustion of fossil fuel causing "acid rains" which contain mainly sulfuric acid and nitric acid. Oxides of nitrogen are also formed when air is irradiated in a nuclear reactor. In the combined state it occurs in form of sodium nitrate (Chile saltpeter) and potassium nitrate.

Methods of Preparation

Until 1924, nitric acid was obtained from the reaction of Chile saltpeter and concentrated sulfuric acid. Since then Ostwald's method of catalytic oxidation of ammonia has been used in the manufacture of nitric acid.

From Chile Saltpeter and Concentrated Sulfuric Acid

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

 $NaHSO_4 + NaNO_3 \rightarrow Na_2SO_4 + HNO_3$

Birkeland-Eyde Arc Process

In this process air is passed through an electric arc at a temperature of about 3000°C.

$$N_2(g) + O_2(g) = 2NO(g)$$
 $\Delta H = +43.2 \text{ kcal}$

According to Le Chatelier's Principle, the amount of NO formed will be greater at higher temperatures and will not be affected by pressure. The equilibrium concentration of NO is 0.4% at 1500°C and 5% at 3000°C. This process is not used currently because of the high cost of electricity. Another variation of the above method was developed at the University of Wisconsin. It consists of passing air through a preheated bed of magnesia and then heating by combustion of fuel gases. After the gases containing NO have been chilled, nitric oxide reacts with oxygen to form nitrogen dioxide which is subsequently absorbed in water.

$$2NO + O_2 \rightarrow 2NO_2$$

 $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$
 $3HNO_2 \rightarrow 2NO + HNO_3 + H_2O$

Ostwald's Method

Catalytic Oxidation of Ammonia. In this method NH₃ is oxidized at 700°C by air or oxygen gas to form NO in the presence of either platinum gauze or platinum-rhodium catalyst. The reaction is rapid and goes almost to completion (95%–98%).

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
 $\Delta H = -229.4 \text{ kcel/mole}$
 $2NO + O_2 \rightarrow 2NO_2$
 $2NO_2 = N_2O_4$
 $3N_2O_4 + 2H_2O = 4HNO_3 + 2NO$

Physical Properties

Nitric acid is a colorless mobile liquid which fumes strongly in moist air. It has a pungent, choking odor. Nitric acid melts at ~41.6°C and boils at 82.6°C. Its density is 1.51 g cm⁻³ at 25°C. It is very soluble in water. It forms a maximum constant-boiling mixture which boils at 120.5°C containing 68.5% HNO₃, and the solution has a density of 1.41 g cm⁻³ at 20°C. "Fuming nitric acid" is the concentrated nitric containing dissolved nitrogen dioxide. The color of fuming nitric acid ranges from yellow to red depending upon the concentration of NO₂ present. The following are some important standard electrode potentials of nitric acid solution.

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$$
 $E^\circ = +0.96V$ $NO_3^- + 3H^+ + 2e^- \rightarrow NO_2 + H_2O$ $E^\circ = +0.98V$ $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$ $E^\circ = +80V$

Nitric acid is a planar molecule containing an sp^2 nitrogen atom. The predominant resonating structures of the acid are

The bond distance and angles in nitric acid are given in the structural formula:

The structure, properties, and uses of a variety of chemicals are highlighted in this feature which is aimed at Increasing the use of descriptive chemistry.

Chemical Properties

Decomposition

Nitric acid is fairly stable at room temperature. However, it is decomposed by heat, especially above 68°C.

$$4\text{HNO}_3 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{NO}_2$$

The familiar yellow color of concentrated nitric acid in reagent bottles is due to its decomposition to NO₂. The following seems to be the most plausible mechanism for the decomposition of nitric acid at room temperature.

$$2HNO_3 \rightarrow N_2O_5 + H_2O$$

$$N_2O_5 \rightarrow NO_2 + NO_3$$

$$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$$

$$NO + N_2O_5 \rightarrow 3NO_2$$

Acidic Properties

Nitric acid is highly ionized (93% in 0.10 M) in water solutions and, therefore, it is a strong monoprotic acid. It reacts with bases, metallic oxides, and carbonates to form salts and water unless the metallic ion concerned is a reducing agent.

$$CdO + 2HNO_3 \rightarrow Cd(NO_3)_2 + H_2O$$

 $3FeO + 10HNO_3 \rightarrow 3Fe(NO_3)_3 + 5H_2O + NO$

Oxidation of Metals

Nitric acid solutions are strong oxidizing agents. Nearly all metals are attacked by nitric acid except Au, Pt. Ir. Ta, and Rh. Metals like Fe, Cr, and Al readily dissolve in dilute nitric acid but are rendered passive by concentrated nitric acid so-Intion due to the formation of an oxide layer on the metallic surface. This feature makes it possible to store and ship concentrated nitric in steel containers. The metalloids Si, Ge, Sn, As, and Sb along with the transition metals Mo and W are converted to oxides by hot concentrated nitric acid. The remaining metals are attacked by nitric acid to form nitrates. The other reaction products depend upon the nature of the metal, temperature, and concentration of the acid. The reaction product may contain one or more of the following substances: N2O, NO, NO2, H2, NH2OH, N2, and NH3. in general, metals which are above hydrogen on the electromotive series yield H2, N2, NH3, NH2OH, or NO when treated with nitric acid. Metals which are below hydrogen in the electromotive series tend to give NO or NO2.

$$Zn + 2H^{+} \longrightarrow Zn^{2+} + H_{2}^{\dagger}$$

$$(<25\%)$$

$$3Zn + 8H^{+} + 2NO_{3}^{-} \rightarrow 3Zn^{2+} + 4H_{2}O + 2NO$$

$$(dilute)$$

$$4Zn + NO_{3}^{-} + 10H^{+} \rightarrow 4Zn^{2+} + 3H_{2}O + NH_{4}^{+}$$

$$(dilute)$$

$$6Zn + 2NO_{3}^{-} + 16H^{+} \rightarrow 6Zn^{2+} + 4H_{2}O + 2NH_{3}OH^{+}$$

$$(concentrated)$$

$$3Cu + 8H^{+} + 2NO_{3}^{-} \rightarrow 3Cu^{2+} + 4H_{2}O + 2NO$$

$$(dilute)$$

$$Cu + 4H^{+} + 2NO_{3}^{-} \rightarrow Cu^{2+} + 2H_{2}O + 2NO_{2}$$

$$(concentrated)$$

$$Sn + 4H^{+} + 4NO_{3}^{-} \rightarrow SnO_{2} + 4NO_{2} + 2H_{2}O$$

$$(concentrated)$$

Oxidation of Nonmetals

Hot concentrated nitric acid oxidizes I_2 to HIO₃, P_4 to H₃PO₄, and C to H₂CO₃.

$$I_2 + 10H^+ + 10NO_3^- \rightarrow 2HIO_3 + 4H_2O + 10NO_2$$

Oxidation of Lower Oxidation Number Metallic Ions
The standard potential of nitric acid solutions range from

+0.80V to +0.96V. Therefore, it can oxidize $V^{2+} \rightarrow V^{3+}$, V^{3+} to VO^{2+} , $Cr^{2+} \rightarrow Cr^{3+}$, Ti^{3+} to TiO^{2+} , Fe^{2+} to Fe^{3+} , and Nb^{3+} to NbO_2^+ .

$$3Fe^{2+} + 4H^+ + NO_3^- \rightarrow 3Fe^{3+} + 2H_2O + NO$$

$$Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$$

brown

These reactions form the basis of detecting nitric acid or nitrate ion by the familiar ring-test method.

Reaction with Nitrogen (II) Oxide

When gaseous nitric oxide is bubbled through an aqueous nitric acid solution uitrous acid is formed.

$$HNO_3 + 2NO + H_2O \rightarrow 3HNO_2$$

The above reaction is catalyzed by hydrochloric acid and small amounts $(10^{-8} \text{ to } 10^{-9}M)$ of silver (I) and mercury (I) ions.

Reactions with Inorganic Compounds

Nitric acid converts SO₂ to H₂SO₄, H₂S to S, HCl to Cl₂, H₃PO₃ to H₃PO₄, and H₃AsO₃ to H₃AsO₄

$$3SO_2 + 2H_2O + 2NO_3^- \rightarrow 3SO_4^{2-} + 4H^+ + 2NO$$

Reaction with Gaseous Fluorine

Dilute solution of nitric acid (1.3 N) are oxidized at low temperature by gaseous fluorine to pungent pernitric acid (HNO_4) , which decomposes to give oxygen gas:

$$2HNO_3 + F_2 \rightarrow N_2O_6 + 2HF$$

 $N_2O_6 + H_2O \rightarrow HNO_3 + HNO_4$
 $HNO_4 + H_2O \rightarrow HNO_3 + H_2O_2$
 $2H_2O_2 \rightarrow 2H_2O + O_2$

Oxidations of Organic Compounds

Many organic compounds undergo oxidation with dilute or concentrated nitric acid. Sawdust reacts vigorously and turpentine oil explodes to produce black smoke. Warm and dilute nitric acid oxidizes the primary alcohol function of an aldose or aldonic acid to a carboxylic acid. Under these conditions, an aldose is converted into a dicarboxylic acid, aldaric acid (the diacid formed from D-glucose is called glucaric acid):

Concentrated nitric acid converts sucrose to oxalic acid and alkyl benzene to benzoic acid derivative on heating.

$$H_3C$$
 CH_3
 $HOOC$
 $COOH$
 $COOH$

Nitrating Property

The nitrating property of HNO₃ is due to formation of NO₂⁺ in presence of concentrated sulfuric acid:

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$

Solutions containing NO₂⁺ are of considerable importance in the aromatic nitration reaction:

Uses

The largest use of nitric acid is still the production of ammonium nitrate, 90% of which is used as a fertilizer and the rest for explosives and as a source of nitrous oxide (N2O). Nitric acid is used for preparation of silver nitrate, trinitrotoluene, nitroglycerine, nitrocellulose, and nitrobenzene which in turn is used to produce aniline for use in the manufacture of dye intermediates, isocyanates, rubher chemicals and hydroquinone, and nitrochlorobenzene to produce insecticides, such as parathions. A growing use of nitric acid is the manufacture of toluene diisocyanate (TDI) which is the raw material for polyurethane plastics, and adipic acid from a cyclohexanol/cyclohexanone mixture to produce nylon-66.

Small amounts of nitric acid are employed in stainless steel pickling, metal etching, rocket propellant, nuclear fuel processing, the separation of gold from silver, the manufacture of sulfuric acid by the lead chamber process, and production of nitrophosphates from phosphate rocks, especially in Europe. Aqua regia is a mixture of concentrated nitric acid and concentrated hydrochloric acid (1:3) which can dissolve gold and platinum.

Production and Price

The amount of nitric acid produced in the United States

was 1.1 million tons in 1947, 9.0 million tons in 1980, and 9.4 million tons in 1981. The 1980 prices were \$0.10 to \$0.14/kg for 58-68% acid and \$0.26/kg for 95% acid.

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A Convenient Method for the Preparation of 2,4-Dinitrophenylhydrazones

Flavanone 2,4-Dinkrophenythydrazone

The preparation of 2,4-dinitrophenylhydrazones is perhaps the most well known and widely used method for the characterization of carbonyl compounds by chemical means, 1.2 The utility of this method is limited by the low solubility of the hydrazine reagent in hydroxylic solvents. To overcome this solubility limitation, the reagent is almost invariably used as a solution in strongly acidic aqueous or aqueous ethanolic sulfuric or phosphoric acid.² These procedures² require that a relatively large volume of the reagent solution be used, often leading to a low conversion of carbonyl compound to hydrazone, and are sometimes accompanied by undesired side reactions (particularly when acid sensitive carbonyl compounds are to be derivatized).

We have adopted a far more satisfactory procedure³ for use in the undergraduate organic chemistry laboratory course. In this case, the carbonyl compound and 2,4-dinitrophenylhydrazine are dissolved in a small amount of dimethylformamide (commercial reagent grade dimethylformamide may be used without further purification; 2,4-dinitrophenylhydrazine is much more soluble in dimethylformamide than it is in common hydroxylic solvents). A few drops of aqueous hydrochloric acid solution are added to act as catalyst and the solution is allowed to stand for crystallization of the product. The time required for complete product furnation varies between a few minutes and about two hours, depending upon the nature of the starting carbonyl compound.

This procedure represents a far more convenient and useful method for the preparation of 2.4-dinitrophenylhydrazones than that described in most current manuals for the undergraduate organic chemistry laboratory course.² The preparation of flavanone 2,4-dinitrophenylhydrazone using this procedure is presented below.

Flavanone 2,4-Dinitrophenylhydrazone. Flavanone (0.50 g, 2.23 mmole) is added to a solution of 0.50 g (2.52 mmole) of 2,4-dinitrophenylhydrazine in five milliliters of dimethylformamide contained in a 50-ml Erlenmeyer flask and the mixture is swirled to obtain a homogeneous solution. Concentrated aqueous hydrochloric acid solution (two drops from a disposable pipette) is added and the mixture is allowed to stand 0.5 hr at room temperature. The solid product is then collected by filtration at reduced pressure, washed with 2 N aqueous hydrochloric acid to remove unchanged 2,4-dinitrophenylhydrazine (20-30 ml), water (30 ml), and cold 95% aqueous ethanol (10 ml). The crude material is allowed to partially dry and is recrystallized from ethyl acetate to provide the hydrazone (0.83 g; 92% yield) as orange-red needles, mp 260-261°C

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Wingrove, A. S., and Caret, R. L., "Organic Chemistry," Harper & Row, New York, 1981, p. 836.

² Moore, J. A., Dalrymple, D. L., and Rodig, O. R., "Experimental Methods in Organic Chemistry," 3rd ed., CBS College Publishing, New York, 1982, p. 347; Miller, J. A., and Neuzil, E. F., "Modern Experimental Organic Chemistry," D. C. Heath, Lexington, MA, 1982, p. 623; Fieser, L. F., and Williamson, K. L., "Organic Experiments," 4th ed., D. C. Heath, Lexington, MA, 1979, p. 354; Lehman, J. W., "Operational Organic Chemistry," Allyn and Bacon, Inc., Boston, MA, 1981, p. 411; Roberts, R. M., Gilbert, J. C., Rodewald, L. B., and Wingrove, A. S., "Modern Experimental Organic Chemistry," 3rd ed., Holt, Rinehart and Winston, New York, 1979, p. 298; Doyle, M. P., and Mungall, W. S., "Experimental Organic Chemistry," John Wiley and Sons, Ioc., New York, 1980, p. 180; Mohrig, J. R., Neckers, D. C., "Laboratory Experiments in Organic Chemistry, 3rd ed., D. Van Nostrand Company, New York, 1979, p. 477; Yip, M. T., and Dalton, D. R., "Organic Chemistry in the Laboratory," D. Van Nostrand Company, New York, 1979, p. 95.

³ Parrick, J., and Rasburn, J. W., Can. J. Chem., 43, 3453 (1965).

⁴ If no solid product separates spontaneously during the period allowed for reaction, the mixture is treated with 10 ml of 2 N aqueous hydrochloric acid solution to precipitate the product which is collected and purified as described.

Modification of a Microwave Oven for Laboratory Use

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University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

The use of domestic or commercial models of microwave ovens for drying analytical samples has been recommended by previous authors (1-7). The savings of time are attractive, and many (but not all) samples, including some electrically conductive ones, are dried without damage (1).

A computer search of the literature using the Chemical Abstracts database yielded a relatively small body of literature and indicated one principal problem. When complete dryness of a sample is approached—a condition never reached in microwave cooking—the oven loses its load. No material capable of absorbing microwaves efficiently remains. Energy is still being supplied to the enclosure. Under these conditions, there is a tendency for the magnetron to arc and destroy itself (2).

We were also concerned about possible interaction of the material being dried with the oxygen of the air, and wished to examine emitted gases from the drying process. These concerns led us to modify a Litton commercial microwave oven (Model 70/08 Menumaster) as follows.

Water Ballast

The oven nameplate states its minimum permissible load is 50 ml of water. Accordingly, a small bottle was made with two sidearms and a threaded neck accepting a standard polyethylene screw cap. A stand made from two pieces of polypropylene sheet held the bottle above the oven floor and away from the wall. The sidearms were joined to two lengths of PTFE bellows tubing by using PTFE/FEP shrink tubing, both from Pope Scientific Inc. of Menominee Falls, WI. The capacity of the bottle to the upper sidearm was approximately 100 ml. Bottle and stand are shown in Figure I.

Inert Atmosphere Enclosure

The polypropylene lid of a Nalge polymethylpentene jar (1000 ml) was put on a lathe, and the upward flange provided for secure stacking was removed. The lid was then mounted on the sidewall of the oven, positioned so the jar itself could be screwed into it. Two \%-in.-diameter holes were made in the lid and in the oven chamber wall, and two similar holes on the same spacing in a polypropylene shelf. These parts were assembled as shown in Figure 2 using glass-filled polypropylene tee-fittings. The through arm of the inlet tee was provided with a glass tube with several lateral holes to sweep purge gas into various parts of the jar beneath the shelf, while the upward-turned stem of the tee was plugged with polypropylene rod. The gas exit tee had its arm extending helow the shelf plugged, and the upward-pointing arm open. When desired, this arm may be fitted with an inverted U of tubing to collect gas from a sample container immediately above the sample. The shelf is braced with a half-slotted support and may be given a platform of ceramic foam to protect it from the heat of drying samples.

Outside the oven chamber, elbows direct the bores to the rear, and polyvinyl chloride tubing is used to lead out through the ventilating louvers of the oven to an appropriate gas supply and vent or analyzer.

Water Flow System

The connections to the water ballast are made to glass-filled polypropylene elbows mounted in the chamber wall, and thence through polyvinyl chloride tubing out through the

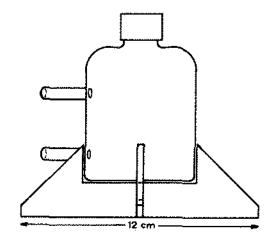


Figure 1. Water ballast for oven on a polypropylene stand.

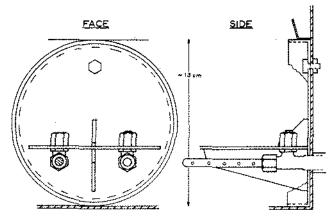


Figure 2. Attachment of enclosure to oven chamber wall. See text for details.

louvers. A water flow monitor (Instruments for Industry and Research, Cheitenham, PA, Model WFM-1800) was connected in the drain line to turn off oven power if the water flow failed. A constant water feed, either through a flow regulator or a constant head device, is helpful in setting a minimum adequate flow.

Materials and Equipment Comments

All construction materials were tested by placing them in the oven for at least 2 min of irradiation. If no temperature rise was observed (apart from the slight general rise of the unloaded oven's temperature), the material was judged suitable for use. Polypropylene, PTFE, polymethylpentene, polyethylene, and nylon were thus tested.

The holes for fittings and the rim of the jar lid were generously coated with silicone bathtub sealant at the time of assembly.

Although polyvinyl chloride tuhing did not heat when

¹ This work was performed by Judith Andrews as her final-year research project for her BS degree.

placed dry in the oven, and although it was successfully used for connecting the water ballast iar in early experiments, its use inside the chamber was abandoned after the oven was once operated with this tubing full of water but without water flow. The tubing swelled and charred to resemble a burned sausage, and melted (but did not otherwise degrade) nylon clamps securing it to the hallast jar.

One disconcerting discovery made when the shell of the oven was removed to fit the modifications was that the air flow channeling fitted by the manufacturer consisted of strips of cardboard secured with carpet tape, and that this cardboard was resting against the glass of the incandescent lamps provided to light the oven chamber. We recommend that these strips be fireproofed or replaced with fireproof material even if the oven is not being modified in the manner described.

Performance

Copper sulfate pentahydrate is reported to lose four moles of water at temperatures below 150°C, and the fifth mole only between 250 and 300°C (8). Our experiments agreed with literature reports that microwave drying can produce only the monohydrate. Drying is nearly complete in 10 min, and variations in time to remove the last traces of the four moles of water probably reflect exposure during weighing to the varying humidity of days on which experiments were conducted.

Drying oxalic acid dihydrate at high heat settings of the oven resulted in sublimation of the \alpha form of the anhydrous acid (m.p. 188.5-189.5°C). The sublimate which collected in the upper part of the sample container was shown by infrared spectroscopy to be unchanged chemically. Such use of the ovens for sublimation from hydrated starting materials deserves exploration. At medium power settings, oxalic acid dihydrate does not sublime, but appears to reach a stable condition after 15 min and then abruptly loses the rest of its water. About one-third of the total weight loss occurs in this second step.

Freshly precipitated calcium oxalate was successfully dried (in sintered-glass filtering crucibles) in 5 min, compared to 60 min in a typical convection oven.

The effect of passing nitrogen through the internal chamber was compared to, and found to be more efficient than, drawing air through with an aspirator. The nitrogen supply used was

the bench nitrogen, which is the boil-off from the liquid nitrogen service to the huilding.

A mass of wet crystals of ammonium nitrate gave a sublimate of ammonium nitrate and also some nitrogen oxides and reached a high temperature after first dissolving in the water which was present. We would recommend that nitrates not be dried by microwave radiation without careful tests with very small samples.

As an additional test of oven performance, portions of "Tel Tale" indicating Silica-Gel (Davison Chemicals Division of Grace Inc.) were spread in Petri dishes to a depth of 4 to 5 mm after exposure to humid air to turn the cobalt indicator salt thoroughly pink. One dish was placed in the nitrogen atmosphere chamber and the other on the floor of the oven outside the chamber. The first batch required 13 min of operation (at Medium-High setting) to become uniformly deep blue, and the second batch 8 min. The appearance of blue color in both cases was in irregular patches which increased in size more than in number. We attribute the slower drying in the nitrogen chamber to the smaller rate of atmosphere exchange compared to the air circulation in the main chamber. We thank the referee who suggested this additional test.

Conclusions

A commercial microwave oven can be useful in drying materials used in analytical laboratories. To protect such a unit against energy buildup when the samples are dry, and to prevent possible destruction of the magnetron tube, a small water ballast may he installed, which will of course decrease the microwave power available for drying the samples.

A chamber made of a polymethylpentene iar, with fittings of other microwave-inert plastics, permits drying in special atmospheres, protects the oven from effluent gases, and allows testing of those gases.

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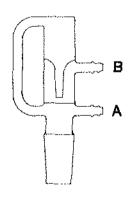
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A Simple, Compact Nitrogen Bubbler

Many chemical reactions require maintaining an inert atmosphere, and many more would benefit from excluding air, to reduce impurities resulting from air oxidation. We have constructed a simple nitrogen bubbler for this purpose. Silicone oil (or Hg) is added through B to a height of 1-2 mm above the tip of the dip tube. The only critical aspects of construction are that B be high enough to avoid splattering of oil out of the tube and that the volume of the upper chamber be large enough to contain all the oil in case a drop in pressure causes the oil to back up the dip

In use, for maintaining an inert atmosphere, the device is attached to the glass joint of a flask, reflux condenser, or dropping funnel, and inert gas is passed through A, adjusting the flow to give a bubble every 1-2 s. For purging apparatus through a separate opening or for monitoring gas evolution, tube A is closed off with a rubber bulb. The gas flow can be led from B into a reagent such as NaOH, for example, when monitoring CO2 evolution in the Hundsdiecker reaction.

The advantages of this unit are that it is compact, occupying about the space of a conventional drying tube, and it is easy to use and store, either by hanging it from the glass loop or by setting it on the pins of a test tube rack.



R. M. Baldwin Medi-Physics, Inc. Emeryville, CA 9460a A. Rhodes Pacific Flame Glass Works Emeryville, CA 94600

Synthesis of Vitamin K Epoxide

An Undergraduate Biochemistry Experiment

M. Thierry-Palmer¹

University of Michigan-Dearborn, Dearborn, MI 48128

The synthesis of vitamin K epoxide is an experiment which introduces the student to many of the techniques used in lipid biochemistry. Most experiments designed to teach the techniques of lipid biochemistry involve the isolation of lipids from animal tissue or plants (1,2,3). In this experiment a metabolite of vitamin K, its 2,3-epoxide, is synthesized and purified. Students are thus able to apply the techniques of lipid biochemistry to a fat-soluble vitamin. The fat-soluble vitamins are not extensively discussed in undergraduate biochemistry courses and recent dramatic advances in the knowledge of vitamin K metabolism and function may not yet be known to undergraduate students (4,5). This experiment can be used to supply current information on vitamin K as well as to introduce students to some techniques of lipid biochemistry.

Experimental Procedure

All manipulations are to be performed in semi-darkness. Vitamin K epoxide is prepared by oxidation of vitamin K (Sigma Chemical Company, St. Louis, MO) with hydrogen peroxide in hasic aqueous ethanol (6, 7).2 Up to 1 g of vitamin K is placed in a 125-ml Erlenmeyer flask, dissolved in 50 ml absolute ethauol, and heated to 80°C in a shaker bath. One inilliliter of 30% hydrogen peroxide and 2.5 ml of 0.5 g/ml sodium carbonate solution are added to the flask and the mixture is shaken for 15 min. A second I ml aliquot of 30% hydrogen peroxide is added to the reaction mixture and the flask is shaken for an additional 45 min while maintaining the temperature at 80°C. The reaction mixture is diluted with 50 ml distilled water and extracted three times with 50-ml portions of hexane. The hexane extracts are pooled and washed with 50 ml of 0.9% sodium chloride. The hexane layer is removed, treated with 30 g of anhydrous sodium sulfate for 1 hr, filtered to remove solids, and concentrated to 10 ml by evaporating under a stream of nitrogen in a 40°C water bath. (CAUTION: No flames should be present in the laboratory during the use of hexane. Hydrogen peroxide should be handled with rubber gloves and never pipetted by mouth.)

Vitamin K epoxide is separated from other components of the hexane extract by reverse phase thin-layer chroinatugraphy. A 20×20 cm plastic thin-layer plate, precoated with Silica-Gel G containing ultraviolet fluorescence indicator (Brinkman Instruments, Westbury, NY), is placed in a tray of 5% mineral oil in hexane for 2 sec. The plate is allowed to air dry before applying the samples. Surgical gloves are used when handling the TLC plate. Capillary pipettes (5 μ I) are used to spot vitamin K (dissolved in hexane) 2.5 cm from the bottom of the plate and 1.0 cm from the left and right edges and to apply the hexane extract as a band to the space on the plate between the two vitamin K spots. The extract and the vitamin are applied in small aliquots and the solvent is allowed to evaporate between aliquots. Aliquots are applied until the spots are slightly yellow.

The plate is placed in a rectangular chromatography tank containing 200 ml of 92:8 acetone:water solution and lined with solvent satorated filter paper. The chrumatogram is allowed to develop fur approximately 90 min and the plate is removed, allowed to air dry, and examined under an ultraviolet lamp. The $R_{\rm f}$ of vitamin K should be 0.4 and that of the epoxide 0.6. The epoxide band is circled with pencil, cut into 10 ml spectral grade hexane and extracted twice by shaking vigorously for 20 min in a shaker bath. Silicic acid particles are removed from the combined extracts by centrifuging for 10 min

in a tabletop centrifuge. A double beam recording ultraviolet spectrophotometer is used to obtain complete spectra (350 nm to 200 nm) for vitamin K and the synthesized epoxide. Initial readings at 226 nm ($E_{236}^{18} = 660$) and at 248 nm ($E_{236}^{18} = 420$) can be taken to determine whether the epoxide and the vitamin need dilution. The volume of the extract and the absorbance value at 226 nm may be used to calculate the amount of the vitamin K epoxide extracted from the TLC plate.

Optional Experiment

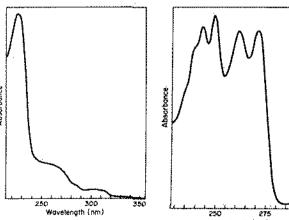
The purity of the TLC-extracted vitamin K epoxide may be tested in a high pressure liquid chromatography system. For such an experiment the hexane is evaporated from the TLC-derived vitamin K epoxide and the epoxide is dissolved in the appropriate HPLC grade solvent. The sample is filtered through a $0.2~\mu m$ filter or centrifuged to remove particles before injection.

Several chromatographic procedures are available for separating vitamin K from its epoxide by HPLC. Three isocratic reverse phase procedures employing different commercial columns are listed below: Methanol:dichloromethane (8:2 v/v) or acetonitrile:dichloromethane (7:3 v/v) on Du Pont Zorbax-ODS column (8); methanol:water (93:7, v/v) on Waters µBondapak C₁₈ column (9); and acetonitrile:water (99:1, v/v) on Varian Micro-Pak CH-10 column (10). A flow rate of 1 ml per min is adequate for all three systems. Detection is achieved readily using the standard fixed wavelength (254 nm) ultraviolet spectrophotometers connected to most high pressure liquid chromatographs.

Results and Discussion

Conversion of vitamin K to its epoxide goes nearly to completion. As little as 0.1 g vitamin K may be used and enough material will be available for ultraviolet and bigh pressure liquid chromatographic analyses. Vitamin K and its epoxide are separated fairly well on reverse phase thin-layer plates. The ultraviolet spectrum of the epoxide produced by one student is shown in Figure 1. This spectrum is to be compared with that of the original starting material, vitamin K. Published literature lists $\lambda_{\rm max}$ for vitamin K epoxide at 226 nm and for vitamin K at 243, 249, 261, and 270 nm. The spectrum for the epoxide closely resembles that in the published literature (7).

The experiment as described can be performed in three



Ultraviolet spectra of synthesized vitamin K epoxide (left) and the vitamin K (right) used as starting material for the synthesis of vitamin K epoxide.

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² The author wishes to thank J. A. Sadowski of the Medical College of Wisconsin for his modification of the method of Tishler et at.

4-hour laboratory periods by a class of 14 students. A schedule for the experiment would be as follows: first day, synthesis and extraction of the epoxide; second day, thin-layer chromatography of the epoxide; third day, UV spectroscopy and high pressure liquid chromatography of the epoxide.

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Events of interest to high school chemistry teachers in various parts of the country and a calendar of important dates and meetings are featured in this column. If you have information about en up-coming event, or if you wish to report on the outcome of a particular meeting or program, write your "What's Happening" editor, or contact the Secondary School Editor.

Northeast

edited by WALLACE J. GLEEKMAN Brookline High School Brookline, MA 02146

February 29, 1984

NEW JERSEY SCIENCE TEACHERS ASSOCIATION 1984 CURRIC-ULUM CONFERENCE to be held at the College of St. Elizabeth, Convent Station, NJ.

For further information, see the January 1984 issue of THIS JOURNAL.

March 5-9, 1984

PITTSBURGH CONFERENCE ON ANALYTICAL CHEMISTRY AND APPLIED SPECTROSCOPY AND EXPOSITION 1984 to be held in Atlantic City, NJ.

For further information, see the January 1984 issue of THIS JOURNAL.

March 17, 1984

THIRD BIENNIAL CHEMISTRY DAY to be held at Drew University, Madison, NJ, co-sponsored by the Teacher Affiliate Group of the North Jersey Section, American Chemical Society, the New Jersey Science Teachers Association, and Drew University.

For further information, see the January 1984 issue of THIS JOURNAL.

March 26-28, 1964

NEW YORK ACADEMY OF SCIENCES CONFERENCE ON MACRO-MOLECULES AS DRUGS AND AS CARRIERS FOR BIOLOGICALLY ACTIVE MATERIALS to be held at the Roosevelt Hotel, New York, NY.

For further information, see the January 1964 issue of THIS JOURNAL.

April 5-8, 1984

32ND ANNUAL CONVENTION OF THE NATIONAL SCIENCES TEACHERS ASSOCIATION (NSTA) will be held at the Sheraton-Boston and the John B. Hynes Auditorium in Boston, MA.

Theme: "Reaching for Excellence."

For further information, contact: Harold "Sandy" Wiper, Newton North High School, Newtonville, MA 02160.

Southeast

edited by NANCY LEMASTER O. W. Daniel High School Central, SC 29630

ADVANCED PLACEMENT SEMINARS

March 13, 1984

University of Virginia, School of Education-Ruffner Hall, 405 Emmett Street, Charlottesville, VA 22903.

For further information, contact: Jean Rayburn, (804) 924-7751,

March 20, 1984

Catawba College, College Community Centre, Saliabury, NC 28144.

For further information, contact: James A. Nesbitt, (704) 837-4402.

March 23, 1984

Mississippi University for Women, The Hogarth Student Center (2nd Floor), Columbus, MS 39701.

For further information, contact: Joe Portera, (701) 329-4750.

April 3, 1984

University of Kentucky, Student Center Annex, Lexington, KY

For further information, contact: Timothy R. Burcham, (806) 257-1806.

April 10,1984

Tennessee Technological University, University Center, Cockesville, TN 38501.

For further information, contact: James C. Perry, (815) 528-3888.

For the state of Florida, the list of AP seminars may be obtained. For further information, see the January 1984 Issue of THIS JOURNAL.

May 10~12, 1984

37TH ACS FLORIDA SECTION ANNUAL MEETING at Florida Southern College, Lakeland, FL.

For further information, contact; Dick Hanley, Program Chairman, Fiorida Jr. College at Jacksonville, 11901 Beach Boulevard, Jacksonville, FL 32216, (904) 646-2165.

Northcentral

edited by ROBERT SUITS D. H. Hickman High School Columbia, MO 85201

April 6-7, 1984

THE 83RD 2YC₃ CONFERENCE at the St. Louis Community College at Florisaant 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 January 1994 Issue of THIS JOURNAL.

April 8-13, 1984

187th ACS NATIONAL MEETING, St. Louis, MO.

For further information, see the January 1984 issue of THIS JOURNAL.

April 9, 1984

"HIGH SCHOOL DAY" at the ACS National Meeting, St. Louis, MO. For further information, see the January 1984 issue of THIS JOURNAL.

Southcentral

edited by JAN HARRIS Cypress-Fairbanks High School Houston, TX 77064

March 2-3, 1984

82ND TWO-YEAR COLLEGE CONFERENCE, Tarrant County Junior Coilege, Northeast Campus, Hurst, TX 76053.

For further information, see the January 1984 issue of THIS JOURNAL.

Southwest

editad by
ERIC STREITBERGER
University of California-Fullerton
Fullerton, CA 96231

March 24, 1984
CALIFORNIA STATE TEACHERS ASSOCIATION SPRING CONFERENCE, Redding, CA.

For further information, contact this editor.

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: W. T. Knauss, Professor of Aeronautics and Applied Mechanics

May 2, 1984

The Atomic Nucleus: Quantum Physics on a Grand Scale

Speaker: S. C. Koonin, Professor of Theoretical Physics

For further information on the above lectures, contact ties F. Browne or Phyllis Brewster, California institute of Technology, Pasadena, CA 91125, (213) 356-6624.



Division of CHEMICAL EDUCATION

American Chemical Society

Report of the ACS Examinations

Committee

The 1984 Testing Program

Four new tests are featured this year.

General Chemistry, scrambled version, Form 1983-S, 80 items, 110 minutes

High School Chemistry, scrambled version, Form 1983-S, 80 items, 80 minutes

High School Chemistry, advanced version, Form 1984-ADV, 60 items, 110 minutes

Organic Chemistry, brief version, Form 1984-B, 70 items, 90 minutes

Note: An "S" form denotes a "scrambled version" which contains the identical items as the original test, but in a different sequence. It is recommended that the two versions be used together to test students seated alternately so as to improve security and discourage copying in crowded rooms.

Users of the new tests are urged to send their data for calculation of extensive and statistically reliable norms. As soon as calculated, these norms will be mailed to those contributing data or serving on the Committee. Thereafter, the norms will be mailed routinely with the new orders.

Norms sent to users are regularly updated from newer or more extensive data.

The following is a complete spectrum of all tests featured this year.

Toledo Chemistry Placement Test, Forms 1974, 1981 General Chemistry, Forms 1979, 1979-S, 1981, 1981-S, 1981-B (Brief), 1983, 1983-S, 1983-B (Brief). Brief Qualitative Analysis, Forms 1973-B, 1977-B Analytical Chemistry (Quantitative Analysis), Form 1982 Instrumental Determinations (Analysis), Forms 1971, 1981 Organic Chemistry, Forms 1978, 1982

Brief Organic Chemistry, Forms 1977-B, 1984-B

Biochemistry, Forms 1977, 1982

Physical Chemistry, Forms 1973-I, 1973-II, 1973-III, 1976-I, 1981-II, 1983-III

Physical Chemistry, Form 1975 (year test)

Physical Chemistry for the Life Sciences, Form 1982-L

Polymer Chemistry, Form 1978

Inorganic Chemistry, Forms 1976, 1981

General-Organic-Biological Chemistry, Form 1979

High School Chemistry, Forms 1979-S, 1981, 1981-S, 1983, 1983-S

High School Chemistry (Advanced), Forms 1980-ADV, 1982-ADV, 1984-ADV

Graduate Level Placement Examinations in:

Analytical Chemistry, Forms 1977-A, 1981-A

Inorganic Chemistry, Forms 1976-I, 1981-I

Organic Chemistry, Forms 1977-O, 1981-O

Physical Chemistry, Forms 1977-P, 1981-P

These tests are confidential and are available only to members of educational institutions. They should be ordered through the official channels in their schools. These tests are not to be used for coaching, nor be seen by students except during the time of testing.

For further information and a brochure describing the tests, write to: T. A. Ashford, Examinations Committee-ACS, University of South Florida, Chemistry Room 112, Tampa, FL 33629, (813) 974-2730.

Condensed Norms: ACS Examinations

Condensed norms for the most recent tests are presented in the following tables. These are selected from a larger body of data sent routinely with orders and are available from the Examinations. Committee-ACS, University of South Florida, CHE 112, Tampa, FL 33620.

For condensed norms of previous tests, see THIS JOURNAL, **60**, 253 (March 1983); **59**, 263 (March 1982); **58**, 286 (March 1981); **57**, 235 (March 1980); **56**, 252 (April 1979); and previous issues.

General Chemistry (Brief Version) Form 1983-B

| Raw Score | %ILE | Raw Score | %ILE |
|-----------|-------|-------------|-------|
| 14 | 4 . | 28 | 68 |
| †6 | 9 | 30 | 78 |
| 18 | 16 | 32 | 63 |
| 20 | 27 | 34 | 90 |
| 22 | 36 | 36 | 94 |
| 24 | 47 | 40 | 98 |
| 26 | 57 | 45 | 100 |
| Median | 25 | đ | 6.96 |
| Mean | 25.54 | KR 21 Flet. | 0.757 |

Based on a sample of 511 students from the 1983 Testing Program.

Equivalent Scores

for the General Chemistry brief version Form 1983-8 and the full length versions Forms 1983 and 1983-8 for a given percentile rounded off to whole numbers.

| Percentile | Score on Brief Form | Score on Full Length Form | Percen- tile | Score on Brief Form | Score on Full Length Form |
|------------|------------------------------|---------------------------------------|-----------------|------------------------------|---------------------------------------|
| 1 | 11 | 20 | 55 | 25 | 42 |
| 5 | 14 | 25 | 60 | 26 | 44 |
| 10 | 16 | 28 | 65 | 26 | 45 |
| 15 | 18 | 30 | 70 | 30 | 47 |
| 20 | 19 | 32 | 75 | 31 | 49 |
| 25 | 20 | 34 | 80 | 32 | 50 |
| 30 | 21 | 36 | 85 | 33 | 54 |
| 35 | 22 | 37 | 90 | 34 | 57 |
| 40 | 23 | 38 | 95 | 37 | 60 |
| 45 | 24 | 40 | 99 | 42 | 68 |
| 50 | 24 | 41 | | | |

Correlation coefficient; brief to full length test, $r \approx 0.96$. Covarience = 70,30. The high correlation coefficient permits giving the brief test if time is limited.

Physical Chemistry Form 1983-III (Quantum Chemistry)

| RAW SCORE | VISCORE %ILE | | %ILE |
|------------|--------------|------------|------|
| 16 | 5 | 31 | 54 |
| 18 | 11 | 32 | 81 |
| 20 | 12 | 34 | 72 |
| 2 2 | 14 | 36 | 80 |
| 24 | 24 | 38 | 87 |
| 26 | 32 | 40 | 93 |
| 28 | 38 | 43 | 98 |
| 29 | 44 | 48 | 100 |
| 30 | 50 | | |
| Mean | 30.5 | σ | 7.80 |
| Median | 30 | KR 21 Ret. | 0.82 |

Based on the scores of 152 students in 9 educational institutions from the 1983 Teeting Program.

Physical Chemistry for the Life Sciences Form 1982-L

| RAW SCORE | %JLE | RAW SCORE | % LE |
|-----------|------------|------------|-------|
| | | | |
| 18 | .8 | 27 | 60 |
| 18 | 14 | 28 | 64 |
| 20 | 21 | 29 | 69 |
| 21 | 27 | 30 | 75 |
| 22 | 36 | 32 | 82 |
| 23 | 40 | 34 | 88 |
| 24 | 47 | 36 | 92. |
| 25 | 52 | 38 | 95 |
| 26 | 58 | 40 | 100 |
| Median | 2 5 | σ | 8.12 |
| Mean | 25.11 | KR 21 9el. | 0.827 |

Based on the scores of 145 students in 10 educational institutions from the 1982 and

1983 Testing Programs.

General Chemistry Forms 1983 and 1983-S Scoring Formula.... Number Right—80 Hems

Norms for the performance of randomly selected groups with various professional goals, as indicated by the students, and for the entire group.

| Professional | | Science other | | Medical | Entire |
|--------------|-------------|---------------|-------------|----------|--------|
| Goal No. of | Chem. Engr. | than Chem. | Engineering | Sciences | Group |
| Students | 63 | 199 | 103 | 309 | 1254 |
| Raw Score | %!LE | %ILE | %ILE | %ILE | %ILE |
| 26 | 2 | 7 | 12 | 5 | 6 |
| 28 | 3 | 11 | 13 | 7 | 9 |
| 30 | 5 | 16 | 20 | 8 | 15 |
| 32 | 8 | 24 | 25 | 13 | 20 |
| 34 | 8 | 28 | 33 | 18 | 25 |
| 36 | 14 | 38 | 45 | 26 | 34 |
| 39 | 19 | 46 | 50 | 30 | 40 |
| 40 | 29 | 55 | 58 | 39 | 47 |
| 42 | 37 | 64 | 64 | 45 | 54 |
| 44 | 49 | 72 | 70 | 51 | 60 |
| 46 | 57 | 77 | 77 | 58 | 67 |
| 48 | 62 | 79 | 82 | 87 | 72 |
| 50 | 65 | 82 | 85 | 74 | 77 |
| 52 | 70 | 85 | 85 | 81 | 82 |
| 54 | 73 | 91 | 87 | 84 | 88 |
| 56 | 79 | 94 | 89 | 89 | 89 |
| 58 | 87 | 95 | 91 | 91 | 92 |
| 60 | 94 | 95 | 92 | 95 | 95 |
| 86 | 97 | 98 | 97 | 99 | 98 |
| 72 | 100 | 100 | 100 | 100 | 100 |
| Валде | 24-69 | 18-75 | 1972 | 15-69 | 12-75 |
| Median | 45 | 39 | 38 | 44 | 41 |
| Mean | 46.57 | 40.45 | 38.8E | 43.72 | 41.19 |
| σ | 9.94 | 10.25 | 12.24 | 10.40 | 12.00 |
| St. Error | 1.25 | 0.72 | 1.21 | 0.588 | 0.339 |
| KR 21 Rel. | 0.813 | 0,820 | 0.878 | 0.827 | 0.87 |

Based on a sample of 1254 students in 21 institutions from the 1983 Testing Program.

High School Chemistry Forms 1983 and 1983-S

Scoring Formula---Number Right---80 Items
Norms for the performance of students in regular, Chem Study, Honors courses
and the entire group.

| No. of | | CHEM | | Entire |
|-------------------|---------|--------|--------|----------------|
| Students | Regular | Study | Honors | Group |
| RAW | 2575 | 1170 | 473 | 3218 |
| SCORE | %ILE | %/LE | %£E | %/LE |
| 26 | 8 | 1 | 0 | 5 |
| 30 | 14 | 4 | 1 | 10 |
| 34 | 25 | 8 | 3 | 18 |
| 36 | 32 | 11 | 4 | 23 |
| 38 | 40 | 15 | 5 | 29 |
| 40 | 47 | 19 | 8 | 35 |
| 42 | 55 | 24 | 11 | 41 |
| 44 | 80 | 30 | 15 | 47 |
| 46 | 85 | 34 | 19 | 51 |
| 48 | 70 | 40 | 24 | 5 6 |
| 50 | 74 | 46 | 29 | 62 |
| 52 | 79 | 53 | 35 | 67 |
| 54 | 82 | 60 | 40 | 71 |
| 56 | 87 | 64 | 45 | 76 |
| 59 | 91 | 72 | 54 | 82 |
| 62 | 94 | 81 | 63 | 87 |
| 65 | 98 | 86 | 73 | 90 |
| 88 | 99 | 93 | 81 | 95 |
| 72 | 100 | 97 | 89 | 98 |
| 79 | | 100 | 100 | 100 |
| ytedian | 41 | 52 | 58 | 48 |
| и о вп | 42.29 | 51.59 | 56.15 | 46.71 |
| σ | 12.96 | 11.79. | 13,15 | 12.97 |
| St. Error | 0.545 | 0.488 | 0.601 | 0.200 |
| (R 21 Rei. | 0.878 | 0.679 | 0.915 | 0.896 |

Number Right—80

BOOK REVIEWS

Chemistry and Our Changing World

Alan Sherman and Sharon J. Sherman, Prentice-Hall, Inc., Englewood Cilifs, NJ, 1983. xxiii + 568 pp. Figs. and tables. 18 X 24 cm.

Written for a one-semester or two-quarter course for nonscience majors, this text provides an interesting addition to those already available for this group of students. It does a reasonably good job of introducing the nonscience student to chemistry, and through a multitude of interesting examples it illustrates how chemistry relates to the everyday world. Simple, easy to read, conversational style language is used aining with numerous black and white cartoons, figures, photographs, and tables. The quality of these is generally good and, for the most part, they add significantly to the text. Each chapter begins with a list of learning goals and ends with a chapter summary and a set of self-test exercises based upon the learning goals. Numerous worked-out examples are given throughout the book. Supplements at the end of the book include a glossary and appendices on basic mathematics, the metric system and measurement, expanded nomenclature rules plus a set of important tables. For those desiring it, a separate instructor's guide is also available to supplement the text.

The book covers the typical topics dealt with in a brief course in general, organic, and biological chemistry and in addition has chapters with such titles as Air Pollution, Agricultural Chemistry, Food, Pharmaceuticals and Drugs, The Chemistry of Home Care and Personal Products, and Chemistry and Outer Space. The book does a nice job of presenting a great deal of historical information; much more than is given typically in most college texts. This feature adds greatly to the book and helps the reader gain a better appreciation of how science operates and a realization that progress in science is due to

the collective contribution of many individuals.

Another feature of the text is a set of short essays referred to as "Scenarios." Frequently futuristic in nature and interesting to read, they tend to dwell on the negative consequences of chemicals in our modern world. The same negative theme seems to underlie many parts of the book not dealing with fundamental concepts. This negative emphasis can detract, at least from a chemist's point of view, from what is a generally well done text. It came across, to the reviewer, as an attempt by the authors to patronize those individuals in our society who like to push the theme that "science is bad." Although truth should prevail above all, such emphasis is not necessary in a chemistry text and gives a distorted perspective of science to the student.

One other aspect of the text that bothered this reviewer was the simplistic and at times incorrect approach of some of the illustrations. For example, using oxygen molecules to introduce double bonds (p. 72) does not seem appropriate even with a disclaimer statement included in the discussion. Likewise, showing 10°C water in equilibrium with ice over a frozen lake (p. 192) is somewhat misloading. Other such problems are picturing glucose molecules as being smaller than water molecules (p. 177), a somewhat confusing picture of the crystal structure of ice (p. 193), "keys" that cannot, as drawn, lit into the "enzyme lock" shown (p. 384), bubbles of CO2 that pass uneffected into the atmosphere above a glass of water containing an Alka-Seltzer® tablet (p. 409), etc.

Although generally well done and interesting to read the reviewer would probably not adopt the book because of its negative emphasis and misleading illustrations.

M. Lynn James University of Northern Colorado Greeley, CO 80639

Elements of General and Biological Chemistry

John R. Holum, John Wiley & Sons, Somerset, NJ, 1983, xv \pm 523 pp. Figs. and tables. 21.5 \times 26 cm.

The sixth edition of this textbook is a combination of the second edition of "Fundamentals of General, Organic, and Blological Chemistry" published in 1982 and the fifth edition of "Elements of General and Biological Chemistry" published in 1979. It is considerably briefer than the 1982 book and somewhat shorter than the 1979 book. The number of chapters and their titles are the same as in the fifth edition but the content has been changed, most notably in the biochemistry sections.

While the book is somewhat briefer than the former editions it is very suitable for a one-semester course in chemistry for students pursuing a professional career in the allied health professions. Also, as the author suggests in his preface, this book can serve as well for a two-term course where students have had no previous chemistry or are very poorly prepared.

The seven chapters that include most of the basic topics usually associated with general chemistry, while quite brief, will provide a basic understanding of the principles of chemistry. The five chapters devoted to organic chemistry provide a basis of understanding that is needed in the subsequent chapters related to biochemistry.

One of the strong points in favor of this book is the inclusion of numerous biochemical applications both in the text and in the problems in the early chapters on basic chemistry and organic chemistry.

The upgrading of the hiochemistry chap-

(Continued on page A68)

-Reviewed in this Issue

Alan Sherman and Sharon J. Sherman, Chemistry in Our Changing World John R. Holum, Elements of General and Biological Chemistry Herman G. Richey, Jr., Fundamentals of Organic Chemistry Titles of Interest

Reviewer

M. Lynn James
P. Calvin Maybury
Victor I. Haubu

A67 A67

Victor J. Hruby

A68 A68

BOOK REVIEWS

ters include many significant advances in research. For example, a unit on neurotransmitters and the kinds of drugs that work at the neurotransmitter level is included. New information is included about the translation of genetic messages in eukaryotic cells as opposed to E. coli. A new unit on recombinant DNA and a special topic on interferon have been added. A chapter devoted to radiation and health is included and a new topic on the PET scan appears for the first time.

This sixth edition represents a major change in design. Worked examples, set off by a color screen, appear throughout. These examples are followed directly by Exercises. (Answers to these exercises are found at the end of the book.) Special topics are found throughout the text and set aside by a color screen. At the end of each chapter separate review questions and problems are provided. Answers at the end of the book are provided for alternate problems. The remainder are included in an instructor's manual. A new design feature is the addition of a full glossary which is a summary of a list of key terms that appear at the end of each chapter.

This sixth edition should be welcomed by those involved in the training of students in the allied health professions.

> P. Calvin Maybury University of South Florida Tampa, FL 33620

Fundamentals of Organic Chemistry

Herman G. Richey, Jr., Premice-Hall, Inc., Englewood Cliffs, NJ, 1983. xvi + 480 pp. Figs. and tables. 18 × 24 cm. \$24.95.

Richey has written an interesting introductory textbook in organic chemistry meant for the student primarily interested in a one-semester introduction to organic chemistry. The length of the book is just about right for this purpose, with suitable material for a 40-lecture sequence. Richey follows a reasonably stardard organization of the book with chapters on the following topics: alkanes; alkenes and alkynes; aromatic compounds; alcohols, ethers, and phenols; chiral compounds; organic halides; amines; aldehydes and ketones; carbohydrates; carboxylic acids; esters and amides; lipids; amino acids and proteins; nucleic acids; and a final chapter on spectroscopy of organic compounds.

This book is distinguished by the clarity of presentation of the material. Even more importantly, though the material is introductory in nature and limited in scope, it nonetheless portrays organic chemistry as an exciting and ongoing enterprise. It does a particularly admirable job of intercalating various aspects of bio-organic chemistry with classical organic chemistry. In general the discussions in the bio-organic area are well chosen and accurate. However, some minor misinformation has crept in. For example, "enkephalins" are not "endorphins" (p. 380). In any case, since the vast majority of students taking a onesemester course in organic chemistry have primary interests in some aspect of the biological or behavioral sciences, a more thorough integration of bio-organic chemistry with classical organic functional group chemistry is needed. This book goes a long way in satisfying this need.

In summary, the book represents an excellent addition to introductory organic chemistry texts. It should be seriously considered by all who are teaching one-semester college courses in introductory organic chemistry.

> Victor J. Hruby The University of Arizona Tugson, AZ 85721

Titles of interest Symposium 1983

Ion Exchange Membranes

D. S. Flett (Editor), John Wiley & Sons, Somerset, NJ, 1983. 0 \pm 210 pp. Figs. and tables. 15.5 \times 23.5 cm. \$49.50.

Topics Covered: Trends in Ion Exchange Membrane Science and Technology; Separation of Anions by Electrodialysis; The Capenhurst Electrolytic Etchant Regeneration Process: Supported Liquid Membranes for Metal Extraction from Dilute Solutions; Ion Exchange and Ion-Selective Electrodes: Application of Solid Electrolyte Membranes to High Temperature Process Control and Metal Refining; The Development of β -alumina Membranes for Use in Electrochemical Devices; Chlor-alkali Electrolysis Using Perfluorocarboxylic Acid Membrane; Perfluorinated Ion Exchange Membrane, Neosepta-F and Its Properties; Equilibrium and Transport Properties of Perfluorinated Membranes Immersed in Concentrated Electrolyte at Elevated Temperatures; The Progress of Membrane Technology for Chlor-alkali Production; Ion Exchange Membrane Application for Electrodialysis, Electroreduction and Electrohydrodimerisation; An Electrochemical Unit for the Recovery of Sodium Hydroxide and Sulphuric Acid from Waste Streams.

Measurement of Suspended Particles by Quasi-Elastic Light Scattering

Barton E. Dahneke (Editor), John Wiley & Sons, Somerset, NJ, 1983. $xiv \pm 570$ pp. Figs. and tables. 16×23.5 cm. \$39.95.

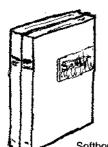
This volume contains papers printed at the Symposium on Measurement of Suspended Particles by Quasi-Elastic Light Scattering in Santa Monica, California on February 18 and 19, 1982.

Molecular lons: Geometric and Electronic Structures, Series B, Volume 90

Joseph Berkowitz and Karl-Ontjes Groeneveld (Editors), Plenum Publishing Corporation, New York, NY, 1983. xii + 495 pp. Figs. and tables. 17 × 26 cm. \$79.50.

This volume contains contributions presented at the NATO Advanced Study Institute on Molecular Ions held on the island of Kos, Greece, from September 30 to October 10, 1980.

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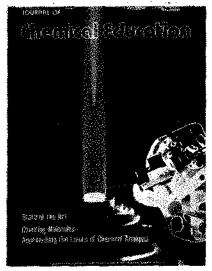


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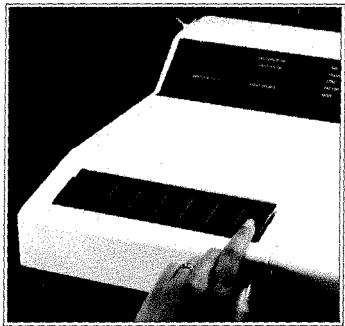
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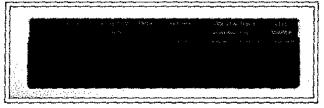
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