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Gilbert Newton Lewis 1875–1946

Report of the Symposium

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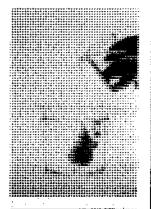
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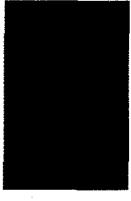
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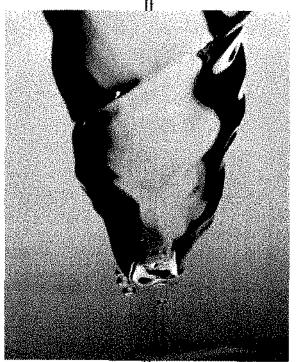
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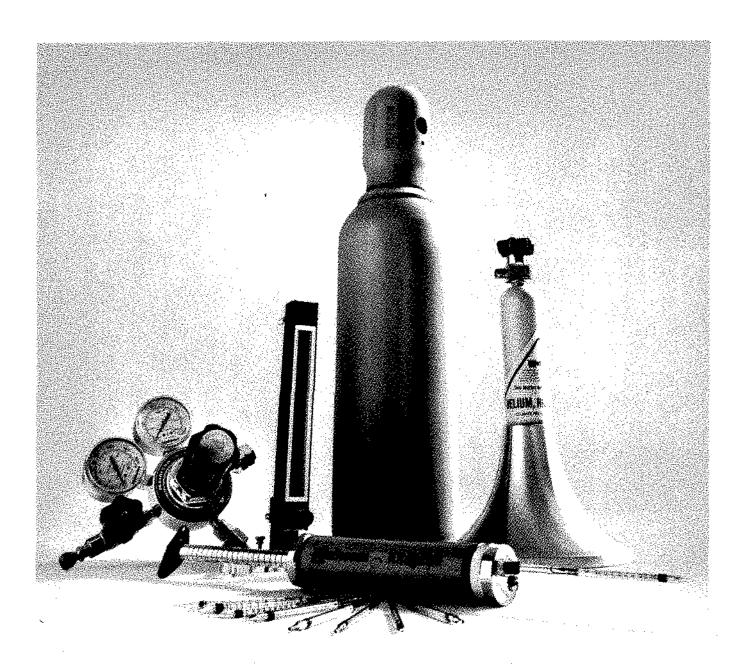








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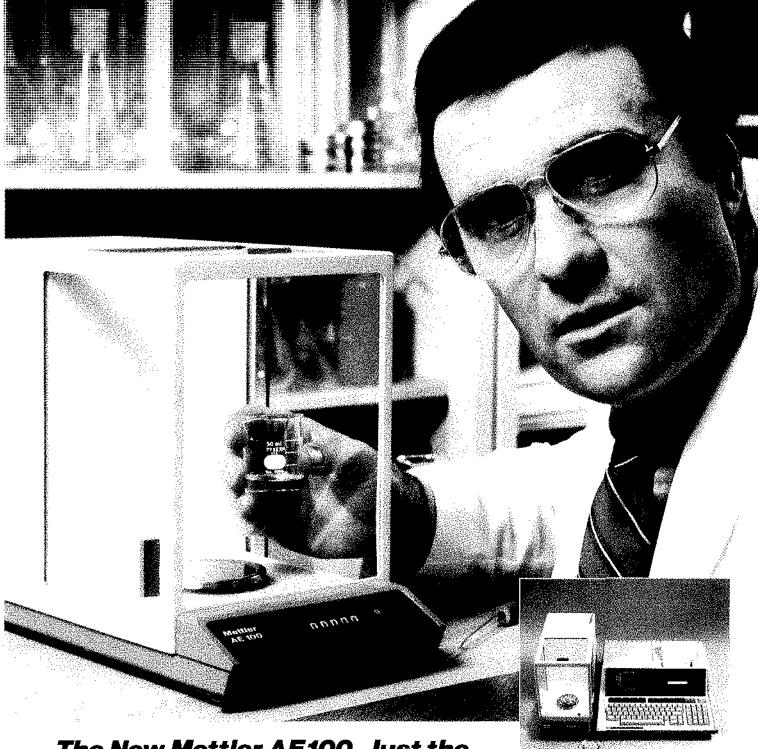
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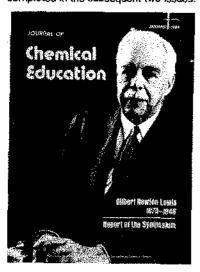
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The Cover

This month's cover portrait of G. N. Lewis introduces the publication of the symposium which was held in his honor at the Las Vegas ACS meeting in March 1982. The proceedings will begin in this issue and be completed in the subsequent two issues.



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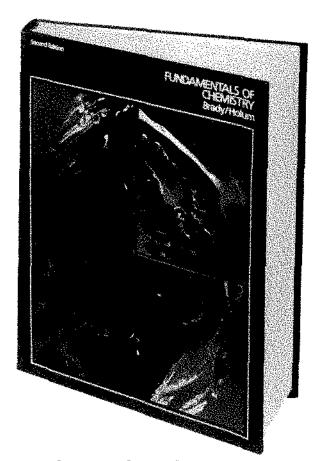
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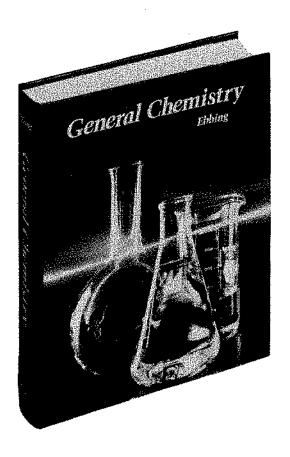


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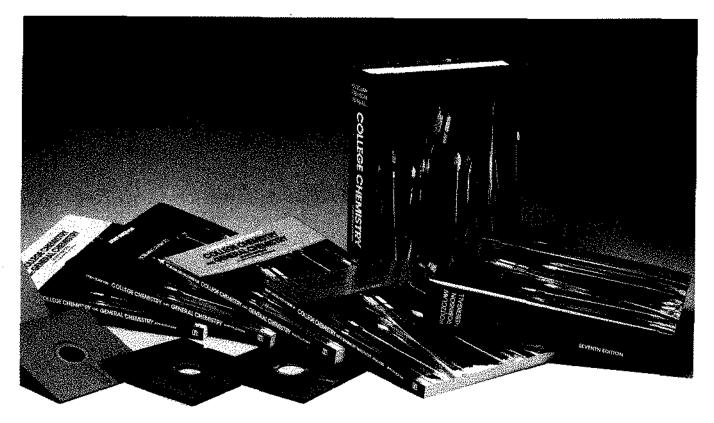
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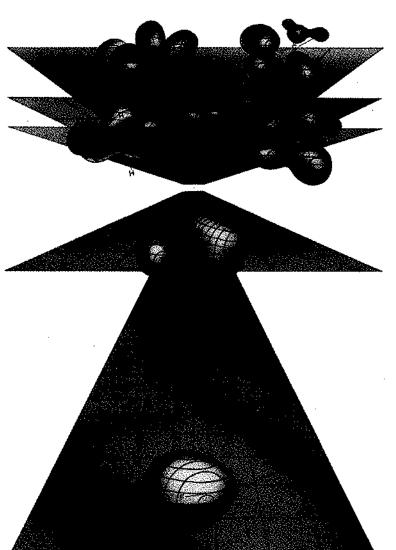
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Elgenenergies of Methyl Fluoride

rafety in the chemical laboratory

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

Good Practices for Hood Use

William G. Mikell and William C. Drinkard

Central Research and Development Department, E. I. du Pont de Nemours, Experimental Station, Wilmington, DE 19898

Laboratory fume hoods are important safety devices. They are provided to protect personnel from chemicals that are being handled or stored which are potentially injurious to health. In addition to protection from chemical fumes they provide some degree of protection from fires and explosions. Hoods, however, are secondary or "back-up" safety devices. Training of personnel, proper design of experiments, and careful operation of equipment are the primary controls. Even the hest hoods cannot overcome poor work practices by the user. Studies (1, 2) have shown that when good work practices are employed with a properly installed and functioning hood, the user is protected. The purpose of this brief article is to outline these good practices for hood use.

Assumptions on Hood Design and Performance

A properly designed, installed, and functioning laboratory hood is a complex device which requires many design and operating compromises such as size, opening, materials of construction, fire and explosion protection, location in lab, air flow, air distribution, services, convenience, cost of operation. To stress some design parameters or to overlook others may seriously affect the performance of the installation. For example, there is a great tendency among hood users to place primary emphasis on face air velocity (or face velocity) as being the single most important

(Continued on page A14)

William Mikeli is the Environmental Control Manager at the du Pont Experimental Station in Wilmington, Delaware. He served with the National Research Council Committees which developed the reports on "Prudent Practices for Handling Hazardous Chemicals in Laboratories" and "Prudent Practices for Disposal of Chemicals From Laboratories."

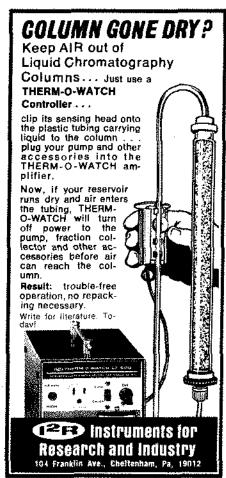
W. C. Drinkard joined du Pont in 1960 and is currently Manager, Facilities and Safety in the Central Research and Development Department at the Experimental Station in Wilmington, Delaware

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safety

parameter. There may be other design or operating parameters of equal or greater importance such as the room air distribution to the laboratory. The hood's ultimate performance is judged by the protection it provides the user not by how rapidly the air may be moving over the bench top. Much exists in the literature (2-5) on this subject. It is assumed, however, that in discussing safe work practices that the chemist has available a satisfactorily installed and well-performing hood.

Preparation for Work

Before beginning work, the user should make sure that all of the sashes are in place and movable as required. The need for any additional safety shields to be used within the hood should be anticipated and they should

Users are responsible for hood operation and should be alert to signs of malfunctions such as unusual sounds or reduced draft. Any suspected inadequacy should be checked immediately. Hoods can be checked by a smnke test, a bit of yarn on a wand, or by observing an air flow gauge if the hood is equipped with one. The user should be alert for any air flow changes or shift in operation and stop work to check it out should either

A plan of action should be prepared for a ventilation or power failure; time may be critical in preventing a serious incident.

Hood Practices

Efficient and safe operation in a well-constructed hood requires good work practices. At all times during operation in the hood sash openings should be kept to a minimum. This is important to minimize operator exposure. In addition, all sources of emission should be kept as far back in the hood as possible (6 in. from the plane of the sash is a good rule of thumb). Recent studies (1, 2) have confirmed the importance of this rule; the degree of protection provided the user has been shown to improve by orders of magnitude when emission sources are placed into the hood away from the plane of the sash. In addition, the user's face should be kept outside the hood while performing chemical operations. Leaning into the hood to adjust equipment when it is operating can result in a significant air turbulance with a corresponding loss in protection.

A sufficient volume of nonturbulent air should flow through the hood at all times. Thus, storage of chemicals and equipment in the hood should be kept to a minimum, and items should not be placed so that they block exhaust ports from the hood. Since air must be supplied to the hood for proper operation it is important that make-up air vents in the laboratory not be blocked by furniture or equipment of any kind. In addition, pedestrian traffic in front of the hood should be minimized and laboratory doors kept closed to reduce air turbulence.

Materials, such as paper, entering the exhaust ducts can lodge in the ducts or fan and reduce hood efficiency. For example, when trouble shooting a poorly performing hood, it is not unusual to find paper towels and/or tissues in the airducts and on the fan.

Traps, scrubbers, or incinerators should be used as primary devices to prevent toxic and/or noxious material from being vented into the hood. This is particularly true when working with highly toxic or odiferous materials such as carcinogens and environmental pollutants.

In conclusion, it is worth repeating that laboratory hoods are secondary safety devices whose effectiveness can be compromised by improper or poor work practices. Primary attention should be focused on the fundamentals of training personnel, proper design of experiments and careful operating techniques.

Literature Cited

- (1) Mikell, W. G., and Hobbs, L. R., "Laboratory Hood
- Studies," J. CHEM. EDUC., 58, A185 (1981).

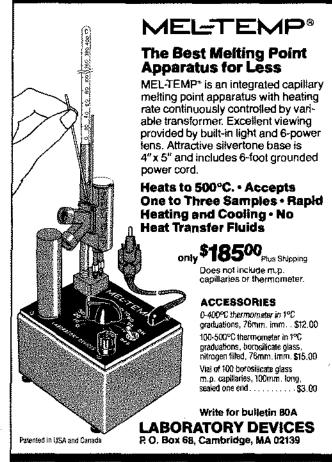
 (2) Pulker, F. H., and Etchells, A. W., "The Rating of Laboratory Hood Performance," ASHRAE Journal, (October 1979).
- (3) Chamberlin, R. I., and Leahy, J. E., "Laboratory Fums Hood Standards," Recommended for U.S. Environmental Protection Agency, Contract No. 68-01-4661, January 1978.
- (4) Hughes, D., "A Literature Survey and Design Study of
- Tunecupboards and Fume-Dispersal Systems, "Occupational Hygiene Monograph No. 4, Science Reviews Ltd., London, November 1980.

 Caplan, K. J., and Knutson, G. W., "Development of Criteria for Design, Selection and In-place Testing of Laboratory Fume Hoods and Laboratory Room Vanilation Air Senature Need Beneral "ACMEDIA". Ventilation Air Supply: Final Report," ASHRAE RP-70, March 1978.

Good Hood Practices

- Sash openings should be kept to a minimum.
- Sources of emission should be kept at least 6 in. inside the bood.
- Users should keep their faces outside the plane of the bood sash.
- · Storage in the hood should be kept to a minimum
- Exhaust ports from hood and supply air vents to room should not be blocked.
- Traps, scrubbers or incinerators should be used to prevent toxic and noxious materials from being vented into the hood exhaust system.
- · Remain alert to changes in air flow.
- Prepare a plan of action in case of an emergency, e.g., power failure.
- To save energy, turn off blower and close sashes when hood is not in use.





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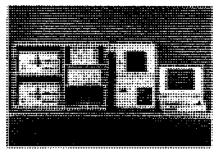
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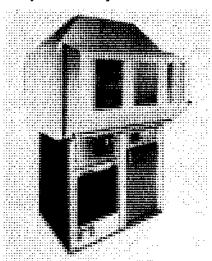
Dual-purpose, Fused-silica Columns



A rugged and highly retentive dual-purpose column has been introduced by Hewlett-Packard Co. The HP Series 530 µ can be used in both capillary and packed-column gaschromatograph analyses. Packed columns have been a tradition in the science of chromatography since its beginning. The need for a column to provide solutions to more complex, multi-component samples resulted in HP's introduction of the fused-silica capillary columns in 1978. Many analyses done with capillary can be handled with the HP Series 530 μ column. A high sample capacity and ease-of-use make the dual-purpose column a practical alternative for packed-column chromatography. The HP Series 530 μ has a stationary-phase film thickness of 1.5 to 3 microns, providing adequate capacity for one-microlitre injections of solutions that normally are analyzed on a 3 to 5% packed column. The use of quality phases and inert fused-silica tubing results in a lower bleed than the corresponding packing, permitting hightemperature analyses like simulated distillation with little need for matched-column compensation. When operated under packed-column conditions, the new column allows the chromatographer to use a technique previously restricted to capitlary operation. Two HP Series 530 μ columns can be installed in the same packed injection port with their exit ends connected to two separate datectors. This "50/50-split" technique will provide significant time-saving benefits in qualitative analyses, HP chemists believe.

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X-ray Diffraction System

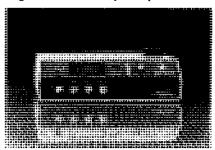


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(Continued on page A18)

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- A separate chapter on solubility equilibrium is included (Ch 17)
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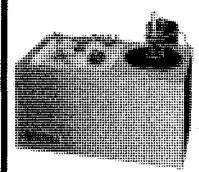
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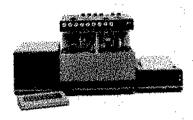
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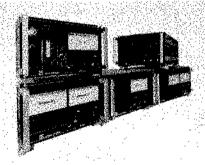
Multidimentional Gas Chromatography



ES Industries, the exclusive U.S. representative for Siemens Gas Chromatographs, has announced the availability of the Siemens Si-Chromat 2 Gas Chromatograph. According to a company spokesman, the SiChromat 2 is a double oven G.C. which features a patented valveless "live" column switching system. With this system, multidimentional chromatographic procedures such as heart cutting sample components for transfer to a second column and backflushing the precolumn can improve resolution and save valuable analysis time. Valveless means the sample does not come into contact with any valves and the 'five'' principle means that the switching times can be determined directly.

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IR Gas Analyzer



The Binos infrared Gas Analyzer makes precise end accurate determinations of changes in CO2 and H2O vapor levels in plant chambers. A measurement range of ±25 ppm CO₂ at a nominal reference point value of 330 ppm CO2 is possible with this equipment. The instrument also measures absolute CO2 (typically 0 to 600 ppm) as well as absolute and differential H2O (typically 0 to 1% as an absolute range and 0 to 5000 ppm as a differential range). Four standard models of the BINOS Infrared Gas Analyzer are available from Tekmar Co., and all have appropriete infrared optics to maximize accuracy and sensitivity for their specific applications. Each model is portable and works on 12 V dc or 120 V ac; heated optics are not required. These models feature analog or digital display of the measured component and provide a 0 to 1 volt recorder output signal over the measured

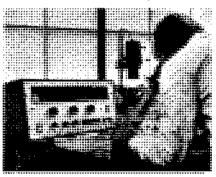
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Autosampler for AA

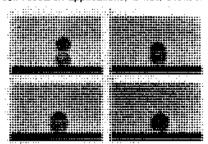
Instrumentation Laboratory (IL) is offering a 6-page report on the IL FASTAC II autosampler. The FASTAC II is the only AA autosampler which employs aerosol deposition of the sample for furance atomization. Because it is a nebulizer based system, the FASTAC II provides automated analyses for both flame and furance atomization. This dual canability minimizes purchase cost, space requirements, and changeover time. Unlike any other furnace autosampler, the FASTAC # converts the sample to an aerosol and deposits it into the furnace cuvette, where it dries immediately on contact. This technique has many advantages: 1. It saves time and simplifies methods development by eliminating the lengthy and complex furnace drying step. 2. It works equally well with aqueous and organic solvents, 3, it eliminates many analytical interferences. 4. It simplifies preparation of standard solutions. 5. It can be set to produce almost any desired analytical sensitivity, 6, it can be used with samples that are too viscous to pipette. 7. The same system is usable for flame and furance. In comparison to the previously offered IL FASTAC autosampler, the FASTAC II offers approximately 10X higher sampling efficiency, and is easier to use.

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Zimmermann Cell Fusion System



The Zimmermann Cell Fusion system that electrically fuses cells, including fusing hybridomas for monoclonal antibody production and fusing cells for plant genetics, yeast transformations and other biotechnology and cell research applications, is now available



from GCA/Precision Scientific Group. With the Zimmermann Cell Fusion system, cells are exposed to a low level electrical field, orienting the cells end to end. Alignment voltages can be varied from zero to 40 volts at a frequency of 10KHz to 5MHz. A short, direct current pulse is then applied, which opens micropores in adjoining cell membranes, allowing mixing of

(Continued on page A20)



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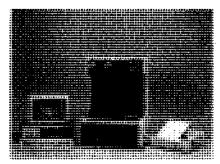
JAMES A. GOLDMAN

cellular contents and resulting in their fusion. Each electrical pulse can be precisely controlled from zero to 250 volts. Up to nine separate pulses can be applied, with durations to 99.9 microseconds. By providing a number of separate small pulses, the Zimmerman Celi Fusion system gives the biologist precise control over the cell fusion technique and is less destructive to the cells than other fusion techniques. The benchtop Zimmermann Cell Fusion system is also designed to be userfriendly. Major process parameters are controfled by large, easily accessible diels with digital LED readouts of their values, in addition to the power supply and an assortment of fusion chambers, the system includes an extensive protocol manual. The manual, which is based on the work of Dr. Ulrich Zimmermann and his colleagues at the Nuclear Research Center of West Germany and by GCA biotechnology scientists, details sample protocols for fusing yeast cells, plant cells. erythrocytes and hybridomas. A technical description of the Zimmermann Cell Fusion process is also provided.

Circle #48 on Readers' inquiry Card

Porosimeter

Micromeritics' Pore Sizer 9305 porosimeter features an RS232 port that allows automatic acquisition, reduction and reporting of porosity



data. The instruments include a demonstration program listing for the IBM PC at no additional cherge. Now data can be presented in tabular and graphic formats. Analysis data can be stored and retrieved for analysis comparison. Sample pore size distributions, total pore area, median pore volume and area, average pore diameter, bulk and apparent density can be stored and manipulated to suit individual leboratory requirements. The Pore Sizer is designed to measure the porosity of powder or solid samples. The data from porosity analyses represents the intrusion and extrusion of a non-wetting figuid (mercury) into semple vold volumes under pressures that are ramped to 30,000 psi.

Circle #49 on Readers' Inquiry Card

Mercury Pressure Porosimeter

Erba Instruments, the U.S. seles and service organization of Carlo Erba Strumentazione of Italy, provides e detailed analysis of their automatic Mercury Pressure Porosimeter—2000 Series. The 8-page brochure details and illustrates the complete, fully-programmable

automatic system for determining pore size, volume, surface area, bulk density and particle size. Six examples demonstrate the Porosimeter's results reported in the field of catalysts, ceramics and cements. Also included is information pertaining to ink-bottle pores and ultramacro porosity.

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Multipoint Ambient Air Monitoring System

The Miran 981 Multipoint Ambient Air Monitoring System, that helps to ensure protection of personnel by monitoring the concentration in air of up to 5 gases or vapors at up to 24 remote locations, is featured in a 6-page data sheet recently published by The Foxboro Co. The Miran 981 can monitor more than 200 of the approximately 400 gases declared hazardous by the Occupational Safety and Health Administration (OSHA). This system can be used to monitor air quality in hospitals and medical supply manufacturing plants, power plant control rooms, industrial environments, and other locations as far as 300 m (1000 ft.) from its enclosure. The operating principle of the Miran 981, discussed in the data sheet, is based on infrared spectroscopy. The system's microprocessor controls the infrared spectrometer, signal averages the infrared transmission measurements at each programmed wavelength, calculates absorbance, and uses a stored coefficient matrix to determine the concantrations of components in the air sample. This microprocessor-based system provides a printed report with eight hour and monthly time weighted averages (TWA) of the toxic gas concentrations in parts per million (ppm) and alarm conditions at each remote location. An interactive keyboard combined with user oriented programs makes the operation of the 981 simple and virtually error free.

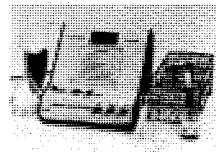
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UV-Vis Absorbance Detector

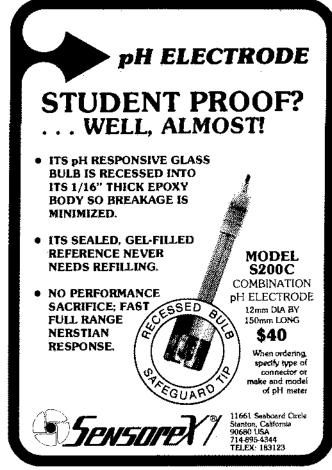
The Spectroflow 757, available from Kratos Analytical Instruments, is a logical alternative to single wavelength detectors because of its price and sensitivity. It is ideally suited for use with analytical scale HPLC, "fast LC", prep and microbore. A touch-sensitive membrane panel operates instrument functions, while a rear panel connector permits comprehensive computer control using any existing controller. The Detector incorporates important features like auto-zero and digital noise suppression.

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Digital Colorimeter



(Continued on page A22)



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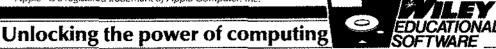
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out of the editor's basket

JAMES A. OZI DMAN

Chemtrix, Inc., announces its Type 24 Digital Colorimeter that features readouts directly in two concentration ranges, 0-199.9 and 0-1999; absorbance and transmittance readouts; plus, a universal cuvette holder. Ideal for water, pollution control, clinical and industrial analyses, it has eight analytical wavelengths from 350 to 660 nanometers which are adjustable by a front panel thumbwheel control. Absorbance, % transmittance and concentration levels are easily read from the instrument's high-contrast liquid crystal displey (LCD). The universal cuvette holder permits the use of square cuvets up to 12.5 mm and round tubes up to 19 mm diameter. Additionally, a full line of water test kits are available for use with tha Type 24.

Circle #53 on Readers' Inquiry Card

pH Meters

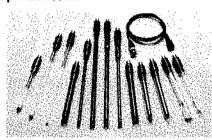


Corning Science Products has introduced e line of five easy-to-operate pH meters with a unique "detta" shape and unified display which allow easy use and quick reading from the laboratory benchtop. Beginning with the Model 120, a lightweight, battery-operated meter for use in the lab or in the field, the line ranges upward to the Model 155, a pH/ion meter for all research applications which features known and sample addition/subtraction modes, step-by-step alphanumeric prompting in five languages, automatic buffer recognition, three-decimal accuracy, a digital clock and timer, and activity and memory functions capable of accommodating a five-electrode testing system. Other models in the line include: Model 140-Ideal for quality assurance or education applications where speed of analysis over a quantity of samples is important. Its four-button control panel is unequalled for ease of use. Model 145--Incorporates all features of the Model 140, plus a sharp, eight-digit alphanumeric LED display that prompts users through calibration and measurements in automatic or manual operations mode. The Model 145 is ideal for basic research functions, containing a microprocess-operated lookup table that automatically matches buffer and temperature calibrations. Model 150---The Model 150 offers all the features of the Model 145 plus direct measure of activity/concentration, clock and timing modes, automatic endpoint sensing, set points, five-language alphanumeric prompting and a five-electrode memory for use with Corning's Multi-Electrode Selector-all operable through

five simple function keys. Simply labeled for quick calibration, the new Corning pH meters are designed for rugged durability in a laboratory or field setting. Cases are made of molded structural foam with keypads of polyvlnyl chloride especially coated to withstand chemical spills. All Corning meters are supplied with a plastic barrel combination electrode with Corning's exclusive replaceable junction feature. In addition, complete lines of accessories and test electrodes are offared by Corning.

Circle #54 on Readers' Inquiry Card

pH Electrodes

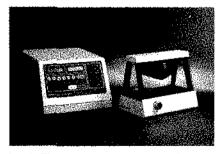


FETURA"-11 PE ELECTRODE Boukman Instruments, Inc. Scientific Instruments Division

The Futura-II pH electrode line from Beckman Instruments, inc., a family of 21 electrodes, is designed for high performence and maximum reliability in any kind of environment. Each Futura-II electrode has a connector/cable system for quick interchanging of 1-, 2- and 6-meter cables. The gasketed connector seals off the electrical contacts from the external environment to protect them against the effects of steam, chemical vapors, liquids and other substances that can produce inaccurate measurements. A self-aligning screw-on connector prevents misalignment. The lownoise, high-rejection design of the cable assures accurate and repeatable results. The Futura-II line of elactrodes includes glass. reference and combination electrodes to meet the requirements of particular applications. The internal design of the electrodes enhances accuracy, repeatability, speed of response and long life, even under adverse measuring conditions.

Circle #55 on Readers' Inquiry Card

Autobalance



Perkin-Elmer's AD-6 Autobalance offers features that simplify weighing tasks. Standard features include automatic zeroing and taring, simple calibration, safe memory for 899 samples, additive or multiplicative factoring of weights and slatistics routine. The control unit includes a keyboard panel with dual LCD dis-

plays and an accessory drawer for convenient storage for forceps and weights. The separate weighing unit allows right or left-handed access and unique pan arrests make sample handling easy. The AD-6 Autobalance has a 5 gram capacity with 0.1 μ g sensitivity. An RS232C accessory allows the addition of a Perkin-Elmer Model 680 printer or interface capability into a computer.

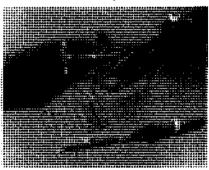
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Analog Interface

VOTEM is a complete package, available from Down East Computers, consisting of hardware and software that enables your computer to measure, display and record "real world" analog signals. Your computer can monitor any physical phenomenon (pressure, light, temperature, etc.) that can be represented by a DC voltage. A probe is provided for air and liquid temperature measurements. Your computer becomes a "smart" digital volumeter and thermometer with storage capability, Just think of the possible applications. Use VOTEM and your computer to monitor the temperature in a home energy conservation project to save money and possibly quality for an energy tex credit on the entire system. VOTEM also amplifles and cleans up the tape signal for reliable program LOADing. The tape signal conditioner circuit will allow you to LOAD tapes with a lower volume setting on your tape recorder, resulting in less noise and more dependable LOADs. You will be able to LOAD from lapas which would previously not comply. VOTEM requires no modifications to your computer and does not use the computer's expansion connector, leaving it free for other add-ons such as the memory pack and printer.

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Multiple Manifold Dispenser



Labindustries' adjustable manifold dispenses simultaneously into microtiter plates with 6, 8 or 12 wells, or into test tubes in a rack. Available as a complete instrument with Labindustries' micropipettor and sampling systems, it can be attached to any repetitive dispenser or pipettor with a Luer tip outlet. This transparent, autoclavable manifold dispenser has interchangeable glass capillary outlets and closures, which adjust to match rows of wells in plates, or rows of test tubes in a rack. This instrument is designed for ELISA, HLA, tissue typing, cell feedings, simple inoculations and chemistries. Dispenser volumes are adjustable from very few microliters to several milliliters, with $\pm 3\%$ reproducibity. A unique feature of the multiple manifold dispenser is that it can

(Continued on page A24)

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out of the editor's basket

JAMES A GRYDMAN

be used T-style (center operation) or offset style (side operation). Three modets are available.

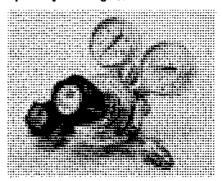
Circle #58 on Readers' Inquiry Card

Chlorinator Alarm Switch

Fischer & Porter announces an economical switch which can be used in an alarm circuit to advise operating personnel that the chlorine gas supply feeding a Chlorinator has been depleted. The switch serves to prevent unchlorinated water from reaching consumers or unchiorinated wastewater from being discharged into receiving bodies of water. Alternately, the switch may be used with automatic chlorine changeover systems to inform operators that the Chlorination system is operating from a standby source. The switch is available in kit form for use with all Chlorinators having capacities up to 2000 lb/day, and may also be used to retrofit Chlorinators which are presently in service.

Circle #59 on Readers' Inquiry Card

Specialty Gas Regulator

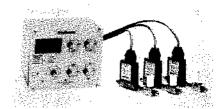


Scott Specialty Gases introduces "The Protector," a high purity two stage regulator designed by Scott Specialty Gases to protect the quality of high purity noncorrosive specialty gases. The Protector is the answer to four non-corrosive, high purity delivery system problems. Performance....The Protactor has two pressure reduction stages for accurate and sensitiva pressure control-from full cylinder pressure to 200 psi--- "just set it and leave it." Contaminant Prevention-The Model 18 has a non-contaminating stainless steel diaphragm in both stages to prevent diffusion and outgassing; it also have Viton and nylon seats and nylon and Tefion seals. Safety--- A safety feature standard on The Protector but extra on meny two stage regulators is a first stage relief device to protect the second stage and the downstream equipment. Savings--The materials of construction used in The Protector provide years of trouble-free service.

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Multichannel Dyna-Blender

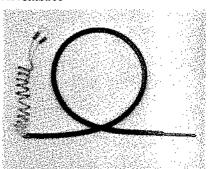
Matheson announces a third generation of its gas blending equipment, the Multichannel Dyna-Blender. The new Multichannel Dyna-Blender delivers on-line, premixed gases at



different ratios regardless of temperature, pressure or flow variations. This unit features up to four channel blending capability, a digital display and separate controls for each channel. It also offers costs savings and space savings over modular systems without compromising control, accuracy and precision. Each of the four channels can be controlled, remain independent with a constant flow, or remain idle with no flow. Control of the channel can be by an external ratio of another flowstream, by internal manual adjustment, or by en external 0-5 VDC signal. The digital LED display and the four channal set-read switch allow the operator to monitor each channel, one at a time, as desired.

Circle #81 on Readers' Inquiry Card

Armored Sheath Thermistor Assemblies



Armored sheath thermistor assemblies, Series A800, are available for Thermometrics for measuring temperatures in arduous atmospheres where extrame temperatures and rough service conditions are encountered. These assemblies are most often used for monitoring or controlling the temperature of hot, corrosive liquids, air or semi-solids; and in process controls. A series A800 assembly consists of a thermistor sealed at the tip of a glass rod, which is then encapsulated into a stainless steel enclosure with a flexible, protective armor sheath over the extension leads, and are available with a variety of matrials and insulations based upon the specific applications. The housing may be a straight tube, or may have an adaptor collar or threaded hex body as desired. The closed end tube is available in lengths from 1 inch to 6 in.; the armored sheath may be 2 ft to 20 ft long. Standard units are rated for use from ~40°C to 300°C. The closed end tube may be immersed to within 1/4-in, of the hub on the sheath.

Circle #62 on Readers' Inquiry Card

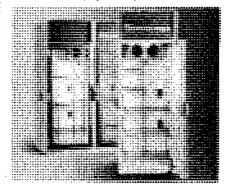
HPLC Column Temperature Controller

Kratos' Delta Temp line of HPLC column temperature controllers is described in a 2-page datesheet. Complete specifications and ordering information are provided. The Delta Temp has a range of 0 to 150°C; with complete thermal insulation to eliminate hot outer

surfaces. Column cooling is possible by using a recirculating refrigerating bath with precise counter-heating by the Delta Temp. Up to 4 columns may be operated at any one time. Maximum column size is $\frac{3}{8}$ in. dia. \times 30 cm long. Computer control is practical via built-in interfaces.

Circle #63 on Readers' Inquiry Card

Chromatography Refrigerators



The Jewett Refrigerator Co., Inc. has announced two refrigerator models designed to meet the axacting demands and specific needs of liquid chromatography. This line of refrigerators compliments their diverse range of hospital, laboratory and pharmaceutical refrigerators and freezers. Available in either single door (25-cubic ft) or double door (55cubic ft) models, both models consistently maintain a dependable uniform cabinet temperature of 4°C. Exterior fronts are provided in a contemporary blue trim with beige cabinet and white ename! interior. Standard features on both units include: triple Thermopane glass door (s); the security of key-locking doors; two convenient vapor-proof covered access portholes; two interior vapor-proof covered duplex outlets; adjustable stainless steel cantilevered and four-position support shelves; and external switches for intarior light and lower outlet shut-off. Optional accessories offered are Jewett's 7-Day Recording Thermometer which monitors temperature variations of stored product with the Mark-A-Matic II continuous-flow inking system. In the evant of a power fallure, its spring wound mechanism provides a complete record of the temperature of stored items. Jewett's Temperature Power Monitor System is an AC/battery operated monitor able to warn of dangerous temperature variations or power failure.

Circle #64 on Readers' Inquiry Card

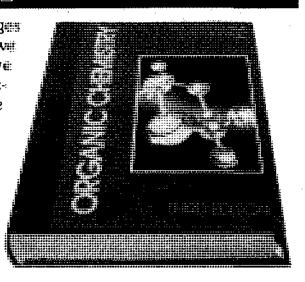
Lo Temp Freezer

The Harris Lo Temp 25LS Freezer is a sturdy, reliable, chest type freezer of large volume. It can be used in medical, life science and industrial applications. Insulation is 5-in and foamed-in-place from polyurethane. Volume is 25 cu. ft. Operating range is from --79.°C to -104°C. The external dimensions are 94-in. long X 32-in. deep X 44-in, working height. The chamber dimensions are 59 ½-in. long X $21\frac{1}{2}$ -in. deep \times 33 $\frac{1}{2}$ -in. high, internally. The freezing unit is a dual cascade system which uses less energy than comparable freezers. Magnetic gaskets assure efficient cooling. The 25LS can be air or water cooled. It can be backed up by a CO₂ standby system and can employ non-flammable refrigerants.

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editorially speaking

Facts and Their Roles in Chemistry

Facts, which are defined as "truths known by actual experience or observation," occupy a unique position in chemistry. Facts must be carefully distinguished from theories, which are "coherent groups of general propositions used as principles of explanation for classes of phenomena." At the same time facts and theories are also intimately interrelated. Facts are necessary to support theories, and hence, are essential in an intellectual sense. Facts are also the medium in which theories operate. The details of theories are structured by facts, and in a real sense facts and theories are synergistic.

The trouble with facts is that we often don't really know which of them are important—or are even likely to become important. This, of course, is a result of the evolutionary nature of chemistry as a discipline. Some facts never achieve the status of long-term recognition for their importance, although they may appear to be momentarily consequential. Consider, for example, the critical role played by the electronic spectra of Ti³⁺ ions in different ligand environments or by the NMR spectrum of the compound with the molecular formula Fe(CO)₃C₄H₄, cyclobutene iron tricarbonyl. Because some facts are widely recognized as being critically important to increasing our understanding of chemistry, interest in obtaining them quickly rises to a crescendo. Once facts of this kind have made their contribution, however, they often disappear into oblivion.

Some facts are wrong, but useful nonetheless. Thus, Lewis chose the octet as the measure of a stable electronic arrangement because it was thought that "inert gases" did not form compounds. We now know that octets are no longer critically important, witness the existence of compounds such as SF₆ and PF₅. Furthermore, some of the "inert gases" do form stable compounds and/or polyatomic anions, and hence the inert gases are now called "rare gases".

Chemistry also incorporates a large body of "facts" that derive from relationships among facts obtained by actual experience or observation. The importance of some of these relationships is without question, e.g., molecular weight. Others have not stood the test of time. For example, the parachor was thought to be an important quantity in helping decide questions of molecular structure for a number of years in the 1920's, (parachor = $M\gamma^{1/4}/(D-d)$, where γ is the surface tension of a substance, M its molecular weight, D the density of the liquid state, and d the density of the saturated vapor, all measured at the same temperature.) Today the parachor finds little use or application, and the idea essentially has been relegated to an historical cul-de-sac.

In a continually evolving subject, some facts which are important have no obvious connection to currently important theories; these facts and/or their existence need to be remembered if they are to be of future use. Still other facts may have a practical usefulness. In a very broad sense facts have come to be cherished. Since facts have such a special position in science, it is not at all surprising that many current instructional techniques stress their acquisition. Indeed facts can have a mesmerizing effect on both teachers and students. But teaching or learning chemistry involves more—much more—than acquiring facts.

Students need to learn to interact with the facts and concepts which underlie their subject. This can be accomplished in a variety of ways, each providing for the development of one or more analytical skills. Students should be encouraged to practice their chemistry using a variety of different methods. Hands-on experiences are critical. Students need to write and learn to receive criticism as well as he given opportunities to rewrite and refine their abilities to express themselves clearly and succinctly. They need to practice their chemistry, try to defend their ideas, test out potential solutions, and discover why a particular approach didn't work. Facts are the medium in which modern chemistry operates. The present educational process works well to help students acquire facts; but we need to give more attention to helping students acquire the skills to manipulate these facts and to articulate the ideas and operations involved in their manipulations.

JJL

in this issue

Gilbert Newton Lewis: 1875–1946

If we yield J. Willard Gibbs to the mathematical physicists then G. N. Lewis must surely rank as the greatest of American chemists. Certainly he has been the most influential. Not only did he achieve great things himself, but he was also, as many of the symposium papers bear witness, a major inspiration to an extraordinary group of students, associates, and colleagues. More than anyone else he led American chemistry from provinciality to world leadership.

There was no significance in the date, 30–31 March 1982, and even less in the location, Las Vegas, for the symposium "Gilbert Newton Lewis: 1875–1946". It merely seemed unwise to postpone such a symposium indefinitely if we were to benefit from the insights and the memories of some of the principal survivors and successors of the G. N. Lewis era. Happily they are legion. Shortly before we met in Las Vegas the following note arrived from Lewis' widow, Mary H. Lewis:

Dear, Dr. Davenport,

I am delighted that Gilbert's memory has been kept alive all these years and that a symposium is now being held in his honor. Thank you all very much for your part in it. I would have loved to be present, but unfortunately am not able to travel. I send my best wishes for the success of the symposium.

Sincerely yours, Mary H. Lewis

Similar greetings were received from Mrs. Margery Selhy, Lewis' only daughter. Gilbert and Mary Lewis' two chemist sons, Richard and Edward, together with their wives, were present in Las Vegas, and Richard Lewis traces the family background in his "A Pioneer Spirit from a Pioneer Family" (page 3).

John Servos, a historian of science whose PhD thesis at Johns Hopkins University was titled "Physical Chemistry in America: Origins, Growth and Definition," tells of the state of the discipline of physical chemistry prior to Lewis' departure from MIT for California in 1912 (page 5). Much later Glenn Seaborg was to become personal research assistant to G. N. Lewis in 1937, working with him on generalized acidbase theory by day while moonlighting in nuclear chemistry. Shortly after joining the staff in Berkeley in 1937, Melvin Calvin assisted Lewis in the development of the theory of color of organic substances and the paramagnetism of the triplet state. Both Scaborg and Calvin have known all hut four of the permanent chemistry faculty at Berkeley since 1912! The photographic essay, "The College of Chemistry in the G. N. Lewis Era: 1912-1946" (page 11), is a collation of their separate but overlapping accounts. The faces peering from these old photographs contributed far more than their share to the development of modern chemistry. This first installment of the symposium proceedings concludes with Melvin Calvin's "Gilbert Newton Lewis: His Influence on Physical-Organic Chemists at Berkeley" (page 14). An important appendix to his paper is an unpublished memoir of Lewis written in 1953



by the pioneer physical-organic chemist Gerald E. K. Branch (page 18).

Exigences of space precluded the publication of all the symposium papers in this one issue of the JOURNAL so it's well that we list what is yet to come.

February 1984

Glenn T. Seaborg, "The Research Style of G. N. Lewis: Acids and Bases."

Leo Brewer, "The Generalized Lewis-Acid-Base Theory: Surprising Recent Developments."

Kenneth S. Pitzer, "Gilbert N. Lewis and the Thermodynamics of Strong Electrolytes."

Jacob Bigeleisen, "Gilbert N. Lewis and the Beginnings of Isotope Chemistry."

March 1984

Anthony N. Stranges, "Reflections on the Electron Theory of the Chemical Bond: 1900-1925."

Linus Pauling, "G. N. Lewis and the Chemical Bond."
William B. Jensen, "Abegg, Lewis, Langmuir, and the Octet
Rule."

Michael Kasha, "The Triplet State: An Example of G. N. Lewis' Research Style."

In the Bancroft Library of the University of California there is a strange box of miscellaneous odds and ends labelled simply "G. N. Lewis." Among them we find visiting cards, several receipted bills, a military order from the time Lewis served under General Pershing, and the manuscript of a speech given on some unknown occasion to an obviously general audience. This latter concludes:

I have attempted to give you a glimpse...of what there may be of soul in chemistry. But it may have been in vain. Perchance the chemist is already damned and the guardian of the pearly gates has decreed that of all the black arts, chemistry is the blackest. But if the chemist has iost his soul, he will not have lost his courage and as he descends into the inferno, sees the rows of glowing furnaces and sniffs the homey fumes of hrimstone, he will call out----:

"Asmodeus, hand me a test-tube."

That last phrase might well serve as Lewis' epitaph.

Derek A. Davenport
Purdue University
West Lafayette, #N 47907

A Pioneer Spirit from a Pioneer Family

Richard N. Lewis

P.O. Box 233, Inverness, CA 94937

Anyone who knew Gilbert Newton Lewis is aware of his ability to strike out into a new field of chemistry, but few are aware of the breadth of his pioneering activities. We will hear of several areas of his chemical interests in this symposium. But his interests also included such areas as relativity, the reversibility of time, origins of the elements, economic theory, glaciology, and anthropology.

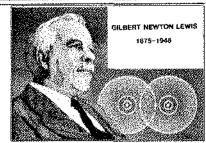
My purpose is to investigate the antecedents and background of Gilbert Newton Lewis in the hope of shedding some light on how such a remarkable man could arise. He himself did not talk much about his ancestors, though he did make an effort to track them down. He was stymied, however, when he got as far back as Barnstable, Massachusetts in the 1700's, where he found all previous records had been destroyed by fire. I have been only slightly more successful.

The first ancestral Lewis of record was George Lewis, who came from East Greenwich in Kent to the Plymouth Colony in 1632, with his wife, the former Sarah Jenkins. He became a farmer in Scituate, took the freeman's oath in 1635, and in 1639 was one of the founders of the town of Barnstable, the first English settlement on Cape Cod. He was a constable there, and a member of the militia. A Congregational Church was established in 1639; the Church building, now the Sturgis Library, was completed in 1646. We do not know George's religion, although his (probable) brother, John, who arrived in Scituate in 1635, is described as a man of some property and a devout Anglican. John's son, Joseph, lived in New London and Windsor, Connecticut.

George had five sons, of whom three, Ephraim, George, and Thomas, were born in England. His son, John, was among six men from Barnstable killed in the bloody "King Philip's War" with the Indians in 1676. Marriage records indicate a Sarah Lewis, probably a daughter, was married to James Cobb in Barnstable in 1663; John Lewis, probable grandson, was married to Alice Bishop, a widow, in 1695.

The census of 1790 listed no fewer than 34 Lewises as heads of households in Barnstable, probably all descendants of George through five or six generations, including a Jabez Lewis, our ancestor. Jabez was an Anglican (Episcopalian) and, therefore, most likely suspected of being a Tory (whether he was or not). Perhaps life became uncomfortable for him, or the town was now overpopulated. In any case he pulled up stakes with his wife, Mary, son, Wilca, teen-age daughter, daughter-in-law (former Betsey Stuart), and one grandchild. (Dad used to say, "There's royal blood in my veins." I suppose he was thinking of the Stuarts.) They joined a party of pioneers under the leadership of John Leet and traveled to the wilds of western New Hampshire, settling in what is now West Claremont.

Wilca had eight children between 1796 and 1804, but times were hard and several died in an epidemic of scarlet fever, along with his first wife and his young sister, whose portrait hung in my Aunt Polly's house for many years. George Gilbert Lewis, born in 1800, survived. He grew up in West Claremont and married Adeline Labaree, a descendant of the early French trapper, Pierre Labaree. He fathered five strong boys and promptly died, leaving Adeline to manage alone. She was made of stern stuff, however, and raised them all successfully, single-handed. Not only that, but she put them all through Dartmouth College.



One of the five, my grandfather, Frank Wesley Lewis, was born in 1840. He became a lawyer and specialized in insurance. He died in 1910 and I know very little about him, except that he wrote a book, "State Insurance" (Houghton Mifflin, 1909), that was a forerunner of our present Social Security system. He was at least 25 years ahead of his time, undoubtedly a radical, certainly a pioneer. I wish I knew whether this book had any direct influence on President Franklin D. Roosevelt. I have a photograph (1890) of him and three of his brothers, all very distinguished-looking men, but I have no information on them or their children.

Frank married Mary Burr White, the daughter of Newton White of Holbrook, Massachusetts—a "great and good man"—according to Aunt Polly. The name Burr possibly indicates some relation to Aaron Burr, but then we probably all have some black sheep in our families. Mary had been educated in a ladies' seminary near Boston; both she aud Frank had definite ideas on education and were sure that the available schools were not for their children. She taught Gilbert to read at the age of three; he read Robinson Crusoe at age five and, thereafter, every book he could get his hands on. Frank taught him his mathematics, a good teacher with an apt pupil. Somewhere, Gilbert received a thorough knowledge of Latin, Greek, German, and French.

Aunt Polly was born in 1871, Gilbert in 1875, and Roger in 1884, the year the family moved to Lincoln, Nebraska, where Frank was a lawyer and hroker. They lived on the outskirts of town on a small farm. I believe this is where Gilbert acquired a love of nature. He noted that birds would gather there as it was one of the few places in the area that had trees. (His favorite was the catbird, a bird of unassuming appearance but great virtuosity of voice.) I believe Polly had a strong influence on Gilbert. She apparently acquired some of her parents' ideas on education and set up a private school in Buffalo where she could teach the way she thought children should he taught. My parents carried on in the same vein. Their three children were taught at home until their late high school years.

I have looked with little success for any scientific background in the family. I once received from Gilbert's cousin, Dr. Marian Bugbee of White River Junction, a hattered chemistry text from about 1840 that seemed incapable of inspiring anyone, but someone in the family must have got some use out of it.

Undoubtedly the most powerful influence in Gilbert's chemical career was that of T. W. Richards, who joined the staff at Harvard in 1894, the year after Gilbert transferred from the University of Nebraska. It seems that Richards was involved both in Gilbert's undergraduate and graduate education. His thesis, published with Richards was, "Some Electrochemical and Thermochemical Relations of Zinc and Cadmium Amalgams."

Other men who influenced his career were the physical chemists Walter Nernst in Leipzig and Wilhelm Ostwald in Goettingen, under whom he studied in 1900–1901. He was certainly influenced hy A. A. Noyes, with whom he worked for seven years at M.I.T. Although he had little, if any, direct contact with Albert Einstein, he was excited by Einstein's ideas of relativity and published four articles on it, including one with R. C. Tolman and another with E. B. Wilson, Sr. In one respect he differed totally with Einstein; that was in his

insistence on the role of chance in the natural world, especially in regard to quantum mechanics and entropy. Einstein had

great difficulty accepting this.

While at M.I.T. he had room and board with Edward S. Sheldon, Professor of Romance Languages at Harvard, whom he greatly admired. Later he married Sheldon's daughter, Mary Hinckley Sheldon—another remarkable woman in Gilbert's life. She still survives at age 91. Both she and her daughter, Margery Selby, are very sorry not to be able to be bere today. So is his grandson, also Gilbert Newton Lewis, Professor of Mathematics at Michigan Technological University.

Ever the student, even while teaching, he learned from everyone around him, especially his associates and his students, among whom may be mentioned especially Joel Hildebrand, Gerald Branch, Ernest Gibson, Harold Urey, Glenn Seaborg, Melvin Calvin, and Jacob Bigeleisen.

Through his own pursuit of learning, I believe that he infected all who came near him with the spirit of inquiry. His associates and his students have gone on to spread the Lewis attitudes toward research and education. His influence continues and will continue.

I am glad all of you have been able to honor him by your presence today.

Sources

- (1) Personal reminiscenses of Gilbert Newton Lewis and Mary Hammond Lewis (Aunt Poliv).
- "The Lewis Family," The American Genealogical Research Institute, 1501 Wilson Boolevard, Arlington, VA 22209.
- (3) Records and gravestones of the West Claremont (N.H.) Union Church (Episcopal).
- (4) Arthur Lachman, "Borderland of the Unknown-The Life Story of Gilbert Newton Lewis-One of the World's Great Scientists," Pageant Press, New York, 1955.
- (5) "In Honor of Gilbert Newton Lewis on his Seventieth Birthday," University of California Press, Barkeley, 1945.
- Press, Berkeley, 1945.

 (6) Giauque, W. F., "Gilbert Newton Lewis," Year Book of The American Philosophical Society, Biographical Memoirs, pp. 317-322, 1946.

The Southwest Chemistry Lecture Exchange Program

A recent note¹ concerning the organization of a chemistry lecture exchange inspires the author to relate the formation of the very successful Southwest Chemistry Lecture Exchange Program which has been in continuous operation for an extended period of time. The mode of operation of this program may be useful to those in other areas of the country that might desire to set up a similar program.

The current program was organized by the author at the Southwest Regional Conference on Graduate Studies in Chemistry at The Southwest Regional Meeting of the ACS in Shreveport, Louisiana. Of the 16 institutions offering doctoral degrees in chemistry in the states of Arkansas, Louisiana, New Mexico, Oklahoma, and Texas, one or more representatives from each of 13 institutions participated in the formation of a lecture exchange program among their schools. The main features of the exchange were the following:

- (1) Lists of topics and speakers from each department were exchanged. A list of all of the participating institutions was sent to all of the doctoral-granting institutions so that each school in turn could send a list of topics and speakers to all of the others on the list. Some of the lists were sent out so that they were ready for lecturer invitations for the following spring semester.
- (2) In order to simplify the problem of travel expenses it was agreed that the school from which the speaker originated would pay travel costs if this was allowed by the particular institution.
- (3) New lists of available speakers and topics were exchanged each year (preferable in the summer or early fall). The list for the preceding year would be used fur inviting speakers for projected seminar programs for the following academic year.

Under this particular setup, the Exchange Program "runs itself" without anyone being responsible for the overall direction:

Several benefits have come from the Southwest Chemistry Lecture Exchange Program.

- (1) The Exchange has been a source of speakers for seminars, colloquia, and for ACS meetings. This has particularly been beneficial to the smaller institutions and ones that are "off the beaten path."
- (2) Benefits to the larger schools are the opportunity to recruit graduate students, to organize and present new material, and to become acquainted with smaller institutions in the Southwest and their faculty.
- (3) The visit of a speaker to an institution has afforded opportunities for the speaker to become acquainted with the members of the department and also to see what facilities are available. This has resulted in a number of cooperative research projects throughout the area.
- (4) Since the members of the department become acquainted with the area of the visitor's research interests, they have frequently been able to recommend the visitor to undergraduate students contemplating graduate study.
- (5) Some departments have given the speaker an opportunity to meet with undergraduate chemistry majors and present to them opportunities for graduate study at their respective schools. This has been particularly convenient at the author's institution since graduate seminars are scheduled at 3:15 p.m. on Fridays whereas an undergraduate seminar for seniors is scheduled each semester on Fridays at 2:00 p.m.
- (6) Lists of names and addresses of senior chemistry majors are being exchanged among some of the schools as potential graduate students.

Since the beginning of the Lecture Exchange Program, a number of schools that have instituted doctoral programs or which have developed viable master's degree programs have joined the Exchange Program. These are East Texas State University, Southern Methodist University, University of Texas at Arlington, University of Texas at Dallas, and University of Texas at El Paso. Since lecture exchanges have tended to occur more frequently between institutions that are closer in terms of distance, some of the schools in the outermost areas of the Southwest region have extended their range of schools beyond the Southwest region.

² The 20th Southwest Regional ACS Meeting, Washington Youree Hotel, Shreveport, Louisiana, Dec. 5, 1964.

Baylor University Waco, TX 76793

¹ Chem. & Eng. News, 34 (Sept. 20, 1982). The lecture exchange being organized by Erwin Boschmann of Indiana University is on a quite different basis than the one described in the present paper.

³ The 16 institutions were: University of Arkansas, Louisiana State University (Baton Rouge),* Louisiana State University (New Orleans) (now University of New Orleans), Tulane University, University of New Mexico, Oklahoma State University, University of Oklahoma,* Baylor University, North Texas State University, Rice University, Texas A&M University, Texas Christian University, Texas Technological College (now Texas Tech University), Texas Woman's University,* University of Houston, and University of Texas at Austin. Representatives who did not attend the meeting but participated in the Lecture Exchange Program are indicated by an asterisk.

A. G. Pinkus

G. N. Lewis: The Disciplinary Setting

John W. Servos

Department of History, Amherst College, Amherst, MA 01002

I should like to begin with a text, a short passage from a letter that G. N. Lewis wrote in February 1922 to his colleague at Lafayette College, Eugene C. Bingham. "The fact is," Lewis wrote (1),

that physical chemistry no longer exists. The men who have been called physical chemists have developed a large number of useful methods by which the concrete problems of inorganic chemistry, organic chemistry, biochemistry, and technical chemistry may be attacked, and as the applications of these methods grow more uumerous, it becomes increasingly difficult to adhere to our older classification.

When Lewis wrote this he was in his mid-forties. He had been at the University of California for almost ten years and had built there a center for chemical research and training that was without parallel in this country. He was then dictating his treatise on thermodynamics to Merle Randall and was preparing a second book on valence, both of which would appear the following year. As much as any man, Lewis had been responsible for developing a vigorous tradition of physicochemical research in the United States. That he, who was widely regarded as America's preeminent physical chemist, should have suggested that the field no longer existed is, to say the least, somewhat ironic.

It is possible of course that Lewis was engaging in his well-known technique of confronting his reader with a surprising paradox, but I do not think so. This was not the only occasion on which Lewis expressed his discomfort with the label "physical chemist" (2). More important, Lewis was in a sense quite correct when he said that physical chemistry no longer existed, for the physical chemistry of his youth, that of Ostwald, Arrhenius, and van't Hoff, had been transformed in such fundamental ways as to be almost unrecognizable. A subject

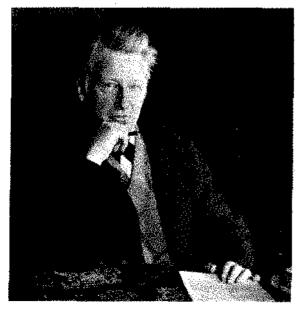


Figure 1. J. H. van't Hoff in 1904. Photo courtesy of the Center for the History of Chemistry.



that was often narrowly defined by the problems of dilute aqueous solutions had become a set of techniques and way of thinking about chemistry that defied any simple definition. A subject that was so closely identified with the study of chemical processes that talk of atoms and molecules was often censured for being subversive had given way to one in which it was increasingly understood that structure was related to process. A subject that was, despite the good intentions and claims of its founders, very remote from meeting the needs of other scientists had been supplanted by a vigorous new physical chemistry that treated real as well as ideal states and hence was of use to chemical engineers, petrologists, biochemists, and scientists of many other stripes. And a subject that had been the preserve of a small and well-defined group of practitioners, sometimes called "the ionists," had become the communal property of all chemists.

This transformation of classical physical chemistry took place during Lewis's early maturity, and it was a transformation to which Lewis himself made vital contributions. Yet despite the significance of Lewis's work, we know very little about the formative years during which he began to make those contributions to chemical thermodynamics and the theory of valence for which he is best remembered. What I should like to do in this essay is to construct a picture of the early stage of Lewis's career—the apprenticeship that he served before arriving at Berkeley in 1912—and to set that picture against the back-drop of the transformation then underway in physical chemistry. What was physical chemistry when Lewis entered the field in the late 1890's? How did his training and early experience mold his conception of the subject? And to what degree did the teachers and colleagues with whom he worked in those early years shape Lewis's interests and the distribution of his efforts? Lewis's achievements, of course, cannot be fully understood in terms of his training, for he possessed au originality that could not be taught, but even men of genius bear dehts to their teachers, and it is these that I should like to assess.

Let us begin by better defining Lewis' starting point, the physical chemistry he encountered as a student in the 1890's. The subject was, in fact, younger than Lewis himself, at least if one thinks of it as a distinct and well recognized specialty. Whereas Lewis was born in 1875, physical chemistry was a creature of the 1880's. That was, of course, the decade that saw the publication of van't Hoff's studies in chemical dynamies and theory of osmotic pressure (Fig. 1), of Arrhenius' theory of electrolytic dissociation (Fig. 2), of Ostwald's massive "Lehrbuch der allgemeinen Chemie" and his famous dilotion law (Fig. 3), and of Nernst's theory of the concentration cell. It was also the decade in which an institutional basis for physical chemistry was created. The Zeitschrift für physikalische Chemie begau publication iu 1887, and, in that same year, Ostwald was called to a chair at the University of Leipzig, where he quickly built up the premier center for training in the new discipline (3).

But startling as this record of accomplishment was and is, it should be remembered that when Ostwald, Arrhenius, and van't Hoff came together in the 1880's they faced serious obstacles in their efforts to win the recognition of their fellow scientists. Physical chemistry was born amid conflicts, and



Figure 2. Svante Arrhenius. Photo courtesy of the Center for the History of Chemistry.

these left durable imprints on the young specialty. In the first place, the founders of the new discipline had to overcome the tendency, especially pronounced in Germany, to identify organic research as the cutting edge of chemistry. This meant competing with organic chemists for chairs, institutes, and the patronage of industrial concerns. It also entailed competition over goals and priorities. In the course of assertion and counter-assertion. Ostwald and his cohorts came to define physical chemistry as the study of the process of chemical change—of the arrow or equal sign in chemical reactions—the antithesis of organic chemistry which dealt with the composition and structure of reactants and products. The organic chemist, Ostwald charged, was like the miner of '49 who had but one thought, to discover golden nuggets (4). In his haste to seek out new compounds, he neglected the questions fundamental to all chemical change: how do physical conditions affect the equilibrium and yield of reactions, and how may the force of chemical affinity be defined and quantified. Ostwald saw himself as a reformer, working to make chemistry an analytical rather than a taxonomic science, a science of process rather than one of composition and structure. He inculcated this attitude in many of his pupils together with a certain contempt for organic chemistry (5). In so doing, he opened a gap between organic and physical chemists that did not begin to heal until the twentieth century.

Second, the theory of electrolytic dissociation was the object of widespread and general debate from its statement in 1887 until well into the twentieth century. At first it was exposed to the skepticism of scientists who simply could not accept the notion that stable molecules might spontaneously dissociate in water. Later, as the limitations and imperfections of Arrhenius' theory became clearer-for example, as the behavior of solutions of strong electrolytes was recognized as a problem—physical chemists themselves began to question the adequacy of the principle. The theory of electrolytic dissociation had been considered the jewel in the physical chemists' crown because of the insight it afforded into the nature of solutions, the sites of most chemical processes. It is no wouder that research on aqueous solutions should have dominated physical chemists' concerns when it turned out that the jewel was flawed (6).

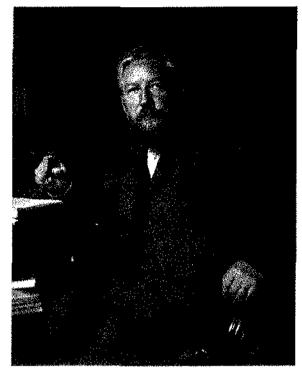


Figure 3. W. Ostwald. Photo Courtesy of the Center for the History of Chemistry.

Third, the development of physical chemistry in its early years was entwined with the debate over atomism that raged among physical scientists at the end of the nineteenth century (7). During the 1890's, Ostwald commenced his public attacks on the doctrine of atomism, charging that it was a hypothesis without value, either as a genuine description of nature or as a guide to research. Natural science, he argued, would be better served if investigators rejected unobservable entities and mechanical models and instead grounded their work in the sure and general principles of thermodynamics. His colleagues, Arrhenius, van't Hoff, and Nernst, did not entirely subscribe to this view, but Ostwald, as the public spokesman for physical chemistry and as the outstanding teacher in the new discipline, won a wide hearing for his ideas and exerted considerable influence over young recruits.

The outcome of these controversies was that, by the turn of the century, physical chemists were avowedly oriented toward the study of process rather than structure. Solutions, the sites of most chemical changes, were their central objects of investigation, and among solutions, dilute aqueous solutions of electrolytes attracted the greatest attention. Finally, many physical chemists shared Ostwald's aversion to molecular-kinetic theory. He had succeeded in sensitizing a generation of physical chemists to the distinction between fact and hypothesis, and even those who disagreed with his extreme view of atomism often showed great hesitance before seeking to explain phenomena in terms of the structure and properties of unobservable entities.

Lewis of course was still a boy in the 1880's, and by the time he reached Harvard in the mid-uinetics, information about the new physical chemistry was only beginning to reach the United States, carried primarily by Americaus who had worked with Ostwald and then returned to teaching positions in American colleges and universities. Lewis had his introduction to the subject in his senior year at Harvard—1896—when he enrolled in a course given by one of these veterans of Leipzig, Theodore William Richards (Fig. 4) (8).

Richards was then a 28-year-old assistant professor, widely regarded by his colleagues as being America's brightest upand-coming chemist (9). His studies of atomic weights, for which he would win the Nobel Prize in 1914, were already

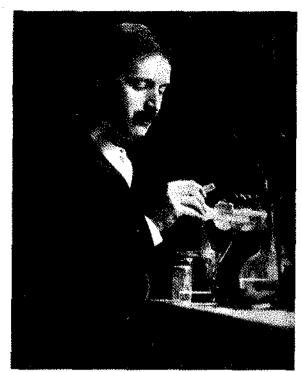


Figure 4, T. W. Richards, circa 1905.

beginning to attract international attention, and the authorities at Harvard were grooming him to step into a professorship. As part of that grooming, the university sent Richards to Europe in 1895 to work with Nernst and Ostwald. There Richards undertook research on the electromotive force of amalgam cells and other topics in the new physical chemistry. The course that Lewis took from him the following year no doubt reflected Richards' new-found enthusiasm for electrochemistry and solution theory. It was a small course, attracting but nine students, and the laboratory in which experimental work was done consisted of one small room in Boyleston Hall, the all-purpose chemistry building (10). But the subject caught Lewis' interest, as did the professor who taught it, and after teaching at the Phillips Academy, Andover, during the year following graduation, Lewis returned to Harvard to obtain a doctorate under Richards.

The training that Lewis received as a graduate student was first and foremost a training in experimental technique. Richards was a perfectionist in the laboratory, determined to search out every last source of error in his measurements, whether those measurements were of atomic weights or of heats of reaction. He worked closely with his graduate students, often treating them as assistants. And, like many perfectionists, Richards found it difficult to delegate responsibilities to his co-workers. "In my experience," he once wrote (11),

assistants who are not carefully superintended may be worse than none, for one has to discover in their work not only the laws of nature, but also the assistants' iusidious if well meant mistakes. The less brilliant ones often fail to understand the force of one's suggestions, and the more brilliant ones often strike out on blind paths of their own if not carefully watched.

Presumably, Richards placed the young and imaginative Lewis in the second category, and this Lewis must have felt confining.

Confining, too, must have been Richards' professed empiricism. He was of that generation of American scientists who identified good science with careful measurements and who thought that theory should flow from precise experiments. In Richards' case, the native strain of empiricism was reinforced

hy his exposure to Ostwald's injunctions against confusing hypotheses with facts. Although Richards spent much of his life measuring atomic weights, at the turn of the century he refrained from placing full confidence in the atomic theory, at least in his public statements. In his papers from that period he repeatedly cautioned his readers that the atomic theory and the edifice of molecular-kinetic hypotheses built upon it might, after all, prove ephemeral (12). The real need, he suggested, was for data that would be of lasting value despite changes in scientific fashion. "Believing in Faraday's methods," he wrote, "I cannot help thinking that fact is more important than theory, and that if one indulges in theory, it should be in physical theory, closely related to fact and not a metaphysical theory which seems able to bear but little fruit in experiment" (13). Richards appears to have consigned talk of chemical bonds to the realm of metaphysics. In his lecture notes there is an entry which reads: "Twaddle about bonds: A very crude method of representing certain known facts about chemical reactions. A mode of represent ation not an explanation" (14).

It was while Lewis was at Harvard—indeed, while he was assisting in the course in which Richards made these remarks—that Lewis developed his first rough model of the cubical atom and the chemical bond (15). We may well imagine the reception that Richards gave to his young assistant's ideas. Years later, in 1919, Lewis himself described his experience during this period in very harsh terms. "I went from the Middle-west to study at Harvard," he wrote (16),

believing that at that time it represented the highest scientific ideals. But now I very much doubt whether either the physics or the chemistry department at that time furnished real incentive to research. In 1897 I wrote a paper on the thermodynamics of the hohlraum which was read by several members of the chemistry and physics departments. They agreed unanimously that the work was not worth doing, especially as I postulated a pressure of light, of which they all derided the existence. They advised me strongly not to spend time on such fruitless investigations, all being entirely unaware of the similar work that Wien was then doing. A few years later I had very much the same ideas of atomic and molecular structure as I now hold, and I had a much greater desire to expound them, but I could not find a soul sufficiently interested to hear the theory. There was a great deal of research work being done at the university, but, as I see it now, the spirit of research was dead.

Clearly the imaginative and iconoclastic Lewis had differences with the cautious Richards, who hedged all of his bets. But whatever Lewis later judged Harvard to have been, he returned to it repeatedly, first for his graduate education, and then, after a brief and unproductive trip to Europe, for his first job as an instructor. There were in fact things to learn there, things that Richards could teach. First, there was discipline. If Richards put the brakes on Lewis' enthusiasm for atomic and molecular structure, it may well have been to Lewis' benefit, for his early model was a crude and speculative affair which would, in all likelihood, have caused him considerable embarrassment if published. Second, there was thermodynamics. It was Richards more than anyone who fostered Lewis' interest in thermodynamics, and it was while he was at Harvard, working closely with Richards, that Lewis developed the concept of escaping tendency or fugacity, from which he later derived the notion of activity. The papers that Richards and Lewis wrote during the years from 1899 to 1902 convey the distinct impression that here were two chemists who were teaching themselves and each other chemical thermodynamics by exploring new methods of organizing the scattered, unconnected, and often imprecise equations which then constituted the field. Although they were joint authors of but one paper, they frequently cited one another's work, they shared a common interest in refining the notion of chemical affinity, and in this connection they both recognized the sigificance of integrating the Gibbs-Helmholtz equation (17). Third, there is no question but that Lewis benefitted from his work in the laboratory with this master of experimental technique. When

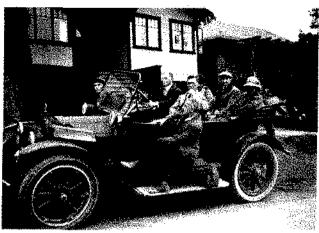


Figure 5. A physical chemistry outling in 1917; from *left* to *right*: David A. Smith, Arthur A. Noyes, G. N. Lewis (on running board), [?], Mrs. G. N. Lewis, James E. Bell, [?]. Photo courtesy of the Archives, California institute of Technology.

Lewis arrived at Harvard, he was an inexperienced novice; when he left he was an inventive and skillful experimentalist.

In 1904, Lewis made his break with Harvard in a rather dramatic fashion by moving to the other side of the globe to become superintendent of weights and measures in the Philippines. In his surviving letters, Lewis makes no reference to his motives for going to this new American colony, and we can only guess as to his reasons for accepting the post. It is perhaps worth noting that he had failed to publish a single paper during the two years preceding his departure from Harvard, the only extended drought in Lewis' career. These were the years in which he was assuming significant teaching responsibilities, and it is not unreasonable to suppose that Lewis found these classroom duties taxing and wished to be free of them. In any event, he did not tarry long in Manila, for in 1905 he accepted an invitation to join the faculty at MIT.

When Lewis arrived at "Boston Tech" (MIT then occupied its original site in Back Bay) he found what was lacking at Harvard-a band of talented, young physical chemists who exhibited not only the form, but also the spirit of research. Among those working with him that first year at MIT were Charles A. Kraus, later to become professor of chemistry at Brown University, Edward W. Washburn, who went on to professorship at the University of Illinois, Richard Chace Tolman, who would work with Lewis again at Berkeley and who ended his distinguished career at Caltech, and William C. Bray, whose future would be linked with Lewis' at the University of California. Kraus, who had just turned 30, was the oldest in the group; every one of these chemists was later elected to membership in the National Academy. It was a remarkable concentration of talent for any American university of that period, and it was all the more remarkable that it existed at MIT, a school that had not yet awarded its first PhD

Their presence in Back Bay was due largely to the efforts of one scientist, Arthur Amos Noyes (Fig. 5). Noyes, then approaching the age of 40, had been among the first and most talented of Ostwald's American students. He had obtained his doctorate at Leipzig in 1890, and then had returned to his undergraduate alma mater, MIT, as an instructor. During the 'nineties, Noyes perforce dedicated much of his energy to undergraduate instruction; young faculty members at the Institute were expected to spend upwards of 20 hours a week in contact with students. But in his free time, often working with undergraduate assistants, Noyes had managed to do an imposing amount of original research. He was not as skillful an experimentalist as Richards, nor did he display the creative instincts of his teachers, Ostwald and Nernst, but he had a

clear head, a sound knowledge of thermodynamics, and the ability to identify important questions (19).

At some point during the 1890's, Noyes conceived the ambition of duplicating at MIT the kind of research school in which he had worked at Leipzig, an institute where, as he told a friend, he might have "associates . . . to work on ions—one for each ion . . . " (20). In 1903, after a year of negotiations with the president of MIT, Noyes obtained what he wanted, an institute which he called the Research Laboratory of Physical Chemistry. This was the site where Lewis worked during his years at MIT.

It was an unusual entity. In the first place, more than half of its operating budget came from Noyes' own pocket and from a grant which he had been recently awarded by the new Carnegie Institution of Washington, MIT supplied a small annual subsidy and agreed to crect a temporary building to house Noyes and his associates. Second, it was created as an autonomous department; as director Noyes reported to the president of MIT rather than to the head of the chemistry department. He had an independent budget and the power to hire and fire. Third, the laboratory was intended to be a research center rather than a site for instruction. A handful of doctoral candidates would be admitted, but Noyes wished to fill most of the dozen or so spots in the facility with chemists who already possessed PhD's. This was perhaps the most striking feature of Noyes' scheme; in effect he was opening up a new option for young, research-minded chemists by creating some of the first opportunities in this country for post-doctoral study. These post-docs, or research associates as Noves called them, would have limited teaching responsibilities; their tenure would depend upon research accomplishment. Finally, Noves instituted a research colloquium at the laboratory, a regular staff seminar at which workers discussed both the current literature and their work in progress. This too was an innovation, for although research colloquia were common in Germany, they were still quite rare in the United States. The post-doc and the staff seminar would, of course, later become essential parts of the chemistry program at Berkeley (21).

Lewis spent seven productive years at MIT. When he arrived, he had already completed his papers on the potential of the oxygen electrode, and in Noves he found a chemist who was alive to the benefits that might accrue from a systematic study of the free energies of formation of chemical substances. In June 1905, several months before Lewis' arrival, Noyes had already begun to discuss the possibility of organizing a cooperative program of experimental work on the problem, involving chemists around the country (22). But after Lewis arrived, and perhaps with his advice, Noyes decided that the experimental work was so delicate as to make a cooperative scheme impracticable. Instead, Lewis, with the help of students and colleagues, undertook the systematic determination of electrode potentials himself. This work, begun at MIT and continued at the University of California, was that part of his research in which Lewis took the greatest pride. "It is one thing," he wrote, "to learn an experimental method and apply it with great exactness to all the problems which come to hand; it is another thing to have a definite problem which requires the use and often the invention of many different methods" (23). This, of course, was the task he faced in determining the electrode potentials of the elements.

Lewis considered his work on free energies of formation to be part of a larger task of weaving together the abstract equations of thermodynamics and the concrete data of chemistry, and during his years at MIT he made other contributions to this goal, in particular, his invention of the useful notion of activity. But thermodynamics was not his only concern during this period. He read widely in physics as well as in chemistry, as is clear from his papers on relativity (24). He also audited at least one course in organic chemistry. Years later, after the publication of "Valence," the teacher in that course, F. J. Moore, wrote to Lewis and complimented him on

his concern with, and knowledge of, organic chemistry. "We seldom expect this," Moore wrote, "from a person so deep in

physical chemistry as yourself" (25).

It is unlikely that Lewis took this course purely for its entertainment value. Any comprehensive theory of valence would have to take account of the evidence of organic chemistry, and valence was still very much in Lewis' thoughts. Although he published nothing on the subject while at MIT, his interest must have been stimulated by his coworkers, who themselves were abuzz with talk of atomic and molecular structure. Thomson's work on the electron was read in seminars. The absolute size of the atom, tautomerism, and Werner's coordination theory were discussed at the staff colloquium (26). Charles A. Kraus spent the years from 1907 to 1909 studying solutions of metals in liquid ammonia in an effort to test the theory that free electrons were the carriers of electrical charges in metals (27). And it is striking how many of the important papers ou valence written during the 'teens were by chemists who had worked at this laboratory. K. G. Falk was still on the staff when, in 1910, he collaborated with John M. Nelson on an influential essay that marshalled the evidence for an electron transfer theory of valence. One year after leaving MIT, W. C. Bray together with G. E. K. Branch developed a dualistic theory of valence, positing two types of bonds, polar and nonpolar. W. C. Arsem, a young physical chemist who had gone to General Electric after working with Bray at MIT, suggested in 1914 that bonds resulted from the sharing of a single electron. And of course Lewis himself published papers both in 1913 and in 1916, the former developing Bray's dualistic concept and the latter outlining his own theory of the shared pair bond (28). The variety of these theories indicates that there was no consensus among the chemists at Noyes' research laboratory, but their number testifies to the intensity of the discussion underway there between 1905 and 1912.

There is something surprising about all of this, for the proprietor of this Research Laboratory, A. A. Noyes, was a physical chemist trained in the classical mode. His research dealt primarily with the phenomena of dilute aqueous solutions and especially the puzzling behavior of solutions of strong electrolytes. His hasic conceptual tool was thermodynamics, and he shared that reluctance to speak in terms of atoms and molecules so common among Ostwald's students. As late as 1902, he could write a textook on the general principles of physical science without once mentioning the electron (29). But Noyes never went so far as his teacher, who denied the existence of atoms altogether, and as physical evidence for atomism mounted after 1902, Noyes dropped many of his inhibitions. By 1907, when he published the results of his five-year investigation of the electrical conductivity of aqueous solutions, Noyes had reached the point where he could suggest that the discrepencies between the behavior of strong and weak electrolytes might well be owing to differences in their modes of combination. Ions, he stated, might unite in two ways. They might combine to form electrical molecules in which the constituents retained their electric charges and characteristic properties, or they might combine in a more intimate fashion to form chemical molecules in which the constituents lost their identities. Strong electrolytes tended to form electrical molecules; weak electrolytes tended to form chemical molecules. Whereas chemical molecules dissociated in solution in accordance with the law of mass action, electrical molecules obeyed an entirely distinct principle whose theoretical basis was not understood (30). Noyes' molecular interpretation of his evidence was a significant departure from the tradition in which he had been trained, but it was of a piece with much of the other work underway in his laboratory.

Our sources do not permit conclusions to be drawn regarding the question of who was influencing whom at MIT, but this question is perhaps less important than the fact that here a group of physical chemists trained in the classical mode were together moving toward the conclusion that molecular considerations deserved an important place in their work. Hypotheses regarding the fine structure of matter and the nature of the chemical bond might afford insight into traditional problems in physical chemistry. As Kraus put it in 1907, "The study of the conduction process cannot be successfully carried out until the molecular state of the system has been established, even in the case of electrolytes the progress of investigation is governed by this condition" (31).

This observation seems trite today, but at the time it represented an important shift in the thinking of physical chemists. It was a shift away from a specialty defined in terms of the study of process toward one in which considerations of structure and bonding would hold a legitimate place. The shift occurred in part because physicists, such as J. J. Thomson, were developing chemically interesting models of the atom and, in part, because physical chemists themselves were finding it increasingly difficult to treat problems, such as those posed by strong electrolytes, using their traditional repertoire of concepts and techniques. Talk of bonds was not so much twaddle, but serious business.

At the Research Laboratory of Physical Chemistry one sees classical physical chemistry evolving into the newer physical chemistry of which Lewis would become a leading proponent. The electrode potentials of the elements were being determined with a new degree of accuracy, and the data so gathered would soon become indispensable to chemists of all sorts. The theory of solutions was being enriched and its field of application broadened by the introduction of the concept of activity. And not least important, constraints on molecular interpretations were being loosened and a new generation of physical chemists was coming to see the fine structure of . matter as an essential subject of study. When Lewis went to Berkeley in 1912, he carried with him the benefit of this experience. His apprenticeship had ended, but the transition to the new physical chemistry had just begun.

Acknowledgment

Students of Lewis's work will recognize my debts to Robert F. Kohler and Erwin N. Hiebert, whose papers, cited above, constitute the starting point for any study of Lewis and his era. I thank Jeffrey L. Sturchio, Larry Owens, and Gerald L. Geison for valuable comments on earlier drafts of this paper, and the Archives of the University of California, Cornell University, and Harvard University for permission to quote from letters in their possession. I also acknowledge the generous support of the National Science Foundation and of the American Council of Learned Societies.

Literature Cited

(1) G. N. Lewis to Eugene C. Bingham, 21 Feb. 1922, copy in 1921-1922 Box, Wilder D. Bancroft Papers, Cornell University Archives.

(2) When Lewis accepted a position at the University of California he insisted that titles such as "Professor of Physical Chemistry" be abolished so that there should be the greatest possible mobility in the department. See, G. N. Lewis to Benjamin Ihde Wheeler, 5 Jan. 1912, CU-5, Box 61, Archives of the University of California,

(3) On the origins of physical chemistry, see Root-Bernstein, Robert Scott, "The Ionists: Founding Physical Chemistry," Ph.D. dissertation, Princeton University, 1980.

(4) Ostwald, Wilhelm, "Die Aufgaben der physikalischen Chemie," Humboldt, Mon-

atsschrift f. d. gesamten Naturwissenschaften, 6, 249 (1887), on p. 252.

(5) See, for example, Loeb, Morris, "The Fundamental Ideas of Physical Chemistry," in "The Scientific Work of Morris Loeb," (Editor: Richards, T. W.), Harvard University Press, Cambridge, MA, 1913, p. 5. Lock was the first of Ostwaid's American students to return to the United States.

(6) Wolfendon, John H., "The Anomaiy of Strong Electrolytes," Ambix 19, 175 (1972), and Dolby, R. G., "Dehates Over the Theory of Solution." Historical Studies in the Physical Sciences, 7, 297 (1976).
(7) See Hiebert, Erwin N., "The Energetics Controversy and the New Thermodynamics," in the Historical Studies of Science and Technology of Technology.

he Hiebert, Erwin N.—The Energetics Controversy and the New Thermodynamics, in "Perspectives in the History of Science and Technology," (Editor: Roller, Dusne H. D.), University of Oklahoma Press, Norman, OK, 1971, pp. 67-86, and Clark, Peter, "Atomism versus Thermodynamics," in "Method and Appraisal in the Physical Sciences: The Critical Background to Modern Science, 1800–1905," (Editor: Howson, Colin), Cambridge University Press, Cambridge, England, 1976, pp. 41-105.

(8) On Lewis' career, see Calvin, Melvin, "Gilbert Newton Lewis," in "Proceedings

Robert A. Welch Foundation Conferences on Chemical Research, XX, American Chemistry—Bicentennial," (Editor: Milligan, W. O.), Houston, 1977, pp. 116–150; Hildebrand, Joel Henry, "Gilbert Newton Lewis," National Academy of Sciences, Biographical Memoirs, 31, 210 (1958); and Lachman, Arthur, "Borderlands of the

- Unknown: The Life Story of Gilbert Newton Lewis," Pageant Press, New York,
- (9) On Richards, see Kopperl, Sheldon J., "The Scientific Work of Theodore William Richards," Ph.D. dissertation, University of Wisconsin, 1970; Conant, James B., "Theodore William Richards," National Academy of Sciences, Biographical Memoirs, 44, 251 (1974); and Hartley, Sir Harold, "Theodore William Richards," Journal of the Chemical Society, 133, 1937 (1930).
- (10) Harvard University, "President's Report," 1895-1896, p. 71.
 (11) T. W. Richards to Julius Stieglitz, 17 Nov. 1916, Professional and Personal Correspondence, 1916 Box, T. W. Richards Papers, Harvard University Archives.
 (12) See, for example, Richards, T. W., "The Possible Significance of Changing Atomic
- Volume," Proceedings of the American Academy of Arts and Sciences, 37, (1902),
- on pp. 5 and 15-16.
 (13) T. W. Richards to Wilhelm Palmaer, 13 Jan. 1914, Professional and Personal Correspondence, 1902–1914 Box, T. W. Richards Papers
- (14) Richards, T. W., Chemistry 8 Notebook, Harvard University Archives, quoted by Kopperl in "The Scientific Work of Theodore William Richards," p. 226.
- (15) Kohler, Robert F., Jr., "The Origin of G. N. Lewie's Theory of the Shared Pair Bond," Historical Studies in the Physical Sciences, 3, 343 (1971).
 (16) G. N. Lewis to Robert A. Millikan, 23 Oct. 1919, Box 3, College of Chemistry Records,
- University of California, quoted by Kohler in "The Origin of Lewis's Theory," pp. 251_352
- (17) Erwin N. Hiebert discusses the work of Lewis and Richards on this problem in his sketch of Walther Nernst in the "Dictionary of Scientific Biography," Supplement 1.
 (18) On MIT, see Servos, John W., "The Industrial Relations of Science: Chemical Engineering Committee of Sciences and Commi
- (18) On MIT, see Servos, John W., "The Industrial Relations of Science: Chemical Engineering at MIT, 1900–1959," Isis, 71, 531 (1980).
 (19) On Noyes, see Pauling, Linus, "Arthur Amos Noyes," National Academy of Sciences, Biographical Memoirs, 31 322 (1958), and Servos, John W., "The Knowledge Corporation: Chemistry at Caltech, 1915–1936," Ambix, 23, 175 (1976).
- (21) A. A. Noyes to H. M. Goodwin, 15 Jan. 1891, H. M. Goodwin Papers, MIT Archives, quoted by Wise, George, "Ionists in Industry: Physical Chemistry at General Electric, 1900–1915," Isis, 74, 7 (1983), on p. 11.
- (20) On the Research Laboratory of Physical Chemistry, see Servos, John W., "Physical

- Chemistry in America, 1890-1933," Ph.D. dissertation, The Johns Hopkins Uni-
- versity, 1979, chapter 3. (22) A. A. Noyes to George Ellery Hale, 5 June 1965, Roll 27, microfilm edition of the George Ellery Hale Papers (Editor: Daniel J. Kevles). See also "Report of The National Academy of Sciences for the Year 1906, Government Printing Office, Washington, D.C., 1907, pp. 19-20.
- (23) G. N. Lewis to J. R. Partington, 7 Dec. 1928, Box 3, College of Chemistry Records, Ar-
- chives of the University of California.

 (24) G. N. Lewis, "A Revision of the Fundamental Laws of Matter and Energy," Phit. Mag., 16, 705 (1908); Lewis, C. N., and Tolman, R. C., "The Principle of Relativity and Non-Newtonian Mechanics," Proc. Amer. Acad., 44, 711, (1909); Lewis, G. N., and Wilson, E. B., "The Space-Time Manifold of Rolativity," Proc. Amer. Acad., 48, 389
- (25) F. J. Moore to G. N. Lewis, 6 Dec. 1923, Box 3, College of Chemistry Records, Archives of the University of California, Berkeley.
- (26) "General Institute News-Research Laboratory of Physical Chemistry," Tech. Rev., 10, 175 (1908).
- (27) Kraus's papers appeared in the J. Amer. Chem. Soc., 29, 1567 (1907); 30, 663, 1197, and 1373 (1908).
- (28) Falk, K. G., and Nelson, J. M., J. Amer. Chem. Soc., 32, 1837 (1910); Bray, W. C., and (29) Falk, N. G., Son (Nelson, J. M., J. Amer. Chem. Soc., 32, 1937 (1919); Bray, W. C., and Branch, G. R. K., J. Amer. Chem. Soc., 36, 1655 (1914); Lewis, G. N., J. Amer. Chem. Soc., 38, 1648 (1913); and Lewis, G. N., J. Amer. Chem. Soc. 38, 762 (1916), Robert Kohler discusses all of these papers in "The Origin of Lewis's Theory."
 (29) Noyes, Arthur Amos, "The General Principles of Physical Science. An Introduction to the Study of the General Principles of Chemistry," Henry Holt, New York, 1902.
 Live Partiling reads this homography in his oxeron. Notes in "Proceedings of the
- Lime Pauling made this observation in his essay on Noyes in "Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research. XX. American Chemistry.—Bicentennial," (Editor: Milligan, W. O.), Houston, 1977, pp. 90–91.

 (30) Noyes, Arthur A., et al., "The Electrical Conductivity of Aqueous Solutions," Carnegie
- Institution of Washington, Washington, DC, 1907, pp. 351-352.

 (31) Kraus, Charles A., "Solutions of Metals in Non-Metallic Solvents; I. General Properties
- of Solutions of Metals in Liquid Ammonia," J. Amer. Chem. Soc., 29, 1558 (1907).

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The College of Chemistry in the G. N. Lewis Era: 1912–1946

Melvin Calvin and Gienn T. Seaborg

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

Gilbert N. Lewis of the Massachusetts Institute of Technology accepted the position of Dean of the College of Chemistry and moved to Berkeley in the Fall of 1912. When Lewis arrived the chemistry faculty already had four members: Edward Booth who served until he died in 1917, Edmund O'Neill who retired in 1925, Walter C. Blasdale who retired in 1940, and Henry C. Biddle who left Berkeley in 1916. From MIT Lewis brought with him William C. Bray, Merle Randall, and Richard C. Tolman, together with several graduate students. Bray and Randall were to stay at Berkeley but Tolman left in 1916. George Ernest Gibson from England and Germany and Joel H. Hildebrand from the University of Pennsylvania joined the faculty in 1913. These proved to be the last non-Berkeley PhD's appointed to the faculty until Calvin's appointment in 1937 (see table). Of the permanent chemistry faculty from 1912 to the present we have known all but Booth, O'Neill, and Biddle.



The accompanying photographs are notable in that they are among the very few substantial ones of the College of Chemistry faculty, including Lewis, that have survived from the G. N. Lewis era. Soon after the Chemistry Annex was completed in 1915, a number of people moved there from the larger old huilding which had been completed in 1890. The first photograph (Fig. 1) was taken in front of the Chemistry Annex on 14 May 1917. It shows Lewis and his graduate students William L. Argo (at this time an instructor); Axel R. Olson; Thomas B. Brighton; Parry Borgstrom; Asa L. Caulkins; Orville E. Cushman; Guy W. Clark; and George S. Parks; Randall and his graduate student, Charles S. Bisson; Bray; Constance Gray, secretary to Lewis; William J. Cummings, glassblower; and Svend Holmstrup, shopman.

The second picture (Fig. 2) was taken in front of Gilman Hall in the fall of 1917, at about the time this building was completed. This photograph includes faculty members



Figure 1. Picture taken on May 14, 1917, in front of Chemistry Annex.

Back row (left to right)

William C. Bray, William L. Argo, Gilbert N. Lewis, Constance Gray, Parry Borgstrom, George S. Parks, Merle Randall, Charles S. Bisson, Asa L. Caulkins, Svend Holmstrup (shopman), William J. Cummings (glassblower).

Front row (seated left to right)

Axel R. Olson, Thomas B. Brighton, Orville E. Cushman, Guy W. Clark.

Eastman, Blasdale, Bray, Randall, Gibson, Porter, Stewart, O'Neill, Argo, and Lewis (Branch was away in the Canadian Armed Services while Hildebrand was apparently out of town); Lewis' secretary, Constance Gray, and clerk M. J. Fisher; graduate students Esther Kittredge, Esther Branch

(wife of Gerald Branch), Charles S. Bisson, Wendell M. Latimer, Charles C. Scalione, Roy F. Newton, William G. Horsch, William H. Hampton, John M. McGee, George S. Parks, Parry Borgstrom, Albert G. Loomis, Angier H. Foster, and Axel R. Olson; undergraduate students Carl Iddings, William D.

University of California, Berkeley---Chemistry Faculty

Year Joined	Name	Degree Date	Where Taken/With Whom	Year Joined	Name	Degree Date	Where Taken/With Whom
Faculty o	n hand at time Gilbert N. Lev	wis arrived i	n Berkeley	1921	Olson, Axel R.	1918	UC Berkeley, Lewis
•	Booth, Edward	1877	UC Berkeley		Hogness, Thorfin R.	1921	UC Berkeley, Hildebrand
	O'Neill, Edmond	1879	UC Berkeley				
	Blasdale, Watter C.	1892	UC Berkeley	1922	Giauque, William F.	1922	UC 8erkeley, Gibson
	Błddle, Henry C.	1900	University of Chicago		(Nobel Prize, 1949)		
1912	Lewis, Gilbert Newton	Newton 1899 Harvard, T. W. Richards	B 4 4 - O	4000	HOD I I I I		
	Tolman, Richard C.	1910	MIT	1923	1923 Rollefson, Gerhard K. 1923	UC Berkeley, Lewis	
	Bray, William C.	1912 MIT, G. N. Lewis 1933 Libby, Willard F.	raid restant	4000	1100 4 1		
	Randall, Merle			1933	UC Berkeley, Latimer		
1913	Hildebrand, Joel C.	1908	Pennsylvania, Edgar Fahs		(Nobel Prize, 1960)		
			Smith	1937 Pitzer, Kenneth S.	Pitzer, Kenneth S.	1937	UC Berkeley, Latimer
	Cibena G Fract 1911 Receipt Lummer	Calvin, Melvin	1935	Minnesota, Glockler (UC			
1915	Branch, Gerald E. K.	1915	UC Berkeley, Lewis		(Nobel Prize, 1961)	1505	Berkeley, 1923, Gibson)
	Argo, William C.	1915	UC Berkeley, Lewis				contolog, rollo, dibdony
1917	Porter, C. Waiter 1915 UC Berkeley, Biddle 1938 Ruben, Sam	Ruben, Samuel C.	1938	UC Berkeley, Latimer/			
	Eastman, Ermon D.	1917	UC Berkelay, Lewis				Libby
	Latimer, Wendell M. 1917 UC Berkeley, Gil	UC Berkeley, Gibson					
	Stewart, T. Dale	1916	UC Berkeley, Tolman	1939	Seaborg, Glenn T. (Nobel Prize, 1951)	1937	UC Berkeley, Gibson

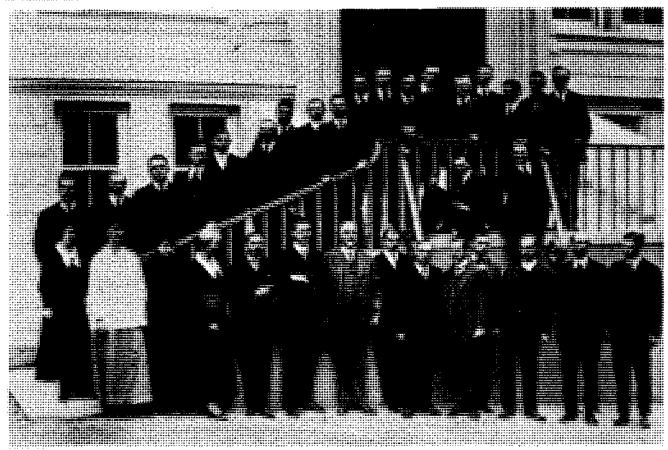


Figure 2, University of California College of Chemistry Staff Members in Front of Newly Constructed Gilman Hall (Fall of 1917).

Front row (right to left)

Ermon D. Eastman, Walter C. Blasdale, William C. Bray, Merte Randall, G. Ernest Gibson, C. Walter Porter, T. Dale Stawart, Edmund O'Nelli, William L. Argo, Gilbert N. Lewis, Constance Gray, Esther Kittredge, Esther Branch, and M. J. Flaher, (bookkeeper).

Ascending Stairs (left to right)

Charles S. Biason, Wendell M. Latimer, William J. Cummings (glassblower), Carl Iddings, Reginald B. Rule, J. T. Rattray (woodworker), Charles C. Scallone, Hall D. Draper, William G. Horsch, William H. Hampton, Willard G. Babcock, John M. McGeo, George S. Parks, Parry Borgstrom, Albert G. Loomls, George A. Linhart, William D. Ramage, and Harry N. Cooper.

Seated (left to right)

Alex R. Olson and Angier H. Foster.

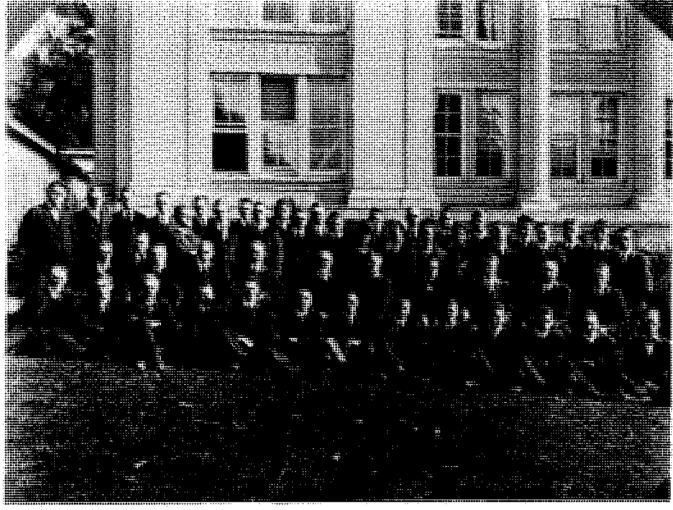


Figure 3. University of California College of Chemistry Staff Members in front of the north end of Gilman Hall, November 1920.

From left to right, seated, first row

Philip S. Danner, H. W. Chapman, James T. Rattray, Hal D. Draper, Nelson W. Taylor, Theophil F. Buehrer, Allyn M. Shaffer, Roscoe H. Gerke, Francis R. Bichowsky, Reynold C. Fuson, T. Fraser Young, Thomas E. Phipps, and Roy M. Bauer.

Seated, second row

George F. Nelson, Wendell M. Latimer, Gerald E. K. Branch, T. Dale Stewart, William C. Bray, Edmund O'Neill, Gilbert N. Lewis, Merle Randall, Joel H. Hildebrand, Walter C. Blasdale, and Ermon D. Eastman.

Standing, third row

Eustace J. Cuy, Robert M. Evans, William M. Hoskins, Roy F. Newton, Albert P. Vanselow, Maybelle J. Fisher, Constance Gray, Edna R. Bishop, Anna L. Elliott, Clarence A. Jenks, and Gustav E. Ostrom.

Standing, fourth row

William J. Cummings, John A. Almquist, Russell W. Millar, W. Albert Noyes, Jr., Albert M. Williams, Maurice L. Huggins, Evald Anderson, Dwight C. Bardwell, Harry K. Hvig, Bruner M. Burchfiel, William F. Giauque, Sherwin Maeser, Kart R. Edlund, Thorlin R. Hogness, James B. Ramsey, and Manuel L. Zavala.

Ramage, Willard G. Babcock, and Reginald B. Rule; assistant George A. Linhart; glassblower William J. Cummings and woodworker James T. Rattray and curator Harry N. Cooper.

The third picture (Fig. 3) was taken outside Gilman Hall in November, 1920. Seated in the second row front are George F. Nelson (chief machinist), and faculty members Latimer, Branch, Stewart, Bray, O'Neill, Lewis, Randall, Hildebrand,

Blasdale, and Eastman (Gibson, Olson, and Porter are missing). Also included are Constance Gray (secretary to Lewis), M. J. Fisher (secretary to O'Neill), Rattray (woodworker), Cummings (glassblower), H. W. Chapman (machinist), postdoctoral fellows Francis R. Bichowsky and W. Albert Noyes, Jr., and Roy F. Newton (instructor). All the others are graduate students and are identified in the caption.

Gilbert Newton Lewis

His Influence on Physical-Organic Chemists at Berkeley

Melvin Calvin

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

My task is to describe the influence of G. N. Lewis on my own research and to indicate how Lewis (Fig. 1) influenced physical-organic chemistry research at Berkeley during the period 1912—46. I was the last of the non-Berkeley-graduate faculty members whom Lewis brought to the Berkeley campus and the first one in 22 years. The first of Lewis' Berkeley appointees was Gerald E. K. Branch who played a central role in the subject I am to discuss. "Jerry" Branch took his first degree in 1911 in Liverpool, England. He came to Berkeley in 1912 on the advice of his professor, F. G. Donnan. Clearly, by that time, Lewis' reputation had already reached Europe. Branch took his PhD with Lewis in 1915 on "The Free Energy of Formic Acid".

Lewis' Electron Pair Bond Concept Initiates Theoretical Organic Chemistry at Berkeley

In 1913, while a graduate student of only one year's standing, Gerald Branch published a paper in the Journal of the American Chemical Society with William C. Bray entitled "Valence and Tautomerism" (1). The authors acknowledge discussions with Lewis, and their paper is immediately followed by one written by Lewis himself which carries the same title and was submitted on the same day (2). At that time the term "valence" was used without sign-it was simply a number. Bray and Branch introduced the terms maximum valence number (with sign) and maximum coordination number. In his follow-up paper Lewis pointed out that the qualifier "maximum" was inappropriate. Those two terms ultimately evolved into "oxidation number," as later defined by Wendell Latimer, and "coordination number." The oxidation number was defined as the number of electrons removed from (or added to) the atom in the particular compound, and this number had either a plus or minus sign attached to it. The coordination number was defined simply as an integer, the total number of atoms or groups bound to a center. The introduction of these two terms and their precise

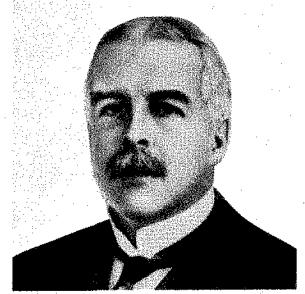


Figure 1. Gilbert N. Lewis, 1912.



definition by Bray and himself in Tillia, which were sometimed by Lewis who related the term "polar number" to the electrons taken away or given to an atom, was a "breakthrough" which led Lewis to the idea that the way in which atoms were actually held together was by virtue of the electrons between them. Of course, it was recognized that there were extreme cases in which the electrons were transferred completely from one atom to another, as in lithium chloride. There were also other cases in which electrons were shared between two atoms, to fulfill the orbital requirements of both atoms between which those electrons lay, giving rise to the concept of the shared electron pair bond. These two papers unified the ideas on bonding of inorganic chemistry (lithium chloride) and those of organic chemistry (methane).

The Shared Electron Pair Bond

In the early days probably the most important concept that Lewis developed was that of the shared electron pair bond, which eventually gave rise to some coherence in the theory of organic chemistry. I would like to quote from Robert Kohler (3) concerning the significance of that particular development

The first satisfactory picture of the chemical bond was proposed in early 1916 by Gilbert Newton Lewis. His book, Valence and the Structure of Atoms and Molecules published in 1923 [(4)], which elaborated the picture of the bond and its ahared pair of electrons, was the textbook of the new generation of organic chemists. Withnut Lewis' conception of the shared pair bond the interpretation of reaction mechanisms already begun by the British school of Lapworth, Lowry, Ingold and Robinson, would not have gotten very far. The shared electron pair concept was really the foundation of physical-organic chemistry. Likewise, without the idea of the ahared pair bond, then being used with increasing competence and success by organic chemists, the application of quantum mechanics to the chemical bond in the late 1920's by London, Schroedinger and Pauling, would have begun on far less certain grounds.

At that time most organic chemists were trying to do mechanistic studies using a line to represent a bond, which, while perfectly adequate for structural chemistry, was not at all adequate when discussions of chemical change were attempted. The English chemists (Lapworth, Lowry, Ingold, and Robinson) were beginning to wrestle with organic reaction mechanisms, and the first theoretical organic chemist in the United States (actually an Englishman!) to try to do the same was Gerald Branch at Berkeley. In this connection, I'd like to read from a letter from Col. A. H. Foster, Air Force (Ret.) who was a student in the College of Chemistry from 1913-17. In my correspondence with Col. Foster some years ago, he listed the faculty he knew here in Berkeley. He talked about Lewis, O'Neill, Tolman, Blasdale, Hildebrand, Randall, and then he came down to "Jerry" Branch, "whose status I never understood, although he and his lovely wife were both evident in the laboratories. Dr. Branch had one of the quickest minds of any person I ever knew, and I have often wondered what he made

Professor Branch wrote an essay on Gilbert Lewis in 1951 and presented it at the History of Science Dinner Club in Berkeley in 1953 (for text of this essay, see Appendix). I'd like to quote from that document, because it shows how close

Branch and Lewis were, and how conscious they were of the transition that chemistry was undergoing under the influence of the electron pair hond

Lewis became interested in the nature of the atom very early in his career. His notebook of 1902 contains the first formulation of his theory, but he published unthing in this field until his interest was revived by the publication of a short article on the nature of bonds by W. C. Bray and the author [G. E. K. Branch] in 1913. This was followed almost immediately by a publication on the same subject by Lewis, and the revival of his ideas of 1902, which were thrown to that den of lions, the research conference. The theory was not published until three years afterwards [in 1916, under the title of The Atom and the Molecule (5)].

Another essay (6) many years later, also confirmed the longterm interest of Lewis in the nature of the atom.

The reference to the research conference by Branch was very significant. It was the way Lewis tried out his ideas. The research conference, when I came to Berkeley in 1937, was held on Thursday afternoons. Lewis would either try out his own ideas, or look around at the faculty members and graduate students and ask "What are you doing?", and that was the start of the discussion. This was where the research ideas of the faculty and students were honed, and where the inconsistencies of the theories were thrashed out (6). This interplay of ideas was the reason why Bray and Branch could write an article (1) defining the oxidation number and coordination number and have it followed immediately in the same issue by an article by Gilbert Lewis on the same subject (2). The research conference had been the arena, so to speak, to clear up any arguments which might have existed, and by the time the papers were published, the various inconsistencies had been overcome.

The two 1913 papers, for example, gave rise to the possibilities of describing the mechanistic way in which atoms change their bonds. The whole basis for theoretical organic chemistry was laid during those years when Branch and Lewis were working so closely together.

Tautomerism

In the 1916 paper by Lewis on "The Atom and the Molecule" he used the terms valence and tautomerism in a special way. In order for you to understand the importance, I'd like to quote directly from the paper (5). This shows how far Lewis had gone in his thinking about how to describe the electron distribution in the molecule.

I wish to emphasize once more the meaning that must be ascribed to the term tautomerism. In the simplest case where we deal with a single tautomeric change we speak of the two tautomers and sometimes write definite formulae to express the two. But we must not assume that all of the molecules of the substance possess either one structure or the other, but rather that these forms represent the two limiting types, and that the individual molecules range all the way from one limit to the other. In certain cases, where the majority of molecules lie very near to one limit or to the other, it is very convenient and desirable to attempt to express the percentage of the molecules belonging to the one or to the other tautomeric form; but in a case where the majority of molecules lie in the intermediate range and relatively few in the immediate neighborhood of the two limiting forms, such a calculation loses most of its significance.

What Lewis is describing here is what Branch, following Ingold, later called "mesomerism" and what Pauling was to call "resonance."

In the 1933 paper (7) Lewis uses the term tautomerism where we would use mesomer or resonance hybrid. The English school of Lowry, Lapworth, Ingold, and Robinson, the school from which Branch came, was developing a whole theory of electron reaction mechanisms. Their terms—mesomeric effects, electromeric effects, polar effects—constituted the language of physical organic chemistry in the middle 1930's.

One last excerpt is given to illustrate Lewis' way of describing this and to show you he really understood what mesomerism, or resonance hybrids, were. He was trying to draw the structure of ethylene (7).

Now if we have two formulae such as (b) and (c) which differ only in their electronic arrangement and are of the same spectral type,

the means multiplicity, he recognized the difference between these two and (a)] and same gauge [Lewis had used the image of electrons running on tracks] then these two formulae (b) and (c) cannot be regarded as two possible separate states of the molecule. They must rather be regarded as two different representations of a single structural state, which ordinarily has lower energy than would be predicted if we should assume that there are two separate states and that some of the molecules are in one state and some in the other.

This is the phenomenon which has been called by Ingold the T-effect and which has been studied recently by Pauling under the name of resonance. We must not think that this phenomenon is due to the fact that we can write two or more different formulae to represent the same structure, but rather we must think that we can write two or more formulae because there has been a considerable inosening, without fracture, of the skeletal structure, so that within the skeletal structure there is far more freedom from the effects of quantum restrictions than in a saturated molecule such as ethane.

Color of Substances

It turns out that Lewis arrived at his concept of the color of substances hy constantly asking the same rather obvious questions from 1902 to 1933. He asks, for example, why is a substance colored, what causes the color? And the attempt to answer the question of why a substance is colored gave rise to the concept of the loose electron, and what we now call polarizability. Lewis recognized that those molecules which had deep color, such as dyestuffs, had many loose electrons, and these electrons can be distributed over a rather large skeleton of atoms. That idea gave rise to his notion of what he called tautomerism, but what we now recognize as mesomerism or resonance. Those two things taken together-questions about the color of molecules, questions of polarity of molecules versus nonpolarity (sodium chloride versus ethane, for example) seem like rather small questions. Lewis, however, was able to put them into the context of the larger question of all of chemistry.

The ability to do this was the heart of Lewis' genius and was something which most people could not do, then or now, Most people can ask a small question and answer a small question, but they are not able to ask a small question and from that answer derive a larger idea. When Lewis asks a question, he asks a question that has some depth to it and that has relevance to the entire structure of chemistry and of science. For example, when Lewis asked the question about color he got into the subject of the nature of light, which has many other permutations. Lewis did not limit the scope of his thoughts to the particular question, but he always had in the back of his mind the relevance of the question to science.

I made my first contact with Gilbert Lewis when I arrived in Berkeley in 1937, and I was not then aware of the things that we have been discussing here about Lewis and his work. Since I was the first non-Berkeley faculty member since 1913, Lewis naturally had a little bit of uncertainty about me, and only in retrospect am I able to see what he did. (Incidentally, it was Joel Hildebrand who was responsible for my coming to Berkeley. We had met in the laboratory of Michael Polanyi at the University of Manchester, England, where I was a postdoctoral fellow working on porphyrin chemistry. Hildebrand discussed with me the possibility of coming to Berkeley,



Figure 2. Gilbert N. Lewis, circa 1940.

and when he returned to Berkeley he "convinced" Gilbert Lewis to hire me.) Lewis (shown in his Gilman Hall Office, Figure 2) was looking for a common interest between us, to see if he could get me closer to him and his research, to find out whether I could stay at Berkeley or not. He found a way through his favorite subject, namely, why are molecules colored, the question he had repeatedly asked from 1902 to 1933. Almost every one of his papers which were concerned with valence and structure of molecules had a little section in it on the color of organic molecules.

We began with that—"let's write a paper on the color of organic substances," he said. In order to do that, we had to review the subject of color, which meant finding out what the status of the knowledge of this field was at the time (1937). We laid out in the seminar room in Gilman Hall all the references to the color of organic substances which were available. The best reference was the large dyestuff compendium, the dye index, which listed thousands of dyestuffs made throughout the world. It contained paragraphs on the properties of the various dyestuffs. Lewis read the references, which took several months. It was also necessary to have the structural formulas. This searching and literature examination went on for months, perhaps a year. Lewis examined the material and absorbed it and then, in his usual characteristic fashion, felt it was time to write. (Other people in the program today have had experiences of writing with Lewis-Seaborg, Kasha, Bigeleisen-and they can confirm the method I will describe to you.) Lewis would walk around the table in the seminar room and dictate, and I would write. It went quite smoothly and very, very nicely. Lewis dictated very carefully, and little revision was necessary. One time he spoke his sentence and I didn't write anything. Lewis looked over my shoulder to see what happened, and it was already written down! That wasn't difficult, because we had discussed the subject so much, and I had heard that sentence before. When the paper on "The Color of Organic Substances" (8) was finished, it was published in Chemical Reviews in 1939. Lewis had decided by that time that I could stay in Berkeley.

Phosphorescent State and Paramagnetism

As a result of writing the color paper we did another experiment (which you will hear more about from other participants). We found in examining some of the dyestuff information that we had assembled for the color paper that characteristics such as fluorescence were described. Lewis got the idea to find out why all dyes did not fluoresce, why did all dyes not re-emit the light they absorbed. He recognized the reason for this was that a molecule in an excited electronic state can either emit the light directly (fluorescence) or transfer that

electronic energy into vibrational-rotational modes (energy loss as heat). If such is the case, it should be possible to reduce that energy loss by freezing the molecule in a rigid medium so it cannot rotate and vibrate. Then it would have to emit light.

We made up a mixture of ether-pentane-alcohol, which could be frozen in liquid nitrogen to give a glass. If the dyestuffs are dissolved in this mixture and frozen in liquid air, they all fluoresce. In fact, some of them phosphoresce, that is, they emit light long after the exciting light is turned off. Lewis wanted to know the reason for that and also wanted to know the reason for that emitted light. When the emission lasted for a long time, it was of a different color from when it lasted a short time. In other words, the phosphorescence and fluorescence were different colors; usually the phosphorescence had a redder color.

Lewis did not really know much quantum theory (he did not really want to know very much), but he did know one selection rule, i.e., you cannot have a radiation transition between two states of different momentum. It is necessary to provide for the change in angle of momentum. If you have an excited state that has two electrons each with spin (by that time, spin had been discovered, even though Lewis had only postulated it in 1916), Lewis thought that perhaps the excited state that normally fluoresces had a way to get into another kind of excited state, by thermal degradation, in which the two electrons are parallel instead of antiparallel as they normally are. This means the spin angular momentum will be different in the two states. The only way for the excited electron to get back down again is by vibrational interaction, which would allow the net momentum to return to zero; without this occurring it would have to wait in the new excited state for a long time. This is the prohibition of the singlet-triplet transition. Lewis surmised that the long-lived state is a triplet state, which is the reason it lasted so long.

Magnetism and color were his two "bugs." In all his papers, Lewis always asks about the color and then asks what are the magnetic consequences of the color. This led Lewis to feel, for example, that ethylene was less diamagnetic than it should be (or a little more paramagnetic than it should be) because of the mobility of the electrons. He used Pascal's magnetism constants to confirm theoretical notions that he had evolved when he asked the question concerning color. The same ideas were recurring in 1938, 20 years after he had first proposed them. If the material is a triplet it has to be magnetic since the electrons are unpaired. If this is true, then the molecule should be paramagnetic and it should be possible to confirm it. This led to an elegant experiment which has been described in detail elsewhere (6). After Lewis was satisfied that the results were correct, the paper on the paramagnetism of the phosphorescent state was published (9). Lewis had satisfied himself once more that this "outlander" from the Midwest who had come to Berkeley was satisfactory.

Gerald Branch and Organic Chemistry at Berkeley

At that stage (about 1939), Lewis gave me the clear impression that I should work with Gerald Branch (Fig. 3) and collaborate with him in the preparation of a book on theoretical organic chemistry. Lewis told me that Jerry Branch had it all in his head, but he couldn't seem to get it written down. Therefore, it was my task, according to Lewis, to write down what was in Branch's head. He must have said something to Branch as well, because he (Branch) invited me to come to work with him in that area.

In any case, we worked out an arrangement by which I would come to Branch's house for dinner once or twice a week. Esther Branch, his wife (also a chemist with a PhD from Berkeley) would cook dinner, and we would then go to work. Branch would have written some material during the week, and I was supposed to write some more. We would rewrite and then plan next week's task. That's how the book was written. I must have had fifty dinners at the Branch's house, and the



Figure 3. Gerald E. K. Branch, 1936.

book was written and finally published in 1941 (10). It was the first book on theoretical organic chemistry that had ever been written in the United States that contained quantum mechanical language in it (those were the chapters I wrote). The chapters written by Branch contained a detailed analysis of the effect of structure on the acidity of hundreds of organic (and inorganic) acids. (Acidity was another of the recurrent Lewis themes: color, magnetism, and acidity. The theory of acids and hases had been formulated much earlier (2,4), but Lewis expanded these notions, with Glenn Seaborg as his personal assistant to do this.) Branch had already in his mind gone over the effect of structure on acid strength, as measured by pH and p K_a , and he used that as the foundation of the analysis of mesomeric (resonance, R_{α}) effects and inductive (polar, I_{α}) effects. These concepts are used to describe the effects of substituents and structure on acidity of any given

series. The total effect is given in terms of a property of the substituent $(I_{\alpha} + R_{\alpha})$ and a property of the skeleton upon which the substituent is placed (A_{α}) . (This same type of explanation was used later by Hammett $(\sigma$ and $\rho)$ at Columbia.) One constant had to do with the effect of substituent (σ) and the other constant had to do with the effect of structure (ρ) upon which the substituent was placed.

The publication of "The Theory of Organic Chemistry" in 1941 by Branch and Calvin was the beginning of theoretical organic chemistry in the United States, and it is related not only to the work of Gilbert Lewis but also to the English school which began with Lapworth, Lowry, Ingold, and Robinson. Branch, because of his English background as an undergraduate at Liverpool, had brought the seeds of these ideas to Berkeley. These concepts evolved, under the stimulus of Lewis' ideas of the electron pair bond, into resonance, coordination theory, etc.

We can trace the effect of Lewis' style and his thinking, not only on chemistry as a whole, but particularly on theoretical organic chemistry which was really founded on the Lewis electron pair bond and all of the things that flowed from it, such as of Pauling's resonance quantum theory and modern molecular orbital theory. The initiation of this new phase of dynamic organic chemistry began with Lewis' invention, or recognition, of the electron pair bond and how it could be modified and used.

Branch's anticipation of this phenomenon has never been properly realized or acknowledged. Branch came to Berkeley in 1912 as a graduate student, the year that Lewis came to Berkeley, at the very heginning of the seminar discussions on the subject of how the molecule is put together. Branch participated in the discussions and was influential in the development of Lewis' ideas. They interacted with each other. When Lewis got through with me on the color and magnetism efforts, he thought that the proper place for my next efforts would be with Gerald Branch in the preparation of the treatise on theoretical organic chemistry. This book, in effect, organized all of organic chemistry in terms of electron theory. Physical-organic chemistry at Berkeley and in the United States depends upon Lewis' initial stimulus in the concept of the electron pair bond and Branch's evolution and development of that concept and stimulus.

Lewis' Administrative Concepts at Berkeley

I'd like to touch hriefly on some of the particular methods that Gilbert Lewis used in establishing the department at Berkeley, shown in 1951 in Figure 4 on the occasion of Joel

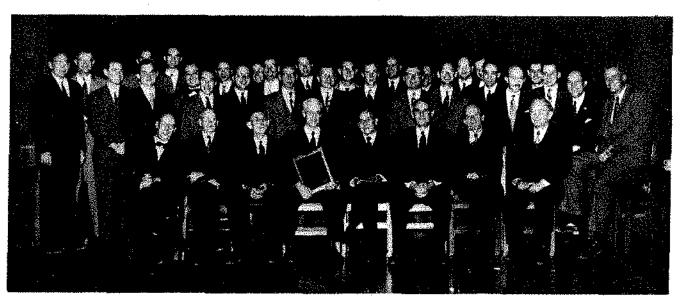


Figure 4. Chemistry Department, 1951. Left to right front row: Latimer, Stewart, Blasdale, Hildebrand, Gibson, Glauque, Branch, and Rollefson. Pitzer and Calvin immediately behind Rollefson.

Hildebrand's seventieth birthday. (Note that even though Lewis himself is not in this photograph—he died in 1946-Latimer, Stewart, Hildebrand, Giauque, and Branch are evident, as well as Pitzer, Calvin, and Seaborg.)

The department of chemistry at Berkeley was (and is) one of the most highly regarded in the United States and worldwide. The reason for this is perhaps best expressed by Gerald Branch in his essay on Gilbert Lewis (see Appendix). As a teacher and administrator, Lewis opposed the tendency toward specialization in curriculum, and he kept the number of undergraduate courses to a minimum with the purpose of preparing students with a thorough grasp of fundamentals rather than a mass of facts. Also, segregation of students was made early, in the freshman year, and the better students, were assigned the better instructors. To quote Branch,

Lewis believed that for a chemist to be useful to the world he should have a superior mind. In consequence, he preached that the department use its time and energy on good rather than average students. This somewhat undemocratic principle was often harshly criticized.

For graduate students, Lewis' methods were also not orthodox, but successful, the general principle being to allow the graduate student the greatest possible latitude. The students acquired initiative, morale, and a fine spirit of cooperation among themselves and the faculty. The weekly research conference (described in Reference (6) and Appendix) was the most important medium through which Lewis educated the graduate students, staff, and himself.

Evaluation of Gilbert Lewis as a Scientist

The success of Lewis and his education of graduate students and faculty is mirrored in the worldwide achievements of those students and staff. As an example, the following people, either students of Lewis or faculty members at Berkeley under Lewis, have received the Nobel Prize in Chemistry: Harold C. Urey (1933), William F. Giauque (1949), Glenn T. Seaborg (1951), Willard F. Libby (1960), and Melvin Calvin (1961), No other single teacher has such a record of students.

There is no doubt that the pre-eminence of the department of chemistry at Berkeley was largely due to Gilbert Lewis' direction for 29 years. The Lewis school of chemistry, with its concepts of intellectual vigor and excellence, has spread throughout the world, as his students, and their students, have created ever-widening circles of teaching and research,

The following quotation concerning the effect that Gilbert Lewis had on chemistry (and science) is taken from the resolution read before the Academic Senate of the University of California, Berkeley after the death of Lewis in 1946. It was written by Professor G. E. Gibson (11):

The half-century which terminated with the death of Gilbert Newton Lewis will always be regarded as one of the most brilliant in the history of scientific discovery, and his name ranks among the highest in the roster of those that made it great. The electron theory of chemical valence, the advance of chemical thermodynamics, the separation of isotopes ..., the unravelling of the complex phenomena of the adsorption, fluorescence and phosphorescence of the organic dyes are among the achievements which will always be associated with his name.

The methods he chose were always simple and to the point. He was impatient of unnecessary elaboration. . . . When the point at issue seemed to him sufficiently important, he would not hesitate to employ apparatus requiring skill and delicacy of manipulation, as in the beautiful hut difficult experiment by which he and Calvin demonstrated the paramagnetism of the phosphorescent trip-

As a man he was a grest soul whose inspiration will never be forgotten by those who knew and loved him. He was one of those rare scientists ... who are also great teachers and leaders of a school, so that their influence is multiplied by the many they have inspired.

Conclusion

Let the final words be Lewis' own, delivered on Charter Day. University of California, Los Angeles, March 22, 1935 (12):

Society is becoming increasingly awars of the power of science to bring weal or woe to mankind. But now when it is seen that the same science that brings prosperity and comfort may lead to dspression and discomfort, men are beginning to look with mixed feelings at this monster which society may exalt or persecute, but cannot view with indifference. Perhaps my topic today should have read 'Ought Scientists to be Burnt at the Stake?' I shall not attempt to decide this question, but only to present in a cursory way some of the pros and cons. . . . But if scientists are to be destroyed, let them not alons be the victims; every creative thought must be extirpated. A philosopher's epigram may kindle a world war. So scientist, inventor, artist, poet and every sort of troublous enthusiast must together be brought before the bar of the new inquisition.

Acknowledgment

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Literature Cited

- Bray, W. C., and Branch, G. E. K., J. Amer. Chem. Soc. 35, 1440 (1913).
 Lewis, G. N., J. Amer. Chem. Soc., 35, 1448 (1913).
 Kohler, Jr., R. K., "The Origin of G. N. Lewis Theory of the Shared Pair Bond," in "Historical Studies in the Physical Sciences," Vol. 3, (pp 343-376), (Editor: McCorromach, R.), Univ. of Pennsylvania Press, Philadelphia, 1971.
 Lewis, G. N., "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923; reprinted by Dover Publications, New York, 1966.
 Lewis, G. N., J. Amer. Chem. Soc., 38, 762 (1916).
 Calvin, Melvin, "Essay on Gilbert Newton Lewis," in Proc. Robert A. Welch Found. Conf. Chem. Res., 20, 116 (1976).
 Lewis, G. N., and Calvin, Melvin, Chem. Rev. 25, 273 (1939).
 Lewis, G. N., and Calvin, Melvin, J. Amer. Chem. Soc., 67, 1232 (1945).
 Branch, G. E. K., and Calvin, Melvin, "The Theory of Organic Chemistry," Prentice-

- (10) Branch, G. E. K., and Calvin, Melvin, "The Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, NJ, 1941.
 (11) Hildebrand, J. H., "Gilbert Newton Lewis," Obit. Not. Fellows of The Royal Society,
- (12) This talk was cited in the book by Arthur Lachman, "Borderland of the Unknown: The Life Story of Gilbert Newton Lewis," Pageant Press, New York, 1955.

Appendix: Gilbert Newton Lewis, 1875-1946

Gerald E. K. Branch

Gilbert Newton Lewis was born in Massachusetts on the 25th of October, 1875, but migrated to Lincoln, Nebraska while still a child. When 13 years old he went to the preparatory school for the University of Nebraska. On graduating from this school he went to the University of Nebraska for two years and then to Harvard College, where he obtained a B.A. in 1896.

After graduation he taught for a year at Phillips Academy in Andover. He then returned to Harvard and obtained the MA and PhD degrees in 1898 and 1899, respectively. After obtaining his doctorate he was appointed an instructor in Harvard. With a break of a year of study in Germany, he remained an instructor at Harvard until 1904.

Why Lewis' career at Harvard came to an end is not clear. In later life he boasted that he was fired. As an instructor he published three papers of high quality in quick succession, and then published nothing for three years. For one who published, on an average, four papers a year for the rest of his life, this lack of publications suggests a serious maladjustment to his environment. The break with Harvard may well have been fortunate for science, for on leaving that college Lewis resumed publication, although

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his next job might have been expected to quench the fire of his budding genius, as it took him far from any center of research. The position was Superintendent of Weights and Measures in the Philippine Islands and Chemist of the Bureau of Science at Manila. Somehow he found time for research in pure chemistry and published three papers while at Manila.

After a year in the Philippines he returned to Massachusetts as a member of the staff of the Institute of Technology, which at that time was a lively center of scientific thought. He remained at M.I.T. from 1905 to 1912, during which time he started his great contributions to thermodynamics. He also worked in other fields including relativity. The article he published with E. B. Wilson (1) was an outstanding contribution to the theory of relativity.

In the seven years Lewis was at M.I.T. he became famous both at home and abroad. In 1912 F. G. Donnan of Liverpool advised the author of this article to accept an opportunity to go to the University of California for graduate study, because he thought that Lewis was the most brilliant young physical chemist at that time.

In 1912 Lewis was appointed Chairman of the Department of Chemistry and Dean of the College of Chemistry at the University of California. These positions he held until he was 65. He continued as professor and professor emeritus until he died suddenly while working in his laboratory on the 23rd of March, 1946.

Just before coming to California, Lewis was married to Mary Sheidon, the daughter of a Harvard professor. Three children, Margery, Richard, and Edward, were born to thie marriage. Mrs. Lewis and the children are still alive. The two boys followed their father's footsteps in becoming chemists.

Lewis' work in California was interrupted by World War I. Shortly after America's entry into the war, he received a commission. He arrived in Frauce in January 1918, and after a visit to the front during the German offensive of that year, he was appointed Chief uf the Defense Division of the Chemical Warfare Service. For his work in this capacity he received the Distinguished Service Medal from his own country and the Cross of the Legion of Honor from France.

During the nineteenth century America was definitely inferior to Western Europe in pure science. At the turn of the century a wave of progress in science started in this country and after 50 years the United States leads the world in pure science. These great movements are common in the histories of civilizations. In such a movement, a man may be a contributor because of his scientific research and its consequent inspiration to others or because of his teaching. We do not limit the latter to conducting classes, but include the organization and leadership which enable others to be successful teachers. In both respects Lewis was a historical figure in the great movement that brought America to the foremost place in chemistry.

The effect of a man's research is not restricted to his own country; it is primarily an advance of science throughout the world. But the effect of his teaching is to a large extent localized. Further, a man's scientific diacoveries are widely known, but his teaching is known only to a few. For these reasons we shall first consider Lewis as a teacher and the founder of a great department of chemistry in Berkeley.

Lewis felt that a chemistry department should both teach the science and advance it. But in both functions the emphasis should be on the fundamental principles of the subject rather than on its industrial applications. There is always some conflict between pure and applied chemistry, and the proper balance between them in a university varies with the conditions in the country. In a young and rapidly developing country the danger is that the applied chemistry will devour the pure one and will in its turn lose originality from being out of contact with fundamental principles. Thus Lewis' emphasis on the pure science was fortunate for California, even though it might have been deleterious to a more developed country.

Lewis believed that for a chemist to be useful to the world he should have a superior mind. In consequence he preached that the department use its time and energy on good rather than average students. This somewhat undemocratic principle was often harshly criticized. That some success was achieved in obtaining a more than average ability amongst the students in chemistry is shown by the unduly high percentage of chemists among the valedictories.

Chemistry is a subject where specialization is rife, with the result

that a curriculum is apt to become gargantuan. Lewis strongly opposed such tendencies and kept the number of undergraduate courses in chemistry to a minimum. These courses were aimed to give a thorough grasp of the fundamentals rather than a mass of facts. Thus at a time when many chemistry departments in the country had no undergraduate courses in thermodynamics, California had two. On the other hand there was no course on petroleum chemistry in the department, aithough oil was a major industry in the state.

The aim of getting the student to think for himself was attained by free discussion between student and teacher and the large use of problems. The value of the former was probably increased by the circumstance that the teacher was often a graduate student. The graduate student is usually not as learned as the professor, but the student is less shy with his instructor when the latter is a graduate student. It may be noted that such contact between undergraduate and graduate student is educational to both parties.

Lewis' belief in the effectiveness of problem eets spread even to so factual a subject as organic chemistry. At the present time many textbooks in organic chemistry contain problem sets that challenge the ingenuity of hoth student and instructor. This might well be traced back to Lewis' influence.

Segregation of students was made as early as the freshman year. The freshman laboratory was divided into rooms that could hold no more than 25. Efforts were made to assign rooms to the better students and the better instructors to these rooms. Many of the upper division courses were restricted to the better students. At one time undergraduate courses were divided into three classes, courses restricted to honor students, those attended by the better students but not restricted to honor students, and finally unreatricted courses. All hunor students were required to do some research. The laboratory course in physical chemistry was divided into two sections, one of which was restricted to honor students. These complicated rules aimed at giving the better teaching to the better students.

In training graduate students Lewis' methods were unorthodux, but on the whole successful. The general principle was to allow the graduate student the greatest possible latitude. They were given the run of the storerooms and laboratory facilities. They chose their own instructors for their research work, and could change horses in the middle of the stream. Lewis was careful to limit the number of graduate students working for him, thus preventing his eminence in chemistry from depriving the other members of the staff of assistance in their work.

The freedum given to the graduate students to nhtain apparatus and materials no doubt led to some unwarranted expenditure, but the avoidance of delays and red tape more than compensated fur this. Further, the students acquired initiative, morale, and a fine couperation amongst themselves. This spirit of cooperation was not limited to the graduate students, but included the staff. No one was ever too busy to help the research of another. Nu one, not even Lewis, was too proud to seek assistance.

The choice of graduate students was carefully made by Lewis, with the assistance of members of the staff. In this choice natural gifts were considered more important than knowledge of chemistry. In many cases the lacunae in the students' education had to be filled hy undergraduate courses. Generally the deficiency was readily made up. Thus Herman C. Ramsberger took junior year coorses in chemistry, yet he readily obtained his doctorate, and went on to contribute much to the advancement of chemistry, until an untimely death put an end to what promised to he a brilliant career.

Having chosen a candidate for the PhD, he next made sure that the choice was a happy one. The aim was to obtain this knowledge early. Constant oral examinations were used. As the number of graduate students increased, the burden of the examinations to the staff became serious. The problem was never solved satisfactorily. In some cases it was doobtful whether the recipient of the degree was really worthy. Still worse, some failed to get the degree yet in later life courributed much to chemistry and became eminent scientists.

One good result of Lewis' efforts to ascertain the worth of the student as soon as possible was the abolition of the final examination for the PhD. This examination was either a farce or an avil

The weekly research conference was the most important me-

dium through which Lewis educated the graduate students, the staff, and himself. In this meeting papers were presented by graduate students, staff, and distinguished visitors. These papers included work in progress in the laboratory, work planned, and excerpts from the current literature. Each paper was followed by an active discussion, in which everyone could have his say, irrespective of his rank or the orthodoxy of his ideas.

In these discussions Lewis displayed a depth of insight and brilliance of thought that were an education to all who heard him. He accepted with good grace the harsh criticisms that were characteristic of the conferences. Needless to say his remarks were enlivened by his wit. This wit often pierced to the heart of a problem. One of the old graduate students has said that he never fully understood entropy until he heard Lewis define the entropy of a system as what we do not know about it. Before publishing Lewis frequently auhmitted his ideas to the criticism of the research conference, or to similarly conducted special seminars.

The success of Lewis' education of graduate students is mirrored in the success of the students. Fourteen of those who obtained their doctorate during his regime are or have been heads of departments or deans in reputable universities. Three have received the Nohel prize, namely, W. F. Giauque, G. T. Seaborg and H. C. Urey. Strange to say, many have achieved outstanding success in industrial chemistry.

Naturally Lewis owed much of his success in California to the other members of the department. Since it is at the beginning of things that contributions are most important, we shall mention William C. Bray, Joel H. Hildebrand, George E. Gibson, and Richard C. Tolman as those to whom Lewis owed most. Of the later additions to the department, Wendell M. Latimer contributed most and succeeded to the deauship.

If Lewis had done nothing else but build a great department of chemistry in the University of California, he would have been an illustrious Californian; but from a wider viewpoint this achievement is trivial beside his contributions to science. These contributions covered a wide field, even extending beyond the confines of chemistry. Nevertheless, two-thirds of his published work relates to the application of thermodynamics to chemical equilibrium, a theory of atoms, molecules and chemical bonds, isotopes, especially deuterium, and the interaction of light with substances. In describing Lewis' contributions to science we shall limit ourselves to these four fields.

At the time when thermodynamics was first applied to chemical equilibrium in Europe, J. Willard Gibbs did the same thing in America independently. In a sense, at that time there were two chemical thermodynamics, European and American. In its second phase of development W. Nernst became the leading figure in Europe and Lewis in America, though somewhat later. Both men wrote textbooks that became standard works, one for Europe, the other for America.

Lewis was quite familiar with European thermodynamics. In fact, he had spent a semester at Göttingen with Nernst in 1901. Nevertheless, he considered himself a disciple of Gibbs, whom he greatly admired. Fundamentally the two thermodynamics do not differ from each other. In the European system equilibrium is tied to the maximum work obtainable, which is usually represented by the symbol ΔA . In the American system it is tied to the maximum useful work obtainable, which is usually represented by the symbol ΔF . The ΔF and ΔA differ hy work done against a uniform pressure by the change of volume resulting from the reaction. To some extent the use of ΔF is simpler than that of ΔA , but both are perfectly permissible. Had Lewis' contribution to thermodynamics merely been the rescue of ΔF , it would have had only academic value. But as we shall see it was much more than this.

Lewis was introduced to thermodynamica by T. W. Richards, with whom he published his first paper on the subject (2). Eight years later he published "The Outlines of a New System of Thermodynamics" (3) which contains the seeds of his later work. The fruition of his work on thermodynamics was reached in 1923 with the publication with Merle Randall of "Thermodynamics and the Free Energy of Chemical Substances" (4). This book is one of the masterpieces of chemical literature and has been translated into many languages, including Russian.

Thermodynamics is logically deduced from axioms concerning energy, work, heat, and entropy. Corrected for the interchangeability of mass and energy, these axioms are exact as far as is known. Chemical equilibrium is measured by analysis. For thermodynamics to be applicable to chemical equilibrium it is necessary that some relationship be found between some quantity measured by analysis and some quantity related to work or energy. This connection was the empirical law of the proportionality between the partial pressure of a substance and its concentration. However, this law is not exact. Lewis' chief contribution to the application of thermodynamics to chemical equilibrium was to use the proportionality between pressure and concentration only for infinitely dilute concentrations, where the proportionality is exact as far as is known. To do this he introduced two quantities, the fugacity and the activity. For infinitely dilute conditions these quantities are equal to the pressure and concentration, respectively.

In reality only one of these quantities is necessary. Although fugacity is perhaps the more fundamental, activity is the one that has survived. This is because it is more nearly related to the concentration of a solution as obtained by analysis, and the deviations between activity and concentration in solutions are normally greater than those between fugacities and pressures in gases.

The introduction of this more exact application of thermodynamics to chemical equilibrium necessitated a change in the equilibrium constant of the old mass law. These equilibrium constants are now expressed in activities instead of concentrations if the activities have been measured. The new equilibrium constants are really constant as long as the temperature is constant, whereas the older constants often varied greatly at the same temperature.

One can measure an extensive property, say volume, of a homogeneous mixture, but how much of this property is to be assigned to a particular component is indefinite. Yet for thermodynamic application it is sometimes necessary to assign a certain amount of this property to a mole of some component. Lewis surmounted this hurdle by using the increase of the property resulting from the addition of a mole of the substance to so large an amount of the mixture that the proportions of the components are not affected materially. These properties were called partial molal quantities.

Lewis introduced the term ionic strength into thermodynamics. In solutions of electrolytes the activities of electrolytes are greatly affected by the electrical charges of ions. So the effects of ions depend on their concentrations and charges. To combine the two effects Lewis introduced the quantity called by him the ionic strength, and defined as one-half the aum of all the products $Z_i^{\ 2}m_i$, where Z_i is the charge and m_i the mobility, of the *i*th species of ion. He discovered the empirical law that the activity coefficient of a salt in dilute solution is fixed by the ionic strength. The dependence of the activities on the ionic strength was later deduced from electrostatics and statistical mechanics by Debye and Hückel, and gave rise to the famous Debye-Hückel equation.

Lewis' experimental work on thermodynamics consisted chiefly in the determination of standard free energies of substances and ions. More than half of the free energies determined were those of ions. In consequence his chief tool was electromotive force determinations.

Calorimetry at very low temperature is another powerful weapon in the determination of free energies. Lewis therefore instigated the development of low temperature calorimetrical technique in Berkeley. Although he himself did not publish many papers involviog low temperatures, the laboratory has become famous for this kind of investigation. The most shining worker in this field at the University of California has been W. F. Giauque, who lately has been awarded the Nobel Prize for his achievements.

Lewis became interested in the nature of the atom very early in his career. His notebook of 1902 contains his first formulation of his theory, but he published nothing in this field until his interest was revived by the publication of a short article on the nature of bonds by W. C. Bray and the author in 1913 (5). This was followed almost immediately by a publication on the same subject by Lewis (6) and the revival of his ideas of 1902, which were thrown to that den of lions, the research conference. The theory was not published until three years afterwards (7). In the same year, a very similar theory was published by W. Kossel in Germany (8).

Lewis' paper was entitled "The Atom and the Molecule." As its title suggests it was essentially two theories. The first part came immediately into conflict with the Bohr atomic theory, for in the Lewis theory the constituents of the atom were quiescent while

in the Rohr theory there was constant motion of electrons within the atom. It was for this reason that the Lewis theory became known as that of the static atom. Actually the essence of both theories was the central location and greater mass of the positive nucleus of the atom, and the classification of its constituent electrons. In the Bohr theory the classification was by orbit, and it achieved the astounding success of predicting the spectrum of the hydrogen atom. In the Lewis theory the classification was by shell. It established the nature of the periodic table as based on the noble gases (helium, argon, etc.) and the dependence of the electropositivities and electronegativities of the elements on their positions in the periodic table. At the present time the two theories have been reconciled, or if one prefers, superseded by quantum me-

Actually neither Lewis' nor Bohr's theory conformed to the laws of physics as then known. For this reason Lewis sought for variation in these laws to fit his theory. In nothing that he published was there anything of this nature that was worthwhile, but actually he often tempered with thoughts that might have led to something similar to quantum mechanics.

Lewis' and Kossel's theory of the atom were essentially the same, but Lewis' theory of the molecule was not shared with anyone, nor was it contained in his early notebooks. The essence of this theory was that a bond between atoms was made by their sharing a pair of electrons of opposite magnetisms. Hence combination decreases the paramagnetism of atoms or radicals and their compounds are diamagnetic unless unpaired electrons lie below the valence shell of electrons.

This formation of bonds by aharing electrons and atoms was an anathema to the laws of physics of 1916. Lewis' attempts to explain it by magnetic forces inherent in the electrons were unsuccessful, although the inherent magnetism of electrons was shown shortly afterwards. Although the theory was very successful in organic chemistry, it almost received its death blow with the discovery of a molecule with the formula H2+, for in this molecule the hydrogen atoms cannot be bonded together by sharing a pair of electrons between them for the very good reason that it has only one electron. But the theory of the electron pair bond was saved by quantum mechanics, for from the postulates of the latter it was shown to be deducible (9) that two atoms or radicals would be bonded together by a pair of electruns of opposite magnetism. Further, quantum mechanics showed that two equivalent units, as for instance the two protons of H2+, would be bonded by sharing a single electron. This limitation to the equivalence of the bonded particles makes the single electron bond a rarity,

Lewis theory of the chemical bond is one of the most important contributions to structural theory and hence to organic chemistry. Linus Pauling in his book "The Nature of the Chemical Bond" (10) expresses a similar opinion. It is a striking coincidence that organic chemistry owes so much to the two physical chemists, Van't Hoff

Quantum mechanics not only freed Lewis' theory of the stigma of unurthodoxy which it had carried at first, but also increased its value by allowing electrons to be used in more than one way at a time. This made possible the ready explanation of the body of facts which in the older structural theory were explained by the somewhat unsatisfactory concept of residual affinity. It also solved the problem of the benzene ring, a problem that had led to the partition of hooks and courses on organic chemistry into aliphatic and aromatic sections.

Among Lewis' own applications of this theory of the electron pair bond to chemistry was his generalized concept of acids and bases. In this theory the base has a pair of electrons to share with

the acid which has room for such a pair. Lewis' definition of an acid was therefore based on phenomena as well as on theory. Thus an acidic hydrogen compound was classed as an acid, not only for its ability to form an addition compound with a base by a hydrogen bond, but also because it gives its proton to a hase in an almost instantaneous process.

Lewis also applied his theory to show the necessity of paramagnetism in free radicals. This has led to the magnetic method for analyzing for free radicals. It is somewhat amusing to note that this phase of the theory led Lewis to assign a new and indubitably correct formula to so simple a substance as oxygen.

In the early thirties Lewis started work on deuterium. The inspiration came from Harold C. Urey, one of the most famous of the men who have obtained the PhD from Berkeley. During 1933 and 1934 Lewis published 26 papers on this subject. This phase of his work lasted a very short time, as nothing about deuterium appears in his writings after 1934.

He was the first to prepare pure deuterium and its compounds. Many of the chemical and physical properties of these were measured. One of the important discoveries made by Lewis was that the chemical properties of deuterium compounds differ from those of the corresponding hydrogen compounds. Theory requires that there should be a difference in the zero point energies of deuterium and hydrogen bonds, and hence difference in the chemical properties of their compounds.

To fully appreciate Lewis' work on deuterium one has to realize that at the time it was done deuterium compounds could not be obtained in bulk, and microchemical technique was in its in-

The last phase of Lewis' work was on the relationship between chemical constitution, absorption of light, and its re-emission in fluorescence and phosphorescence. Actually this subject had interested him for many years. He had written a paper concerning the color and hydration of ions in 1906. In 1920 when he gave the Faculty Research Lecture of the University of California the subject was the relationship between color and chemical constitution.

His serious work on this subject began when he was 64 years old and continued until his death at the age of 71. Leaving out posthumous work, he published 18 papers in this field. The first of these papers and the last before his death were in collaboration with Melvio Calvin. It is fitting that this last publication was about an outstanding piece of work, in which it was experimentally shown that the phosphorescent state is paramagnetic.

Needless to say, Lewis was showered with honors at home and abroad. The most apprupriate of these was the Richards Medal, for he was the most famous of Richards' students. To the regret of all his friends he was not awarded the Nobel prize. His contributions to thermodynamics and his theory of the chemical bond deserved this honor

Literature Cited

- (1) Lewis, G. N., and Wilson, E. B., Proc. Amer. Acad., 48, 389 (1912).
- Richards, T. W., and Lewis, G. N., Proc. Amer. Acad., 34, 87 (1899).
 Lewis, G. N., Proc. Amer. Acad., 43, 259 (1907).
- (4) Lowis, G. N., and Randall, Merle; "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill, New York, 1928.

 (5) Bray, W. C., and Branch, G. E. K., J. Amer. Chem. Soc., 35, 1440 (1913).

 (6) Lewis, G. N., J. Amer. Chem. Soc., 35, 1448 (1913).

- Lewis, G. N., J. Amer. Chem. Soc., 38, 762 (1916).
 Kossel, W., Ann. Physik., 49, 229 (1916).
 Heitler, W., and London, F., Z. Physik., 44, 455 (1927).
- (10) Pauling, Linus, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1939.

Symposium Honoring Debye to be Held

On March 22, 1984, the Cornell University Department of Chemistry and the Cornell Section of the American Chemical Society will hold a symposium to commemorate the 100th anniversary of Peter J. W. Debye's birth. L'ectures will be presented by Mansel Davies, Manfred Eigen, Paul J. Flory, Mark Kac, Linus Pauling, and E. Bright Wilson; in addition, Hans A. Bethe will speak at the evening banquet. Those interested in attending this symposium should contact: Dr. Earl Peters, Executive Director, Department of Chemistry, Cornell University, Baker Laboratory, Ithaca, NY 14853.

Enduring Distributions that Deny Boltzmann

Leonard K. Nash

Harvard University, Cambridge, MA 02138

Equilibrium distributions of atoms and molecules are ordinarily Boltzmann distributions (1), while nonequilibrium distributions that escape the rule of Boltzmann usually elude also any other comparably simple description. We examine here two steady-state distributions that are (a) at least approximately describable, and (b) of substantial practical interest.

The Atmosphere and its Lapse Rate

Imagine a homogeneous atmosphere of ideal gas with molecular weight (M) approximating 29, i.e., the weighted average molecular weight of air. Writing the ideal gas law in the form PM = (nM/V)RT, we see that the local density (δ) will be expressible, in terms of the local temperature and pressure, as

$$\delta = PM/RT$$

To establish the variation of pressure with altitude (h), consider an infinitesimal slice of the atmosphere, with cross-sectional area A, height dh, and mass dm. Consequent to the decrement in superincumbent mass, passage from the lower to upper surface of the slice is reflected in a difference of pressure

$$dP = -g dm/A$$

where g symbolizes the gravitational acceleration. The mass decrement is in turn expressible in terms of the local density and the volume of the slice, as $dm = (A dh)\delta$. Substitution of our expression for δ then produces

$$\frac{\mathrm{d}P}{P} = -\frac{Mg}{RT}\,\mathrm{d}h\tag{1}$$

Over the lower reaches of the atmosphere (troposphere) at which our analysis is aimed, g is effectively constant. Hence, if this part of the atmosphere were *isothermal*, integration of the last equation would give

$$\ln P/P_0 = -Mgh/RT$$

where P_0 is the pressure at altitude h=0 (e.g., sea level). Since in an isothermal atmosphere the number of molecules (N) per unit volume is directly proportional to the local pressure, the last equation is equivalent to the Boltzmann distribution law in the form

$$N/N_0 = e^{-mgh/kT} = e^{-\epsilon/kT}$$

where m is the molecular (not the molar) mass and ϵ is the excess gravitational potential energy of a molecule at altitude h > 0.

Though a fair approximation in the troposphere, this simple law does not properly apply to our atmosphere—a nonequilibrium system that, far from being isothermal, displays a large vertical temperature gradient. One striking manifestation of this gradient is the well-known fact that it is much colder on a mountain's peak than at its base. How does it happen that, closer to the sun and with less of the atmosphere to shield it from that luminary, mountain peak is much colder than mountain base?

As glider pilots well know, large bodies of air are constantly rising or sinking through the atmosphere. With air a very poor conductor, the displacement of these large air masses must be approximately adiabatic. And because the moving air

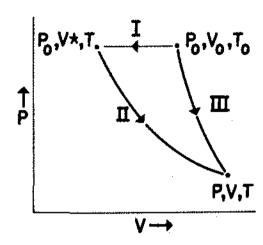


Figure 1. Two routes that link sea-level conditions (P_0 , V_0 , T_0) with the conditions (P, V, T) at any final altitude.

parcel remains throughout in pressure equilibrium with the surrounding atmosphere, the displacement must also be approximately reversible. The qualitative situation is then quite clear. As it ascends into regions of diminishing atmospheric pressure, a rising mass of air expands and does work on the surrounding atmosphere. In an adiabatic process this work must be done at the expense of the internal energy of the air parcel, which must therefore cool as it rises.

Most simply to quantify this effect, we observe that a reversible adiabatic displacement must be isentropic. Along the path of the actual displacement (III in Fig. 1), expansion from sea-level conditions (P_0, V_0, T_0) to the conditions (P, V, T) characteristic of any final altitude must yield

$$\Delta S_{\rm HI} = 0$$

Another route between the same original and final states involves (I) constant-pressure cooling to the final temperature, followed by (II) isothermal expansion to the final pressure (and volume). With entropy a function of state, necessarily

$$\Delta S_{\rm I} + \Delta S_{\rm II} = \Delta S_{\rm III} = 0$$

Insertion of familiar expressions for $\Delta S_{\rm II}$ and $\Delta S_{\rm II}$ produces

$$nC_P \ln \frac{T}{T_0} + nR \ln \frac{P_0}{P} = 0$$

$$\ln \frac{T}{T_0} = \frac{R}{C_P} \ln \frac{P}{P_0}$$

Since P_0 and T_0 are constants, they vanish in a differentiation that yields

$$\frac{\mathrm{d}T}{T} = \frac{R}{C_P} \frac{\mathrm{d}P}{P} \tag{2}$$

From the general equation (1) we substitute for $\mathrm{d}P/P$, and so find

$$\frac{\mathrm{d}T}{T} = \frac{R}{C_P} \times -\frac{Mg}{RT} \, \mathrm{d}h$$

After cancellation of R's and T's, hy integration we obtain

$$\Delta T = -\frac{Mg}{C_P} \Delta h \tag{3}$$

Insertion of $M \simeq 0.029$ kg/mole, $g \simeq 9.8$ m/s², and $C_P \simeq 7R/2$ = (7/2)8.314 joule/mole-°K now gives $\Delta T/\Delta h = -0.0098$ °K/m. What meteorologists call the *dry adiabatic lapse rate* is thus established as

$$\Delta T/\Delta h \simeq -10^{\circ} \text{K/km}$$

This is a very large effect we can measure against the conditions on, say, Mt. Kilimanjaro—a 5.9-km peak close to the equator. That equatorial setting notwithstanding, conditions at the top of Mt. Kilimanjaro are quite literally arctic, characterized by all-season snow and ice fields. If we suppose a base temperature of 38°C ($\simeq 100^{\circ}\text{F}$), our calculated lapse rate implies a crest temperature of $38-58=-20^{\circ}\text{C}=-4^{\circ}\text{F}$, which is quite low enough to explain the permanence of the snows of Kilimanjaro.

Our analysis has justifiably ignored kinetic-energy effects: even with an air parcel moving at 30 mph, the kinetic energy is equivalent to no more thermal energy than is required to warm that air by 0.1°K. Thus all but exceedingly high air velocities will have only a negligible effect. On the other hand, these vertical displacements do proceed rapidly enough that we can also properly ignore both conduction effects and all those due to absorption or emission of radiation by a dry air that is comparatively transparent to both solar and terrestrial radiation. And more generally, in the steady-state atmosphere the vertical displacements that engender temperature differences are much swifter than the equilibrative processes thus rendered incompetent to dissipate the temperature gradient—which is to say insufficient to return the atmosphere to the rule of Boltzmann.

A tacit assumption of the foregoing analysis has been dryness of the displaced air masses. Recognizing that they may contain water vapor, we can give at least a zero-order (2) explanation of an enlarged roster of striking facts (3). Consider for example any mountain(s) on one face of which a prevailing wind blows air rendered humid by passage over a warm sea. With the arrow indicating the prevailing direction of the wind, the observed constellation of conditions around the mountain(s) is likely to be as indicated in Figure 2, not wholly unreminiscent of an alchemical diagram. As the humid influent air is driven up the windward slopes, it is cooled as before by adiabatic expansion. But when at last the dew point is reached, precipitation of rain discharges a latent heat of condensation into the air. This checks the fall of temperature, and as the air continues its ascent the rate at which its temperature declines is diminished by the release of further heat of condensation consequent to further precipitation of rain and, ultimately, snow. When at last the summit is attained, initially moist air will have declined in temperature rather less than initially dry air. (The average observed lapse rate approximates -6.5°K/km.) But if the peak is sufficiently high, the air will be cooled enough to precipitate virtually all its original charge of moisture. This means abundant rainfall on the windward slopes (apt also to be enveloped in condensation clouds).

What happens when, on the leeward side of the mountain(s), the air mass becomes free to descend into regions of

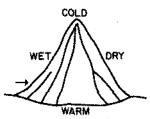


Figure 2. Observed conditions around a mountain. The arrow indicates direction of the prevailing wind.

greater atmospheric pressure? Already dried by orographic precipitation during its ascent of the windward slopes, air that reaches the summit cold now undergoes a reversible adiabatic compression that vigorously reheats it (up to 10°K/km) as it descends the leeward slopes. (The chinook wind, or foehn, is a spectacular special case.) The leeward slopes are thus bathed in dried air heated well above its dew point, and in this region there can be scant prospect of rain. And that "rain shadow" stretches further to leeward the greater the altitude and extent of the mountain(s) concerned. On a major scale, in California (where the prevailing wind blows from the West, across the Pacific) the windward slopes of the several mountain ranges are well watered, while off to leeward lie the deserts of Nevada. On a minor scale, a modest peak on the small Caribbean island of St. Croix produces tropical rain forest on its windward slopes, and also a desert landscape that stretches leeward to the end of the island.

The Ocean and its Vertical Quasi-Uniformity

Consider an ocean vertically uniform in temperature ($\simeq 2^{\circ}$ C) and in salinity ($\simeq 35$) i.e., ca. 35 g of mixed sea salts per 1000 g of water. Levenspiel and de Nevers indicate (4) that, apart from a surface "skin" that extends to a depth of only a few hundred meters in oceans with depths running as great as some 10,000 m, a real-world ocean can be significantly approximated as a uniform ocean (5). Such a uniform ocean may plausibly be supposed an equilibrium ocean; but the falsity of that conclusion is demonstrated by some striking incongruities to which Levenspiel and de Nevers have drawn attention.

Between our uniform ocean and fresh water, the osmotic pressure difference (π) is calculable from the standard relation

$$\pi = \frac{RT}{V_v} \ln \frac{1}{X_v}$$

Here $X_{\rm v}$ and $\overline{V}_{\rm v}$ symbolize respectively the mole fraction and the molar volume of the solvent in the solution. We make no great error if we approximate $\overline{V}_{\rm v}$ as the same as in pure water. In that case $\overline{V}_{\rm v} = \overline{M}_{\rm v}/\rho_{\rm v}$, where $\overline{M}_{\rm v}$ and $\rho_{\rm v}$ symbolize respectively the known molecular weight and density of water. With this substitution, the last equation assumes the form

$$\pi = \frac{\rho_{\rm v} RT}{\overline{M}_{\rm v}} \ln \frac{1}{X_{\rm v}} \tag{4}$$

As to X_v , summation over a standard recipe (6) for seawater yields $\sum v_i m_i$, where v_i is the number of moles of ions freed by one mole of the *i*th sait present at molality m_i . But when we assign to each v_i its limiting integer value, our neglect of activity effects means that, from the sum $\sum v_i m_i = 1.16$ mole/kg, we can obtain for π no more than a maximum estimate by writing

$$\pi = \frac{1.00 \text{ (kg/l) } 0.0821 \text{ (l-atm/mole-°K) } 275 \text{ (°K)}}{0.0180 \text{ (kg/mole)}} \ln \frac{1.16 + 1000/18}{1000/18}$$

= 25.9 atm

The osmotic coefficient ($\phi \simeq 0.9$) appropriate to seawater (7) perfectly reconciles this upper limit with the $\simeq 23$ atm cited by Levenspiel and de Nevers as the observed osmotic pressure of seawater.

Into a uniform ocean let us sink a very long pipe closed at its lower end by a membrane selectively permeable to water only. The interior of the pipe remains dry until the membrane reaches such a depth that the ocean's hydrostatic pressure at last rises to 23 atm. At this point reverse osmosis yields a thin film of pure water on the inner surface of the membrane. And at still greater depths, where the seawater presses ever more strongly against the outside of the membrane, osmotic equilibrium is attained only after a lengthened column of pure water has built up inside the pipe. A little algebra based on

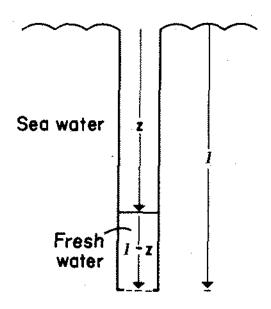


Figure 3. Hypothetical device that produces an upwelling of pure water in a uniformly safty sea.

Figure 3 supplies an explicit expression for the equilibrium distance (z) of the pure water from the surface when the membrane is at any depth (l). With $\rho_{\rm v}$ the density of the pure water on the inside, let $\rho_{\rm s}$ symbolize the density of the seawater outside the pipe. At osmotic equilibrium we must now find

$$g \rho_{s} l - g \rho_{v} (l - z) = \pi$$

$$z = \frac{\pi}{g \rho_{v}} + l \left(1 - \frac{\rho_{s}}{\rho_{v}} \right)$$
(5)

Under 1 atm pressure at the surface, $\rho_{\rm v}=1000~{\rm kg/m^3}$, and $\rho_{\rm s}=1028~{\rm kg/m^3}$. A rise of pressure from 1 to 1000 atm (i.e., the pressure at a depth of $\simeq 10,\!000~{\rm m}$) increases the density of pure water by rather less than 5%, and the corresponding density increase for seawater is comparably small (8). Mutual cancellation of these small changes thus ensures that, at all depths in a uniform ocean, the ratio $\rho_{\rm s}/\rho_{\rm v}$ must retain a value very close to the 1.028 prevailing near the surface. The other key ratio, $\pi/\rho_{\rm v}$, is similarly insensitive to total applied pressure, as is at once demonstrable by rearrangement of equation (4). At all depths in a sea uniform in T and $X_{\rm v}$, the ratio $\pi/\rho_{\rm v}$ must then retain its surface value—which, in convenient units, is

$$\frac{\pi}{\rho_{\rm v}} = \frac{23 \text{ (atm) } 101325 \text{ (newton/m}^2-atm)}{1000 \text{ (kg/m}^3)} = 2330 \text{ m}^2/\text{s}^2$$

For a uniform ocean, substitution in equation (5) of appropriate numerical values yields (in meters) the relation:

$$z = 237.6 - 0.028 l$$

Two special cases are of particular interest. First, at that critical depth where reverse osmosis first produces a film of pure water inside the membrane, with $z \rightarrow l$ we easily calculate the critical depth as

$$l = 237.6/1.028 = 231 \text{ m}$$

in agreement with the figure obtained by Levenspiel and de Nevers. Second, at that depth where pure water wells right up to the surface, with $z \rightarrow 0$ we find

$$l = 237.6/0.028 = 8500 \text{ m}$$

in acceptable agreement with the 8750 m that Levenspiel and de Nevers draw from a far more difficult analysis.

Here is the first striking incongruity arising from the pre-

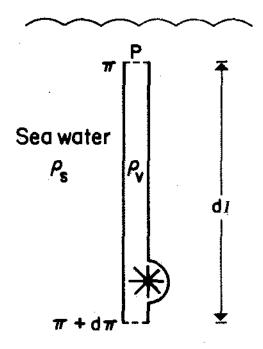


Figure 4. Hypothetical device that extracts useful work from a uniformly salty sea.

sumption that the uniform model ocean is an equilibrium ocean. For surely a wholly spontaneous welling up of fresh water in the midst of a salt sea is no small incongruity. And from this first incongruity arises a second no less startling. For remixing of this fresh water, with the saline ocean whence it came, is an obviously spontaneous change from which a work output is in principle recoverable; and Levenspiel and de Nevers sketch a direct recovery of work from such an osmotic pump. Where a better known alternative approach (9) to energy recovery exploits the disparity of temperature between surface "skin" and ocean deep, the Levenspiel and de Nevers approach is remarkable precisely because it aims to exploit the uniformity of real-world oceans. But is not any such exploitation of uniformity itself a thermodynamic incongruity?

Away from ultracentrifuges, all our everyday laboratory experience teaches chemists to think of equilibrium systems as homogeneous both in temperature and composition. And one is thus strongly predisposed to view the uniform ocean as an equilibrium ocean. But in the extended laboratory of an ocean deep, the variation of gravitational potential energy may be big enough to make an equilibrium ocean significantly nonuniform. The spontaneous production of pure water and useful work from a uniform ocean will then cease to be incongruities precisely when we can demonstrate that a uniform ocean is not an equilibrium ocean.

This conclusion is established by Levenspiel and de Nevers with a chemical-potential argument that thermodynamic novices may find opaque. A wholly transparent but still compelling alternative analysis draws on thermodynamics only for the proposition that, by itself, no system at equilibrium can spontaneously yield a work output. The argument is similar in style to a classic derivation of equation (4) from the Boltzmann law (10).

Into a deep isothermal column of seawater—now supposed wholly at equilibrium—we lower the device sketched in Figure 4. Two membranes selectively permeable to the solvent water provide access to a pure-water shunt of length dl. At the level of the upper membrane let the equilibrium osmotic pressure difference be π ; at the level of the lower membrane let the osmotic pressure be $\pi + d\pi$. (This does not at all discount the possibility that the uniform model ocean may yet prove an equilibrium ocean, since in that event we would simply find $d\pi = 0$.) Whatever may be the character of the equilibrium

ocean, however, it must exclude the possibility of any continuous cyclic flow through the pure-water shunt-because such a flow could be yoked by the paddlewheel to a continuous production of work no equilibrium system can supply.

If p symbolizes the pressure on the outer face of the upper membrane, the salt-water pressure on the outer face of the lower membrane must be

$$P + g \rho_s dl$$

On the inner face of that lower membrane the pure-water pressure is similarly expressible as

$$P - \pi + g \rho_v dl$$

A continuous, work-producing flow through the pure-water shunt will be excluded if, and only if, the difference between the two above pressures matches the equilibrium osmotic pressure at the lower membrane-which entails

$$\pi + d\pi = (P + g\rho_s dl) - (P - \pi + g\rho_v dl)$$

$$\frac{d\pi}{dl} = g(\rho_s - \rho_v) = g\rho_v \left(\frac{\rho_s}{\rho_v} - 1\right)$$
(6)

The right side being positive, the osmotic pressure must increase with depth (l) in the sea-and we dissipate all incongruities by thus showing that a uniform ocean characterized by constant π cannot be an equilibrium ocean.

Why does π increase with depth in an equilibrium ocean? Presumably because the solute concentration here increases with depth, which is to say that the mole fraction of the solvent water decreases with depth. That there is just such a decrease is easily demonstrated. Observing that the derivative in equation (6) refers to the variation of π in a sea where ρ_{ν} (and $ho_{
m s}$) remain constant over the short span dl, we impose the same condition in drawing from equation (4) the corresponding derivative:

$$\frac{\mathrm{d}\pi}{\mathrm{d}l} = -\frac{\rho_{\mathrm{v}}RT}{\overline{M}_{\mathrm{v}}} \frac{\mathrm{d}\ln X_{\mathrm{v}}}{\mathrm{d}l}$$

Elimination of $d\pi/dl$ between this and equation (6) produces

$$\frac{\mathrm{d} \ln X_{\mathrm{v}}}{\mathrm{d}l} = -\frac{\overline{M}_{\mathrm{v}g}}{RT} \left(\frac{\rho_{\mathrm{s}}}{\rho_{\mathrm{v}}} - 1 \right) \tag{7}$$

Comparing this with equation (1), we see that in an equilibrium sea the distribution of water conforms to a simple Boltzmann distribution modified only by the insertion of a buoyancy correction. The density of the pure water being less than the density of the salt solution, the solvent is found more abundantly in the upper levels of the sea where l is small. Flouted in the (real) uniform ocean that is not at equilibrium, the Boltzmann distribution thus duly commands the (purely hypothetical) equilibrium ocean that is not uniform.

Finally, we should demonstrate that the equilibrium ocean supports no spontaneous welling up to the surface of pure water, of the sort we found so incongruous in the uniform ocean. Under the familiar condition of constant ρ_{ν} and ρ_{s} , differentiation of equation (5) gives

$$\frac{\mathrm{d}z}{\mathrm{d}l} = \frac{1}{g\rho_{\mathrm{v}}}\frac{\mathrm{d}\pi}{\mathrm{d}l} + \left(1 - \frac{\rho_{\mathrm{s}}}{\rho_{\mathrm{v}}}\right)$$

Elimination of $d\pi/dl$ between this and equation (6) now vields

$$\frac{\mathrm{d}z}{\mathrm{d}l} = \left(\frac{\rho_{\mathrm{s}}}{\rho_{\mathrm{v}}} - 1\right) + \left(1 - \frac{\rho_{\mathrm{s}}}{\rho_{\mathrm{v}}}\right) = 0$$

In an equilibrium ocean, therefore, the distance z is not a function of the depth (1) of the membrane, and at all depths the top of the pure-water column remains a constant 231 m below the ocean surface.

Acknowledgment

For much useful criticism I am indebted to D. E. Carritt. C. M. Delaney, and W. H. Eberhardt.

While this essay awaited publication, the lapse rate of planetary atmospheres has been discussed by Blanck (11), and a delightful paper by Bachhuber (12) touches lightly on both examples discussed in this essay.

Literature Cited

- Naah, L. K., "ChemThermo," Addison-Wesley, Reading, MA, 1972, p. 25.
 For a full treatment see Iribarne, J. V., ands Goodson, W. L., "Atmospheric Thermodynamics," Reidel, Boston, MA, 1973.
- (3) The full complexity of climatological phonomena is indicated by Barry, R. G., and Chorley, R. J., "Atmosphere, Weather, and Climate," 3rd ed., Methuen, London,
- (4) Levenspiel, O., and de Nevers, N., Science, 183, 157 (1974).
- (5) See for example the data for the Mindanao Trench cited by Green, P., "The Waters of the Sea," Van Nostrand, Princeton, NJ, 1967, p. 56.
- (6) Leyendekkers, J. V., "Thermodynamics of Seawater," Marcel Dekker, New York, 1976,
- Reference (6), p. 108.
 Horne, R. A., "Marine Chemistry," Wiley-Interscience, New York, 1969, pp. 479-80.
 Marland, G., Endeavour, N.S., 2, 185 (1979).
- (10) Nash, L. K., "Stoichiometry," Addison-Wesley, Reading, MA, 1966, pp. 177-79.
 (11) Blanck, H. F., J. CHEM. EDUC., 60, 637 (1983).
- (12) Bachhoher, C., Amer. J. Phys., 51, 259 (1983).

Summer Employment Program Polymer Science

The Industrial Sponsors Group of the Division of Polymer Chemistry of the American Chemical Society announces a new summer employment program. Outstanding juniors are provided the opportunity to work in the field of polymer science with one of a select number of U.S.-based chemical companies.

The first phase of the program involves a unique opportunity offered by the Plastics and Coatings Division of Mobay Chemical Corporation for the summer of 1984. The selected candidate will be sent to Uerdingen, West Germany for a work/training assignment in the Research Laboratories of Bayer AG, Mohay's parent company. All transportation and lodging expenses along with a monthly salary will be paid by Mobay.

Program announcements will be mailed to a large number of colleges and universities this fall. Interested students should send a letter outlining their academic and personal interests and goals along with a transcript or equivalent listing courses and grades before February 1, 1984 to Dr. G. E. Reinert, Mobay Chemical Corporation, Pittsburgh, PA 15205.

Additional industrial participants are currently being sought for ther summer of 1984. Program details will vary according to the interests of the individual companies.

Will Computers Replace TA's? Professors? Labs? Should They?

A Symposium Report

Introduction

John W. Moore and Elizabeth A. Moore

Eastern Michigan University Ypsilanti, MI 48197

The number and variety of applications of computers in chemical education have grown at an ever-increasing pace since the introduction of the Altair microcomputer in 1976. It is becoming commonplace for students to have their own computers, and most chemistry departments have micros available for students to use. There has been a tremendous growth in the number of computer programs available for instructional purposes, although the old bugaboo of re-inventing the wheel is still evident. Commercial publishers have produced extensive sets of lessons to cover entire courses, and NSF-supported projects like SERAPHIM¹ can supply both programs and information about nearly all sources of instructional software.

Therefore, the time seems ripe for assessing where we are and more importantly where we ought to be going in this field of chemical education. Collectively we have by now had enough experience to at least begin to make some judgments about which applications of computers are most valuable and appropriate. We can consider carefully how computer-based instruction ought to affect our approaches to the subject matter of chemistry and the pedagogical approaches we can take to our subject. We can develop new ideas about how to use this new tool, paying attention in this process to the results of educational research. We can do these things, but for the most part we have not been doing them, and we are in danger of getting into the situation depicted in Figure 1. A new tool that is not used innovatively and imaginatively may simply perpetuate and amplify all that is less than satisfactory with the old-fashioned way of doing things.

In hopes of opening discussion of many of the points listed above, Project SERAPHIM organized a symposium at the Fall 1983 ACS National Meeting in Washington, DC. Speakers were selected with an eye to broad coverage of various types of computer applications: Stanley Smith is a commercially published author with nearly 20 years of experience in tutorial CAI; Allan Smith is a faculty memher charged with training colleagues in a university where every freshman will have a computer this year; Stanley Burden is one who has developed and tested a battery of analytical experiments involving online data collection and analysis; Jeff Davis is a jack-of-all-trades with respect to instructional technology; John Moore

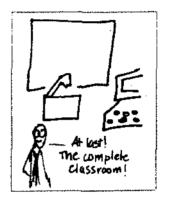








Figure 1. Cartoon by M. Sanders, State University of New York, College at Old Westbury and taken from "Marginalia," The Chronicle of Higher Education. Reprinted with the kind permission of The Chronicle of Higher Education, Copyright © 1983.

is a proponent of instructional simulations; J. J. Lagowski is an old hand in handling large freshman chemistry courses with computer assistance; and Derek Davenport is a devil's advocate whose spicy comments can be expected to keep everyone else on their toes. This report consists of manuscripts submitted by the speakers and a summary of the panel discussion that closed the symposium. Speakers were charged at the beginning of the symposium to consider the challenge made in an editorial in THIS JOURNAL last summer (1):

Fulfillment of the true promise of the application of computeroriented high technology to education requires an uncommon quality of thought and breadth of vision. Such vision implies high costs and high risks, but the stakes are so high that they warraut—indeed demand—an answer formulated by the most creative minds we have available.

¹ Project SERAPHIM—A Model System for Dissemination of Microcomputer-Based Instructional Materials, J. W. Moore and J. J. Lagowski, principal investigators; sponsored by NSF-DISE, SED 81-07568. Opinions expressed in this article are not necessarily those of NSF.

The title of the symposium was made provocative in order to attract the attention of many who have not yet considered the promise or the limitations of computers. We hope that many who read this article will be challenged to take on some of the costs and risks inherent in experimenting with a new medium of instruction, and will contribute to the discussion we hope the symposium began. The greater the number of creative minds applied to the problems of chemical education, the better. There are certainly plenty of intellectual challenges for those who attempt to apply computers to the task of teaching.

Teaching with a Microcomputer: The Current Status and What's in Store for the Future

Stanley G. Smith

University of Illinois Urbana, IL 61801

When considering the current status of computer use in teaching and what's in store for the future one can ask: Can professors be replaced? should they be replaced? and will they be replaced? To answer these questions, it is necessary to define what a computer can do for both the professor and the student. The ability of a computer to put text and graphics on the screen, accept and interpret student input, store and recall data, and do calculations can be molded into an interactive instructional system (2). The major limitation on the ability of such a system in instruction is the imagination of the lesson designers and programmers. Typical applications (3) include tutorial dialogs, simulations of experiments, practice problems, data collection, control of experiments, and chemical games (4). These types of programs have been used to supplement lectures (5), provide interactive homework, and prepare students for laboratory work (6, 7).

Can Computers Teach?

Because of its highly interactive nature and the ability to do animations, the instructional approach used with a computer can and should be very different from that in a textbook or a lecture. For example, instead of explaining a phenomenon the computer can allow the student to experience it through simulations that are designed to illustrate the important features. When coupled with tutorial material designed to assure that the student understands the simulation and suitable practice problems the computer becomes a new kind of instructional medium that supplements the approaches available in printed matter, discussions, and laboratory work. In a textbook, for example, words may be used to describe what happens if you compress a gas in a cylinder. The process can also be described in lecture along with pictures. But on a computer each student can, through a simulation, push the piston in and out and collect data on various pressures and volumes. The experiments can be monitored by the computer and individualized help provided to the student only if needed. Even with something as simple as halancing equations the computer can help by giving a table with the number of atoms of each of the elements in the reactants and the products. As you start to balance the equation computer updates the table dynamically so you can see what balancing an equation really means (Fig. 2). It is clear that:

A computer is not a book.

A book is passive; a computer is interactive. It is also clear that:

A computer is not a lecture.

Lectures tend to be passive. And:

A computer is not a book.

Books have lots of text. Computers have animations. Also,

A computer is not a lab.

You can do a simulated laboratory experiments on the computer, but that isn't real laboratory work. You can't burn your fingers on hot glass or discover what something smells like on a computer. And remember,

A computer is not a book.

It is easy to tell the difference between a computer and a book—they are very different media. A computer requires new pedagogical approaches.

The effectiveness of computer-assisted instruction, as with all types of instruction, depends on the content, the way it is presented, and the instructional design. Students seem to like working and learning with a computer (5), and, although studies are still limited, the available data suggests that CAI is an effective teaching tool (8, 9, 10). Thus there appear to be many circumstances under which a computer can replace a professor.

Should Computers Teach?

If a computer can teach the same material in less time and with greater long-term retention by students than could be achieved by a teacher, then there is a reasonable argument for replacing the teacher.

Anyone who can be replaced by a computer should be.

However, we should also recognize that

A computer is a tool: good teachers cannot be replaced by a computer.

A computer will only replace those TA's, professors, and labs that are limited to those types of things that can be done better on a computer. A good teacher will not be replaced by a computer; a good teacher will use the computer to be even better. The objective is not to replace anybody, but to do a hetter job of teaching. The computer, as demonstrated by experiments, does serve that role.

Will Computers Teach?

The extent to which computers will be used for teaching is critically dependent on the cost of the hardware and the availability of suitable programs. The rapid proliferation of relatively inexpensive microcomputers that have the capability of supporting high quality instructional material is making CAI generally available (11). In 1975 one had to have access to a powerful mainframe computer just to try to do something with computers in instruction. In 1976 if you could put together an Altair kit you could have your own computer for a few thousand dollars. Now, in 1983, for a few hundred dollars you can purchase a computer that is able to support a wide range of instructional techniques. Furthermore, it is likely that in the near future students will have their own

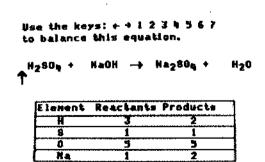


Figure 2. Computer display during equation-balancing drill. Note the table of number of atome of each type. This is updated as each coefficient is entered

computers, just as they used to have their own slide rules.

But, will we have software for all of those millions of computers? In 1980 there was hardly any software for teaching chemistry on a microcomputer. Now, in August 1983, John Moore and I have figured out that there are probably about 400 individual microcomputer programs for use in teaching chemistry and the curve is going up very rapidly (Figure 3).

The ultimate impact of the computer on instruction depends on how it is used. If the existing course content and instructional techniques are simply programmed into the computer, then it will become just another way to do the same thing. Unfortunately, a reasonable prediction for the future (defined as the the next two years) is

- 11 more titration simulations
- 57 more nomenclature drills
- 113 more multiple-choice quizzes
 - new way to use computers to help students learn

The challenge for teachers who do not want to be replaced by a microcomputer is not just to write more nomenclatural drills or multiple choice quizzes but to develop ways to use this new tool to enhance the content and quality of their courses (1) and to find new ways to help stodents learn chemistry.

Suppose Every General Chemistry Student had a Microcomputer. . .

Allan L. Smith

Drexel University Philadelphia, PA 19104

The supposition in the title of this piece will describe reality for all 1800 entering freshmen at Drexel in the academic year starting in the fall of 1983 and, thus, for the 1200 students enrolled in general chemistry. The decision to require microcomputer ownership was not the Chemistry Department's but was made after study and planning at the university level (12). I chaired the faculty committee that was charged with the responsibility of exploring present needs for and possible uses of a student-owned microcomputer in the undergraduate curriculum, developing a set of specifications for the personal microcomputer, and identifying commercially available microcomputers that met or exceeded these specifications. An abridged version of the Microcomputer Selection Committee's report is being published elsewhere (13). The computer selected is a new Apple product not on the market as of this writing (September, 1983). It operates with a 16-bit microprocessor and has a minimum of 64 Kbyte of user-available RAM. The computer system, including the CPU, video

Chemistry Programs

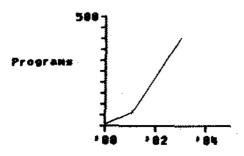


Figure 3, Graph of number of instructional programs versus time. Data from 9, G. Smith and J. W. Moore,

monitor, a disk drive, and software, will be sold to students for \$1,000 which can be financed.

An important part of Drexel's preparation for using microcomputers in the undergraduate curriculum has been a faculty development effort made possible by a \$2.8 million grant from the Pew Foundation, administered by the Glenmede Trust. Some of the projects (workshops, microcomputer seminars, support for courseware and software development, etc.) are described elsewhere (12, 14).

Using Microcomputers in Chemistry

A recent issue of the Computers in Chemical Education Newsletter contained a description of some projected uses of microcomputers in our chemistry curriculum (15). Because microcomputers will be phased in class-by-class over the next few years, most of our thought so far has been on how to use microcomputers in freshman chemistry.

The most immediate use for micros will be of the standard applications packages provided with the system: word-processing, an electronic spreadsheet, and graphics capabilities. For example, we are considering requiring all general chemistry students to write up portions of their lab reports using the word-processor, thus enabling us to ask for revisions of both the scientific content and the prose of the report. Obviously insisting on good writing as well as good science requires careful thought and commitment on the part of both faculty and teaching assistants.

Another application I have been interested in is the use of electronic spreadsheets as a computational tool in general chemistry. Much of the content of today's general chemistry course involves calculations—and it should remain that way. While there are many wonderful chemical ideas whose essence can be stated without using mathematics—molecular structure, for example—many of these ideas can profitably be elaborated with well-chosen computations.

Ideally solving problems, for example those involving aqueous equilibria, requires that students be aware of what chemical species are present and what chemical reactions are taking place. Then the student can "set up the problem," that is, find a logical structure that makes the solution straightforward. Once this is done, a linear sequence of instructions can be given to any calculating device to find the answer. Unfortunately, most people don't think in a sequential manner, and the structure imposed on the problem by the linear medium of a programmable calculator with its single-line display often hides from students the key relationships between quantities and procedures so important in understanding the problem.

Enter the stand-alone personal computer and an electronic spreadsheet program like VisiCalc® (a trademark that is an abbreviation for "visible calculator"). The spreadsheet organizes numeric data in tabular form and allows the use of this data to calculate new rows or columns. If a value in the table is changed, all other values that depend on the first one are immediately recalculated and the table on the screen is updated. Rows and columns can be labelled to show clearly what they contain, it is easy to enter or change numeric values, and once a useful table has been devised it can be saved as a template for later use.

These spreadsheet features are quite attractive for many typical general chemistry calculations. The computational capacities of the typical spreadsheet eliminate the need for ad-hoc approximations along the way to solutions of even complex equilibrium problems. For example, I have developed a spreadsheet template to solve for equilibrium concentrations of the general chemical reaction

$$aA + bB = cC + dD$$

given initial concentrations and the equilibrium constant. A special case of this template solves the weak acid dissociation problem. The immediate updating of the whole sheet after

changing an initial concentration or an extent of reaction permits "what if" exploration on the student's part, which is quite useful when he or she is trying to understand how changing the initial concentration of the conjugate base in a huffer solution might affect the pH, for example.

The first uses of microcomputers in general chemistry were as programmable calculators: the "let's write a BASIC program" syndrome. It would be a major mistake, however, to view today's personal computer as a glorified calculator. A calculator displays a single line of 10–20 characters, while a microcomputer has a screen which holds two-thirds as many lines as a piece of paper. A calculator has a numeric keypad, while a computer has a full keyboard and often other interactive devices (e.g., a "mouse" for moving a cursor on the screen). Microcumputer programming languages are structured, powerful, and often use effectively the full graphics capability of the screen, whereas calculator languages are rather limited. It behooves us to expend some thought, effort, and creativity in developing ways to use these new features effectively.

At Drexel we have been working to capitalize on the opportunities personal computers afford. By this time next year we will also be able to report on the results of our students' creative applications of the new tools they all will have.

Improving Undergraduate Experiments with On-Line Microcomputers

Stanley L. Burden

Taylor University Upland, IN 46989

During the past several years, assisted by an NSF LOCI grant, we have been developing software, hardware, and courseware to use microcomputers on-line in the undergraduate chemistry laboratory. The primary goal of these systems is to increase students' proficiency in the laboratory. This is achieved by permitting the student to perfurm functions that would be inconvenient or too time-consuming to perform manually in normal laboratory time blocks.

We chose systems that span a variety of experimental techniques and principles. We tried to minimize sample preparation time, keep the time per trial short (so if a mistake was made the trial could be easily repeated), and choose experiments in which automation was really needed.

Specific proficiencies that we focus on include experimental design, interpretation of data, and reporting. These are in addition to the more common laboratory technique skills.

Frequently, experimental design and interpretation of data proficiencies are less well-developed in undergraduate laboratory experiments because inordinately long time blocks are needed to collect and analyze sufficient data to give statistically meaningful results. Use of on-line microcomputer systems can improve this situation significantly.

Applications for which on-line systems have been developed or are in the process of being developed include (a) computer-controlled titrations; (b) computer-assisted generation of calibration curves and data logging for use with ion-selective electrodes; (c) computer-controlled multiple standard addition analysis using ion-selective electrodes; (d) computer-assisted logging and analysis of gas chromatographic data for studying the stepwise kinetics of a reaction; (e) computer-assisted logging, plotting, and analysis of spectrophotometric data used in a Lineweaver-Burk analysis of enzyme kinetics data; and (f) logging temperature and pyronometer data for solar collector performance studies. For brevity, we describe only two of these applications in detail. Emphasis will be placed on the use of the systems rather than the details of the systems themselves.

The computer-controlled titrator is used in several courses. In freshman chemistry it is used by the instructor to demon-

strate titration curves from a variety of titration systems. It has also been used effectively with high school students. In analytical chemistry the titrator is used in an experiment that attempts to give students some introductory experience with experimental design. Students are given three commercial antacids and are asked to determine the acid neutralizing capacity of each. Directions for a similar experiment are available commercially and in the literature, but the students have no initial knowledge of this; they must rely on their own ingenuity in designing and carrying out the procedure. They must work alone but are encouraged to use the literature and make appropriate citations in their final report. No specific directions are given but a list of questions leads the student to think about some of the practical details of designing experiments. Answers are handed in prior to laboratory, and the instructor comments on these individually. This assignment is made while the students are studying acid-base titration curves. Generally, the students decide to make titration curves of each of their samples and use these to determine what endpoint is appropriate. If desired, the students can also be asked to identify some of the major species being titrated by identifying their pK's. Since the students normally discover that they must dissolve the samples in acid, they are led to consider using the back-titration technique. This encourages them to think about what species are formed when the acid is added and which are being titrated. While all of this could be done manually, running the titrations and plotting the titration curves using the computer-controlled titrator speeds the process greatly. Students are asked to take sufficient data, do the appropriate statistics, and present the results in an appropriate fashion to support any conclusions they draw. After some discussion of formats, the students are asked to report results as if they were being submitted for publication. From one to three 3-hr laboratory periods are required, depending on how much direction the instructor chooses to give the students.

Principles that are brought to the students' attention in a new or different way as they design and carry out their experiments include: (a) literature searching; (b) sample preparation; (c) back titration; (d) use of titration curves for selection of endpoint, choice of indicator, and/or identification of the species being titrated; (e) use of small-scale preliminary runs to determine general hehavior and appropriate sample size; (f) statistical analysis; and (g) reporting.

The second major on-line system assists students in using ion selective electrodes. The system is also used in our Scientific Instrumentation course after discussing concepts of experimental design such as the "paired-data" and "twogroup" designs. In one of the projects, students are asked to design and carry out a set of experiments to compare analyses by multiple standard additions with those using the direct calibration curve approach. Students must decide which of the two experimental design procedures is most appropriate for this problem and then set up their experiments to use it. For multiple standard additions the same Sargent constantrate buret as is used in the computer-controlled titrator delivers a user-specified number of aliquots of standard solution into an unknown. The computer then calculates the concentration of the unknown after each addition and averages the results. This same system can be used to evaluate various ion-selective electrodes by using it to determine electrode slope or electrode response time under varying conditions. These are experiments that would be extremely time-consuming and tedious to run by manual methods.

A third on-line system assists students in preparing a series of standard solutions. It then automatically logs data from an ion-selective electrode immersed in each standard and makes a real-time plot of millivolts versus log concentration. The student then selects either a linear or cubic fit to the data and a re-scaled, labelled plot is automatically made of the data with the fitted curve. The user then merely immerses the

electrodes in the samples to be analyzed. The potential is automatically logged and the concentration is computed from the fitted equation and printed. In this system, as well as the multiple standard addition system, user attention is minimized during the typical 40–150 s equilibration period of the electrode with each new sample since the system will not log potentials until equilibrium is reached. This frees the user to do other things during this interval. This same system is used in a separate experimental design project in which the students are asked to evaluate the reproducibility of the calibration curve for a given electrode. For this they discover that they should use the "paired-data" design in contrast to the "two-group" design. The "two-group" design is more appropriate for the previously mentioned problem of comparing the multiple standard additions method with the direct calibration curve method.

In general, we have found that when properly used, these on-line systems significantly improve the experiences undergraduate students can have in the chemistry laboratory. Students' laboratory experiences are closer to the situations they will encounter in the real world, and students can be made to think about experimental design, interpretation of data, and preparation of adequate reports much more than they would in a conventional laboratory course.

Let the Medium Fit the Message

Jeff C. Davis, Jr.

University of South Florida Tampa, Fl. 33620

Consciencious teachers have long used a variety of supplemental tools to stimulate their students and to clarify the concepts they are teaching. Table 1 lists some of the media most used in the classroom to supplement the spoken word and chalkboard illustration. Many of these have proven particularly useful for supplementary instruction outside the classroom as well. It should seem obvious that a particular technology is not necessarily best suited for every educational goal or situation. Yet most of us have experienced the euphoria and excitement of discovering a valuable new tool only to slip

Table 1. Instructional Media

Technique	Advantages	Disadvantages
Slides	Clarity, detail	Static, ramote equipment
Overhead Projection	Clerity, detail-	Static
Slide/audio Cassette	as above plus sound	True tutorial difficult
Film	as above plus motion	Sequences fixed, equipment
Film Loop	Motion, short	as above, no sound
Microfiche/Cassette	Size, semi- interactive	Static
Videocassette	Clarity, motion, sound	Sequences fixed
Computer	Interactive, data, computation	Visual limitations
Computer-Video	as above plus visual	Speed of visual access

eventually into discouragement when students have not responded to having that tool thrust upon them at every turn. In Table 1 I have included some comments regarding the advantages and disadvantages of the various media listed.

We are seeing today a wave of excitement generated by the availability of remarkably powerful personal microcomputers. This excitement extends throughout the business and educational world to say nothing of those engaged in technological applications and entertainment. There is no doubt that in the years ahead this excitement will wear thin and many of the rosy promises will not be realized. Nevertheless we can easily recognize educational applications for which the computer is ideal and provides the best tool to accomplish our goals. In other applications, a marriage of the computer with other media will be far more effective for instruction than either the computer or the audio-visual medium alone.

One of the most striking educational applications for which the computer is ideally suited is the generation of objective examinations, scoring examinations and recording scores, analysis of the examination items, and manipulation and analysis of student scores and grades. While it is clear that subjective essay and problem-solving tests must be designed and graded by the instructor, we also should recognize that the time has come when there is no reason for an instructor to put together all the items for an objective exam, grade them, and analyze student and class performance by hand. Tremendous savings in time obtained by having these jobs done by a computer are obvious. Perhaps less obvious is the additional information about exam items and about students that becomes available. Equally valuable are the new means for communication between instructor and student. Table 2 summarizes some of the aspects of managing objective examinations. Two decades of development make it clear that there is tremendous versatility in what kind of computers we can use, whether we develop printed examinations or use the computer terminal directly, whether exams are individualized for each student, whether responses are multiple-choice or not, and what kind of reports are generated for the instructor and for the student. While complete versatility requires imaginative and sophisticated programming skills, more and more tools are becoming available for the non-programming teacher.

In many other applications the computer clearly is a useful tool. However, it often is not as effective by itself as when merged with other audio-visual techniques. We have come to appreciate the fact that tutorial lessons can be programmed with considerable flexibility for individual student differences of understanding. The limitations to accomplishing true tutorial instruction are less in the capability of the computer than in the ability of the author to design a truly effective instructional plan.

With many topics, however, the most serious limitation is that the computer cannot portray real things as well as photographs, film, or videotape. On typical low-cost microcomputers, even the best high resolution display is only an approximate representation in which important aspects and details may be lost. Animation of motion is difficult and often unrealistic.

The most obvious examples of this visual limitation are the portrayal of actual substances, reactions, and the manipula-

Table 2. Objective Exams on Computers

Exam Types	Exam Formats	Exam Construction	Computer Advantages
 Fill-in Response 	Computer-Printed Forms: Response forms batch scored by computer.	 Select items randomly from stored question-answer sets. 	Time and Effort Savings Fast Response for Student
 Multiple-Chaice Response 	 On-Screen Query: Typed-in response scored and stored by computer. 	 Generate random or sequential numbers for data in items. 	 Fiexibility Instructor-Student Feedback Item Analysis

tion of laboratory apparatus. This limitation is easily overcome, however, by utilizing videocassette or videodisk material on the same monitor as an integral part of the computercontrolled tutorial program. This technique permits the display of "live" action when needed in the lesson, including repeat viewing of the appropriate scenes as determined by student responses to questions in the program.

Table 3 suggests some of the kinds of tutorial programs in which interactive computer programming combined with video illustrations can be most effective. From the standpoint of speed of access and volume of video material available, it is clear that videodisk offers the greatest potential. There is no reason, however, why any instructor should besitate to develop video material suitable for his or her needs and to utilize it in tutorial programming via videocassette until the costs for videodisk production become more realistic.

Exploring Chemistry's Mathematical Models with Computer Simulations

John W. Moore

Eastern Michigan University Yosilanti, MI 48197

In many cases what I call "instructional simulations" can provide a new pedagogic approach to teaching chemistry. Such simulations can place students in a role similar to that of a research chemist, requiring the student to formulate significant questions, design appropriate simulated experiments, and interpret intelligently the data obtained from such experiments. At the same time the computer can provide a set of tools for dealing with experimental data (e.g., software for plotting or transforming data) that compresses time, bringing the satisfaction of successfully prohing nature's secrets much more quickly than is usual in real life. Curiosity and disciplined inquiry can be rewarded rapidly, and students are afforded the opportunity to play with our models of how nature works, thereby discovering implications of the models that even experienced chemists may not be aware of.

The student user of an instructional simulation is able to interact with a mathematical model through the medium of a computer. The student chooses parameters and the computer responds by calculating results on the basis of model

Table 3. Computer-Video Instructional Topics

Operation of Analytical Balance
Use of Buret
Use of Pipet
Technique of Filtering
Use of Separatory Funnet
Handling of Solid and Liquid Chemicals
Accident Procedures
Simple Stereochemistry
Principles of Spectrophotometry
Prepartion of Samples for Spectrophotometry
Operation of pH-my Meter
Principles of Crystal Structure

equations. These results are usually displayed graphically or in some other non-numeric format, and they are available almost immediately. On the basis of one round of simulation the student can modify parameter choices and experiment further, playing with the model to see what will happen. Such play can be motivated solely by curiosity, by the challenge of understanding and controlling the model system, or by an assignment from a teacher. Such an assignment can be in essence a research problem, can elicit research-like behavior, and can include the requirement of oral and/or written presentation of results and conclusions.

Instructional simulations make several demands on the

chemist/programmer and on the computer. The situation to be simulated must be well enough understood that model equations are available and provide a reasonable approximation of reality. The situation chosen for simulation should be one where real-life experiments are too dangerous, too slow, too fast, too complex, or too expensive for the student to do. In some cases, such as display of electron densities from quantum calculations, there may not even be a real experiment that could produce the simulated output. The programmer must make student/computer interactions flexible and convenient---the computer should not get in the way, but rather must be an essentially transparent medium that lets the student focus on chemistry and chemical models. Finally, the computer must calculate rapidly enough so that almost instantaneous results can be gotten from realistically complex models. Currently this last is often a stumbling block, but faster, more powerful microprocessors are just down the road, and numeric coprocessors, such as the 8087 now available for IBM Personal Computers, can achieve considerable speed-up in cases where overall response of a simulation is limited by calculation speed.

Several examples will serve to illustrate the diverse ways in which simulations are already applied. Gordon Barrow (16) has described the possibility that physical chemistry could be made a "playground" with an appropriate collection of simulations, and he has written a large number of these. In one, the trajectory of the center of mass of one gas molecule is plotted as it collides with another under the influence of a Lennard-Jones potential. Students can vary relative velocity and impact parameter and then watch the trajectory as it is drawn on a video screen. This sample graphic illustration provides a great deal of insight into what is meant by the size of an atom and how collisions occur.

Another good example of a simulation that contains much information that can be discovered by students was provided to me by Chris Bigum of Melbourne State College in Australia. Bigum has programmed an Apple so that the user can take a single atom and add or remove subatomic particles. Thus a student could tell the computer "add 4 protons" or "subtract

Table 4. Some Sources of Computer-Controlled Videotape/ Videodisk Hardware and Software.

ITAT, Inc.

Allen Productions 500 Lakeside Plaza 2 5225 Witey Post Way Salt Lake City, UT 84116 **BCD** Associate 5809 S.W. 5th Sulte 101 Oklahoma City, OK 73128 CAVRI Interactive Video Systems 26 Trumbull St. New Haven, CT 06511 Colony Productions 1246 Bloumstown Hwy. Tallahassee, FL 32304 Digital Controls 2551 Blairstone Pines Tallahassee, FL 32301 Gentech 1101 N. Fulton Evansville, IN 47710 Informational Technologies, Inc. P.O. Box 72 Punta Gorda, FL 33951 Interactive Video Corp. 7500 San Felipe Suite 100

Houston, TX 77063

20010 Century Blvd. Suite 101 Germantown, MD 20874 New Media Graphics 145 Main St. Cambridge, MA 02142 Pioneer 200 W. Grand Montvale, NJ 07645 Reactive Systems, Inc. 40 N. Vanbrant Englewood, NJ 07631 Regency Systems, Inc. P.O. Box 3590 1610 Interstate Dr Champaign, IL 61820 Texas Instruments P.O. Box 10508 Lubbock, TX 79408 Whitney Educational Services 1777 Borel Place Suite 402 San Meteo, CA 94402

2 electrons" or "add 1 neutron," and the simulated atom would be changed accordingly. If the resulting atom is unstable it will decompose by an appropriate process, such as electron capture, producing a more stable structure. All processes that occur in the simulation are those that are found in a table of nuclides. In simulated time a student has about 10 s to add or remove more subatomic particles; if he does not, decomposition will occur. When a student achieves a stable atomic configuration he is rewarded with some information about the history and discovery of the element formed.

A third example is a program under development by Robert Rittenhouse of Walla Walla College for the SERAPHIM/ ChemCom Interface Project. This program is based on Rutherford's equation for scattering of α particles by metal foils. A student is supplied with several experimental tools: an α-particle scattering apparatus; several metal targets; a detector and pulse-height analyzer; a digital microscope for viewing things on the atomic level; a data-disk notebook; a data analyzer that can perform mathematical operations such as squaring all X values in a set of X,Y pairs; and a data plotter. With these tools at his disposal the student can be assigned simple or complex research projects. For example: "Show that the number of α particles scattered at 30° is proportional to the number of particles that strike that target;" or "Find the relationship between angle of scattering and number of α particles that strike the detector at that angle." In the first case the student is told what to look for and the relationship is direct proportionality, so a simple plot will do. The second case is much tougher and should only be assigned to a good student. By tailoring assignments to students' abilities one can use the same simulation at several levels.

The last example involves an environmental simulation, where the real experiment would involve potential harm to people and the rest of the biota. It is being developed for the SERAPHIM/ChemCom Interface Project by John K. Estell, a computer science student at the University of Toledo. The program casts the student into the role of an operator of a sewage treatment plant who must decide what percentages of sewage flow to treat by primary, secondary, and tertiary methods. The student must stay within a budget while maintaining water quality. Taxes and fines are levied for polluting, and the incompetent student's stimulation will end with his being fired. Students compete to see who can achieve the greatest budget surplus.

The simulations described here all make use of the computer's ability to store, process, and recall data, to calculate quickly and accurately, and to display results in non-numeric or graphic forms. They allow us to invert the normal process of learning about models. Students can vary parameters, observe the effects almost immediately, and become familiar with the outcomes of realistically complex models. Students can be placed in the positions of real-life chemists and can learn the insights and modes of thought those chemists use in their work. The challenge to us as teachers is to devise a broad range of such interactive, instructional simulations that combine flexibility and convenience of use with general and realistic models. Such programs will not replace TA's, professors, or labs, but they will challenge all of us to replace time-honored but less-than-optimal pedagogic approaches to many aspects of chemistry.

Computers in the Freshman Course; Where Do They Perform Best?

J. J. Lagowski

University of Texas at Austin Austin, TX 78712

Over the past 20 years the experience of a few groups in using academic computing in mainstream chemical education has indicated the modes where computer-based methods can

be successful; there is ample evidence, both objective and subjective, to support these suggestions.

The modular nature of computer programs leads to pedagogical and administrative benefits. A program that has been designed carefully to achieve a specific objective, e.g., to simulate a chemical phenomenon, probably can be used to advantage at numerous places in the curriculum; indeed, it may be used several times to help achieve a different overall impression of the subject. Programs may be made available to different students in different sequences, depending upon differing student background characteristics and career goals. The existence of modular programs leads to an educational flexibility that encourages self-paced and personalized instruction. Finally, such computer methods are easily adaptable to detailed record-keeping for a variety of purposes, including student evaluation or counseling, program improvement, and pacing the course to the student's needs.

All too frequently, teachers become overly involved in logistical and administrative functions to the detriment of teaching; that is, they have the burden of assigning, grading, and giving feedback on homework and tests, helping students with their assignments, conducting tutorial/remedial drill group interactions, and organizing individual laboratory work. Successful computer programs have been written that engage students in a tutorial interaction which can be used for drill, review, or remedial purposes; which simulate portions of laboratory experiences; and which produce interactive examinations or quizzes on demand. It is apparent that such programs mimic many of the tasks in which teachers normally engage. To a large extent the computer can perform these tasks (on an individual basis) as well as, or better than, the instructor, since programs are infinitely patient. Indeed, we can imagine a learning system incorporating such programs as extending the capabilities of the teacher in space and time. In such a system, the teacher retains his/her usual teaching role but trades the roles of bookkeeper, grader, and all-around paper shuffler for the roles of counselor, guide, and mediator.

Tutorial/Drill Programs

In chemistry, as in all subjects, there are many pedagogical situations that require a patient tutor to guide the student through a logical sequence of steps in a (relatively) closed subject with respect to information content. Usually the point is driven home by the use of numerous examples that are variations on a theme. Classically, such situations have been exploited by recitation or discussion periods and the use of homework problems. It is possible to write highly sophisticated programs for interactive computer systems that capture the detailed strategy that an individual teacher would use in a tutorial session. In essence, that teacher (in the form of the program) is unbounded in space and time since the program can be run at any time of day and can be transmitted to any geographic point the communications system permits. The alleviation of the logistic constraints imposed by the availability of rooms and/or instructors is obvious.

Laboratory Simulation Programs

Laboratory courses are usually designed to provide experience in experimental techniques as well as to develop a facility for manipulating raw experimental data. Computer methods can provide experience in the latter phase of laboratory work but do little with respect to the former unless the computer is treated as a laboratory tool interfaced between the student and the experiment. Basically, simulation programs can be designed to have a student engage in all the decision-making he or she normally would do in a real experiment, i.e., collect data and draw conclusions based on the data. It is possible to introduce experimental errors in the results of computer-simulated experiments which reflect the accuracy expected from the equipment normally used in the laboratory

as well as gross random errors. Thus, the students' experience in manipulating experimental results can be extended by simulating experiments that (a) might be conceptually simple but which require apparatus too complex for them to manipulate at a given educational level (e.g. atomic spectroscopy, X-ray diffraction at the general chemistry level), (b) consume a disproportionate amount of time if performed in their entirety, (c) are potentially dangerous, and/or (d) involve expensive equipment or chemicals which cannot be supplied for large numbers of students on an individual basis. Simulated experiments can be used in various ways, e.g., as extensions of laboratory work as well as supplements to conventional lecture material.

It should be pointed out that the terminals on which students might perform simulated experiments need not be located in a laboratory; they may be placed in study rooms, library carrels, or even in dormitories. Further, simulated experiments need not be performed at the conventional laboratory periods, nor do the programs need to be available in an interactive mode. Thus, a part of a student's laboratory experience can be provided in a more flexible manner than is now possible under the logistic constraints imposed by conventional laboratory work. The savings in costs for equipment and chemicals using computer-based methods is obvious.

Homework Problems

Homework problems have been used traditionally to provide the student with practice in problem-solving, but there are several difficulties with such strategy. First, grading and record-keeping become important considerations in classes with large numbers of students. Second, feedback on problems (grading) is generally slow and individual error analysis virtually non-existent when a large number of problem sets are hand-graded. Many of the programs written for tutorial/drill mode or laboratory simulation contain drivers or subroutines well suited for generating problems. Separate homeworkgenerating programs have also been developed as well as programs to grade the homework, for a program that can generate problems can contain information on the details associated with common student errors. Thus, it is possible to give not only full credit for a problem, but also partial credit if intermediate steps are correct but the final answer is wrong. In addition, such grading programs usually incorporate subroutines that automatically yield appropriate statistical analysis of the student's performance on individual prob-

Examinations

An important element of computer-based techniques is the development of programs and data bases that generate examinations. The ability to generate a large number of examinations that are statistically equivalent gives the instructor a very powerful teaching device. With such programs available, it is possible to create self-paced courses for relatively large numbers of students; such flexible courses generally depend upon the availability of a "readiness test" on a student-demand basis. Input of the marked examinations into the grading program can be either in a batch mode using inexpensive mark-sense readers or interactively. The latter operation permits immediate feedback to the student. It is apparent that for larger numbers of students at various points in a self-paced course the logistics of creating, administering, grading, and maintaining security for a large number of different examinations becomes virtually unmanageable using conventional methods. Computer-based methods not only expedite all aspects of examination-taking, but they can also incorporate relatively sophisticated record-keeping and statistical routines with little additional difficulty. Most of the successful applications of computer-based methods have occurred at the learning-teaching interface. Programs either help students learn and/or expand the functions of teachers.

Successful methods are those in which computing is *sup*plemental to the normal teaching functions rather than those in which attempts are made to try to replace them.

Of Babbages and Strings

Derek A. Davenport

Purdue University West Lafayette, IN 47907

To talk of many things, Of cherubims and SERAPHIMS, Of Babbages and Strings. And if the Apple's worm is bit, Will we be underlings? Indeed will we be there at all, When to the Dean's delight. Professors are superfluous And students spend the night Transfixed before their tiny screens, Preprogrammed to be hright? The laboratory a cenotaph, The T.A.'s on relief, No need for books or chemicals, Savings beyond belief. O brave new world of Academe, All Indians, no chief! Yet students' minds take random walks, Spelling tends to frolic, And chemistry most often is More concrete than symbolic; So may they both small quarter give, To simple two-bit logic! But if they mind their p's and q's, And keep their whiskers clean, Computers surely have a place Upon the college scene, Their gentle flips and muffled flops, Echoing o'er the green. For unlike aging Faculty, Whose lids are apt to flip, Their patience is quite awesome, Their fluppy discs don't slip, So let us hear a guarded cheer, Hip, chip, hooray, hip, chip!

The time has come our Chairman says

To answer the first three questions in Chairman Moore's little red catechism: "no, no, and again, no. What I tell you three times is true."

Should Computers Replace Professors?

Only in selected cases, but the AAUP won't allow even those few replacements to occur. If only the pious hope "anyone who can be replaced by a computer, should be" were true! As for the competent majority, the teaching professoriate will happily remain indispensable in the computer age. Man is, after all, a tool-making animal and the computer is merely the latest tool, though just possibly one of an entirely new kind. Around 1450 Johann Gutenberg was advanced 800 guilders for the development of new "tools" and within a few years those tools had produced his unsurpassed Latin Bible. In the case of computers in chemical education, even Stan Smith has not yet got past "in the beginni . . . " though to listen to some of the apocalyptic advertising one might think we had already programmed the Book of Revelations. My prejudice is best stated in the language of Paseal. "L'homme n'est qu'un roseau, le plus faible de la nature; mais c'est un roseau pensant" which for those still struggling with enbasic English may be translated as "Man is only a reed, the weakest thing in nature; but he is a thinking reed." It might however be well to remember that L. S. B. Leakey has claimed that in the hands of the great apes a reed is one of the most useful of tools.

Should Computers Replace TA's?

In recitations/tutorials perhaps but my research-minded colleagues are not about to let it happen. After all, the first two or three years of chemistry graduate school may be defined as a work-study program financed not by the federal government but by the involuntary subsidy of the parents of undergraduates. It is hard to envision any chemistry department head in the near future responding to a newly redundant graduate student in the terms a French king used to a lowly petitioner: "Il faut que je vive." "Je n'en vois pas la nec-éssité." If he made such a response, he would not remain department head for very long.

Should Computers Replace Labs?

Certainly, if fact abdicates in favor of fiction, which fortunately nature is unlikely to allow to happen. There are times, however, when my faith wavers. Only today, I saw the latest PhD prelim examination written by illustrious physical chemistry colleagues. Two things struck me: physical chemists still use ergs and dynes and in none of the twelve questions is any specific chemical species invoked nor any set of chemical data cited. One is reminded of Donald Hall's two-line poem

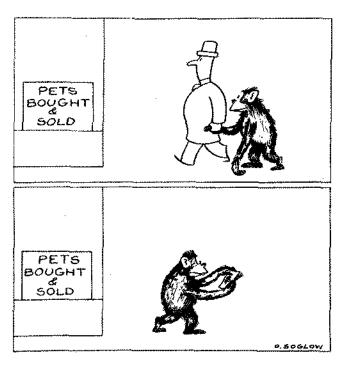


Figure 4. Drawing by O. Sogiow; © 1947, 1975, The New Yorker Magazine, Inc.

Poetical Philander only thought to love He went to bed with what he thought the girls were symbols of.

Jean Martin Charcot had some rather odd ideas but he was on the right track when he claimed, again in the language of Pascal: "La théorie c'est bon, mais ça n'empêche pas d'exister." Theory is fine but it doesn't prevent things from happening. As a preparation for, supplement to, and extension of the teaching laboratory, computers clearly have a great future. But with the possible exception of the chemistry (or at least the physics) of phosphors, beginning science cannot be done on a TV monitor. Words, symbols, mathematical formulae, and graphics may be manipulated on the screen with marvelous dexterity, but it is words, symbols, mathematical formulae, and graphics that are being manipulated—not chemical substances.

As designated devil's advocate for Project SERAPHIM my final comment on this latest wonder of educational technology is shown in Figure 6.

The immemorial problems of teaching endure but at least we have been vouchsafed a marvelous new tool with which to chip away at the darkness.

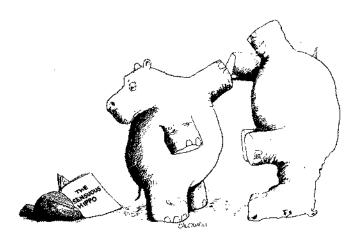


Figure 5. Cartoon by John Caldwell from "Animals, Animals, Animals," (Editors: George Booth, Gahan Wilson, and Ron Wollin) and used with the kind permission of Harper & Row Publishers, Inc., New York, Copyright © 1979 by The Cartoonists Guild, Inc.

Summary and Conclusions

John W. Moore

Eastern Michigan University Ypsitanti, Mi 48197

Summarizing and drawing conclusions about the remarks of as diverse a group of experts as were involved in this symposium is a tall order. However, there were a number of parallels in the talks presented, and I think the symposium at least began to delineate where and how computers can contribute to chemical education.

There was agreement that the computer provides new ways of approaching problems, for faculty, for students, and for chemists in general. Examples are Stan Smith's equation-balancing exercise in which the screen is constantly updated to show how many atoms are present and Allan Smith's use



away, haw many have you got left?"

Figure 8. Cartoon from "Certoons from Punch," (Editor: William Hewiston) and used with the kind permission of St. Martin's Press, Inc., New York. Copyright © 1979 by Punch Publications Limited.

cases a teacher has examined the problem of teaching a particular concept or procedure and devised a method of showing the student a different aspect than would be shown in a book, or in a non-computerized lecture. Simulations such as those I described can be used to induce students to approach mathematical models in a different way, and automated laboratories like Stan Burden's expose students to experimental design and data analysis aspects of laboratory work that would be difficult to access any other way. In designing computerbased materials we should be constantly on the alert for new approaches to the problems of teaching or learning that the computer allows us to try.

Nearly every speaker alluded to the computer as a tool. At the end of Stan Smith's talk we heard, "... we have added one more thing to the list of tools that we have for teaching." Derek Davenport closed with, "The immemorial problems of teaching endure, but at least we have been vouchsafed a marvelous new tool with which to chip away at the darkness. In between we heard from Jeff Davis about how that tool might be linked with others we are more familiar with, and from Joe Lagowski and Jeff about many of the logistic and administrative burdens from which that tool might release us. Stan Burden uses the computer as a timesaving tool for students, and puts the students' time to use on thinking instead of collecting data. Allan Smith alluded to several uses of this new tool that parallel those popular in the business world. We would do well to examine the many applications that have made microcomputers the success story they are in business. with an eye to how these can be adapted to the specific problems of chemistry teachers.

Several speakers identified the computer as a new medium of instruction and attempted to describe how the characteristics of the computer make it more or less useful for different kinds of instructional tasks. Patience in drill and practice situations, rapid and error-free calculations and handling of textual or numeric data, ability to interact with students and take account of previous input from a student, graphics and animation, and ability to keep records and analyze large quantities of data were all mentioned as positive characteristics we ought to take advantage of. The main negative characteristic can be generalized as: the computer is not chemistry, and to learn chemistry one needs to do chemistry. According to Stan Smith, "You can do simulated laboratory experiments on the computer, but that isn't real laboratory work: you can't do real laboratory work on a computer." And according to Derek Davenport, "But with the possible exception of the chemistry . . . of phosphors, beginning science

cannot be done on a TV monitor." Of course it is hard to do chemistry on a book, too, unless you burn it or take it to lab, and the same is true of most other media.

Computers seem to be especially good at teaching ideas and concepts and at manipulating symbols; they are less well suited to situations where real-life experience is necessary, except in the case where the experience is to be with handling a computer/instrument combination or with handling and manipulating symbols and ideas.

Finally let's summarize the answers that were given to the four questions in the title of the symposium. Not everyone addressed the questions explicitly, but there was consensus. Joe Lagowski said, "Yes, Yes, Yes, NO!" and Derek Davenport said, "No, No, No," but then he qualified the first two no's as being for the wrong reasons in some cases. Actually these two responses were probably in much better agreement than a computer analysis of the symbols on the page would reveal. The consensus was stated by Stan Smith, "A computer is a tool: good teachers cannot be replaced by a computer." And so there was agreement that the answer to "Should computers replace. . .?" was a resounding no. But there was also agreement that we are nowhere near using that tool to its capacity. Perhaps the reason lies in a statement that Stan Smith made when he visited Allan Smith and Drexel University.

'The world is overpopulated with programmers who can get the computer to do anything, but who don't know what they want it to do. The greatest limitation of the use of computers in education is the creativity of the people trying to use them."

Literature Cited

- (1) Lagowski, J. J., J. CHEM. EDUC., 60, 529 (1988).
- Smith, S. G., J. CHEM. EDUC., 47, 608 (1970).
 Lower, S., Gerhold, G., Smith, S. G., Johnson, K. Jeffrey, and Moore, J. W., J. CHEM. EDUC., 56, 219 (1979).
- (4) Smith, S. G., and Chabay, R., J. CHEM. EDUC., 54, 688 (1977).
 (5) Chabay, R., and Smith, S. G., J. CHEM. EDUC., 54, 745 (1977).

- (6) Cavin, C. S., Cavin, E. D., and Lagowski, J. J., J. CHEM. EDUC., 55, 602 (1978).
 (7) Wiegers, K. E., and Smith, S. G., J. CHEM. EDUC., 57, 454 (1980).
 (8) Smith, S. G., Ghesquiere, J. R., and Avner, R. A., J. CHEM. EDUC., 51, 243 (1974).
- (9) Moore, C., Smith, S. G., and Avner, R. A., J. CHEM. EDUC., 57, 196 (1980).
- (10) Francis, L. D., J. CHEM. EDUC., 50, 556 (1973).
 (11) Moore, J. W., and Moore, E. A., J. CHEM. EDUC., 60, 563 (1983).
- (12) Smith, A. L., "Suppose Every Freshman Owned a Microcomputer," Proceedings of the IEEE CompCom Fall '83 Conference, September 28, 1983 (to be published).
 "On Selecting a Microcomputer for 1800 Freshmen at Drexel," Drexel Microcomputer
- Selection Committee Report, submitted for publication in Collegiate Microcomputer.
- (14) Smith, A. L., "The Personal Computer Project at Drexel; Selection of the System and Development of the Faculty," SIAM News, July, 1963.

 (15) Smith, A. L., Computers in Chemical Education Newsletter, September, 1983.
- (16) Barrow, G. M., J. CHEM. EDUC., 57, 697 (1980).

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 has 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.



chem i supplement

edited by: MICHAEL R. SLABAUGH HELEN J. JAMES Weber State College Ogden, Utah 84408

Geochemical Exploration of the Moon

isidore Adler

University of Maryland, College Park, MD 20742

The most important keys to understanding the formation of the solar system and its subsequent evolution lie in the chemical composition of the planetary surfaces and interiors, the meteorites, the comets, and the asteroids. An exhaustive study of the geochemical exploration of the planets would require a very lengthy text. This paper is based on examples from my own experience in the Apollo program. These examples represent only a small part of the findings of the space program.

The abundance of certain elements relative to cosmic abundances, their mode of condensation, and condensation temperatures are important clues. For example, the evolutionary processes that have occurred in our solar system can be studied by examining the abundances of potassium and thallium relative to uranium. These elements are indicators of the abundance of volatile elements relative to refractory elements. Such studies also provide important information about the pre- and post-accretionary stages in the evolution of the solar system.

Since we have yet to penetrate even the Earth's mantle, it is obvious that information about planetary interiors can be obtained only by inference. On the other hand, for surface investigations one can employ classical methods such as geological sampling, mapping, and laboratory analysis. Space-age technology using remote analytical techniques, mainly spectroscopic and photographic, are also used. An example of the latter involved the use of photogeologic methods in the Landsat program. We are presently constrained to the use of remote techniques when dealing with celestial bodies other than our moon. Study of our own moon is unique in that we have heen able, hecause of the samples collected, to employ a largely classical approach under decidedly new circumstances. Remote methods have also been used.

Questions about the Moon

Prior to space travel, our knowledge of the moon rested on earth-based telescopic studies. With the advent of space exploration, numerous programs carried out by the United States and the Soviet Union have provided a wealth of new information. Among the various programs were the Ranger fly bys and impacters, Surveyor landers, Lunas, Orbiters, and the Apollo and Luankhod flights. The first truly remarkable in-situ chemical analysis of the lunar surface resulted from the Surveyor missions (1). Surveyor 5 landed at Mare Tran-

This feature presents relevant applications of chemistry to everyday life. The information presented might be used directly in class, posted on bulletin boards, or otherwise used to stimulate student involvement in activities related to chemistry. Contributions should be sent to the feature

quilitatis, Surveyor 6 at Sinus Medii, and Surveyor 7 on the rim of the very large crater Tycho. The instrument deployed to the lunar surface used the principle of alpha-particle back-scattering developed decades earlier by Rutherford and others (2). This provided chemical information about the landing sites.

The first reasonably successful attempt at chemical analysis from orbit was during the flight of Luna 10 (3) which orbited the moon and carried a gamma-ray spectrometer. In 1969 the Apollo 11 mission landed men on the moon for the first time; the site, Mare Tranquilitatis. This was the first instance in human history that documented samples from another body in the solar system has been obtained. By the end of the Apollo 17 mission, astronauts had returned about 400 kg of soil and rocks. The study of these samples employed a great variety of the most sophisticated analytical methods. The samples from the large lunar basins were essentially basalts, while those from the highlands were essentially feldspathic anorthosites. The highlands were found to be the most ancient of the lunar features, somewhat over four billion years old. The basalts were found to range between three and four billion years old. They apparently came to fill the large basins after their formation, which likely occurred as a result of the impact of enormous meteorites and planetesimals some four billion years ago.

The data mentioned above was obtained from analysis of the samples collected at a few chosen sites on the moon. Our view of the whole moon is an extrapolation from these facts. There are many reasons, however, for seeking chemical information from other sites (many of which will be beyond the possibility of manned landings for years to come). Global compositional maps could be of great value in understanding the moon. Thus a series of orbital experiments was proposed which began with the Apollo 15 mission. These experiments have helped considerably in answering a number of questions relating to the early history and origin of the moon.

Orbital Remote Sensing

How does one plan experiments to give compositional information about a celestial body which can be conducted from an orbiting satellite? There are only a limited number of observational phenomena from which one can infer unique elemental identifications and concentrations. A survey of the electromagnetic and particulate spectrum yields only a few possibilities. Certainly one cannot expect to obtain results which are precise by laboratory standards. Nevertheless, such techniques as gamma-ray or X-ray spectroscopy can provide much useful information.

A summary of the radiation environment at the lunar surface is shown in Figure 1. Based on this view of the lunar ambient radiation, a series of orbital experiments were designed to supply chemical information. As we can see, both natural

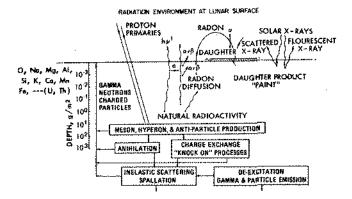


Figure 1. The radiation environment at the lunar surface. Particularly important is the natural radioactivity, the solar X-rays, the gamma rays produced by the cosmic rays and perhaps the alpha particle emission.

and induced sources of radiation are present. Among the principle naturally occurring radioactive constituents are the long-lived nuclides ⁴⁰K, ²³²Th, and ²³⁸U and their decay products. These sources emit alpha, beta, and gamma radiation of various energies. Importantly, the gamma radiation is characteristic and can be used for identification of the elements that emit them. Special processes such as radon and thoron diffusion may also occur (4). Bombardment of the lunar surface by cosmic rays and energetic protons will also produce a variety of short-lived nuclides and, as a consequence, induced radioactivity. Cosmic ray interactions with the lunar surface will also produce a prompt emission of neutrons and protons.

Even under "quiet" conditions, the sun is a copious emitter of soft X-rays. Because of the filtering nature of our atmosphere, it has been possible to determine the spectral distribution of these X-rays only by flights above the atmosphere. These solar X-rays are absorbed by the lunar surface and produce secondary (fluorescent) X-rays which again are characteristic of some of the elements making up the lunar surface. One can then predict the yield of the secondary X-rays, which depends on the intensity and spectral character of the solar X-ray flux and the abundance of the elements in the lunar surface. Finally, the radon and thoron which are diffusing through the lunar surface would be expected to produce alpha particles having energies characteristic of the various decay processes.

Lunar X-Ray Experiment

We see that the "quiet sun" is energetically capable of producing measureable amounts of characteristic X-rays from all the abundant elements with atomic numbers of approximately 14 (Si) or smaller (Fig. 2). During brief periods of heightened solar activity, one can expect characteristic X-rays from higher atomic number elements.

As for the design of the X-ray experiment, calculations had shown that the moon's X-ray brightness was low, and it was therefore necessary to design a highly efficient system for detecting the X-rays from the lunar surface. Not only was the orbiting X-ray spectrometer required to have a high efficiency, but it also had to provide spectral information that could be reduced to chemical quantities. Therefore, an assembly was built which consisted of three large proportional counters with thin windows of beryllium. One detector was operated "bare" and the other two had selected X-ray filters consisting of a magnesium foil and an aluminum foil, respectively. Further, the X-ray output from the detectors was energy-analyzed by eight energy discriminator channels which covered in equal intervals 0.5 to 2.75 keV X-rays. In this manner, three differential X-ray spectra were obtained from the lunar surface which, by simple mathematics, could be reduced to intensity

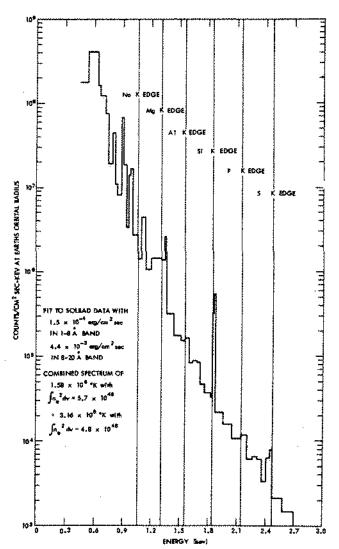


Figure 2. The "quiet" sun X-ray output.

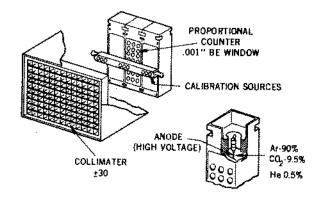


Figure 3. An exploded view of the X-ray spectrometer.

ratios of Al/Si, Mg/Si, and Mg/Al. The detectors viewed the moon through mechanical collimators so that the field of view was 60°. This meant that at orbital altitudes of 100 km, resolution on the lunar surface permitted analysis of features about 10 km across. A view of the X-ray spectrometer is shown in Figure 3.

Gamma-Ray Experiment

From the very beginning of the lunar program it was assumed that K, Th, and U would be key elements in the un-

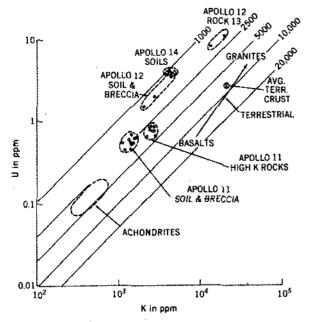


Figure 4. Potassium versus uranium in various materials.

derstanding of lunar evolution. In terrestrial processes the radioactive decay of these elements is considered to be a major source of the energy leading to volcanism and magmatic differentiation. Further, the abundance of these elements becomes an indicator of the extent of chemical differentiation since K, Th, and U tend to concentrate in the late stage crystalline rocks such as granites. By the Apollo 15 flight, excellent determinations of K. Th. and U had been made in various returned lunar samples. As an example, K versus U values have been plotted for various lunar materials (Fig. 4). As a comparison, a line is drawn for terrestrial materials ranging from basalts to granites. The relative position of the achondritic stony meteorites is also shown. The diagonals on the graph represent K/U ratios. Note that the lunar materials have lower K/U ratios than terrestrial magmatic rocks. This has been traced to high U values and low K values. A similar situation exists with regard to K/Th ratios. Furthermore, it was found that there was a distinct variation from one collection site to another. Because K, Th, and U are such important indicators of chemical processes, the attempt to map the global distribution of these elements around the moon was considered of very great importance.

The gamma-ray assembly flown on Apolio 15 and 16 was composed of three major subassemblies: the scintillation detector (a thallium-activated sodium iodide crystal), the electronics, and the thermal shield. In flight the gamma-ray spectrometer was deployed at the end of a 7.5 m boom in order to remove it as far as possible from the radioactivity, both natural and cosmic ray induced, in the spacecraft. While the X-ray experiment described was useful only for the areas illuminated by the sun, the gamma-ray experiment supplied data for the entire flight path.

Alpha-Particle Experiment

There are a number of possible sources for alpha-particles from the lunar surface. The principal ones are alpha radio-active decay of radon and thoron (and their daughter products) which, if circumstances are suitable, would have diffused out of the first few meters of lunar soil. As on the Earth, this is a reflection of subsurface activity. If one assumes thermal velocities for the escaping radon and thoron, then nearly all the molecules would be trapped in the moon's gravitational field. Radon with its 3.8-day half-life should travel a considerable distance before undergoing radioactive transformation. Thoron on the other hand, with a 55-sec half-life, would be

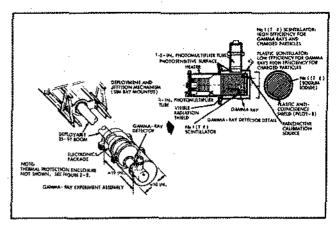


Figure 5. The alpha-particle experiment.

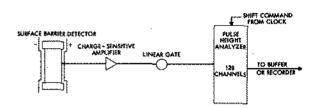


Figure 6. The Science Instrument Module (SIM).

expected to decay near its source. The necessary equipment for alpha particle measurements is shown in Figure 5. The detectors are solid-state surface barrier types. The flight instrument which was contained in the same housing as the X-ray experiment consisted of a series of detectors and alpha-processing electronics.

The Apollo Science Instrument Module (SIM)

Figure 6 shows the Apollo SIM bay. The SIM bay was part of the Apollo Command-Service Module (CSM). Beginning with the Apollo 15 flight, the CSM was used for the first time to carry an ambitious array of instruments for orbital surveys of a variety of lunar characteristics of which surface chemistry was a prominent part. The instrumental complement consisted of an X-ray fluorescence spectrometer, an alpha-particle spectrometer, a mass spectrometer, a panoramic camera, a laser altimeter, and a subsatellite. (The latter was launched into an orbit of its own for the purpose of making geophysical measurements.) The X-ray, gamma-ray, and alpha-particle spectrometers were used for obtaining chemical information about the moon's surface. The mass spectrometer was employed in a study of the moon's tenuous atmosphere at orbital altitudes. It is noteworthy that the X-ray and gamma-ray instruments were also used to obtain astronomical data during the trans-Earth coast.

Results

The orbital experiments described thus far proved to be successful and informative. Before detailing the X-ray results, it is important to describe some of the constraints that entered into the interpretation of the data. Since the sun is not a stable X-ray source, it was necessary to devise methods of correcting for solar flux variation. Instrumentally, a small proportional counter was pointed towards the sun while the large detectors were pointed towards the lunar surface. In this manner, the sun's X-ray output was monitored during surface measurements. Other sources of variation included the sample matrix effects, the solar illumination angle, and surface roughness. These factors were minimized by the use of intensity ratios (5). In view of the near constancy of the silicon abundance, the

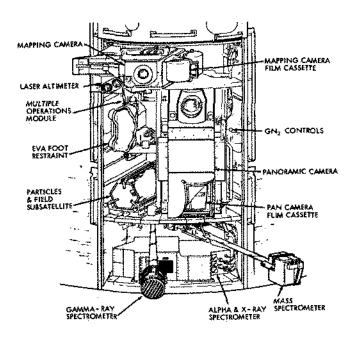


Figure 7. Al/St intensity ratio along the Apollo 35 trajectory.

other elements, such as Mg and Al, were referenced to the silicon. There were other boundary conditions such as the depth of the surface samples (in the X-ray case about $10~\mu m$), the resolution of surface sampling was about 10~km and, of course, the observations were only from the sunlit portions of the moon.

The compositional profile in terms of Al/Si along the Apollo 15 trajectory is shown in Figure 7. The ratios for various analyzed lunar materials are shown on the right-hand axis. A number of conclusions have been drawn based on such results: the Al/Si ratios are greater in the highlands (characteristic of feldspathic materials) and considerably lower in the mare areas (typical of basalts); there is a general tendency for Al/Si values to increase from the western maria to the eastern limb highlands; there was good agreement between the Al₂O₃ values determined by classical techniques obtained from analysis of lunar samples gathered during the Apollo 17 mission and from that inferred from the X-ray measurements. This latter fact showed us that the X-ray measurements were indeed a reliable guide to at least this aspect of the lunar chemistry.

The X-ray results clearly demonstrated that the moon's crust is chemically differentiated. On a global scale, one could define the extent of differentiation and clearly the mare basalts from the highland anorthosites. The X-ray results have also been correlated with optical albedos (the way in which the lunar surface reflects light). It was clearly demonstrated that the reflectivity was a good clue to the chemical composition. High reflectivity was positively correlated to materials of high Al/Si.

The gamma-ray experiment performed in two areas provided both a survey of natural radioactivity as well as considerable information about the chemistry of the surface. Data was gathered from a belt around the moon. In the X-ray experiment, samples were taken at a depth of about 10 μ m. The gamma-ray experiment probed to depths of the order of tenths

of centimeters. The data gathered by such experiments on the Apollo 15 and 16 missions yielded information about the relative intensities of the natural radiation of the moon. For example, the regions within and bounding the western maria (Oceanus Procellarum) show higher levels of radioactivity than any others on the lunar surface. There is, in fact, a striking contrast between this region and the rest of the moon, particularly the eastern maria. Further, there is a detailed structure in the distribution or radioactivity within the high radioactive regions. The highlands showed a relative radioactivity except on the borders of the western maria where lateral mixing is a good possibility. One interesting result is the observed ratio of K/Th. (Potassium is representative of volatile elements while the thorium is representative of the refractory ones.) These measurements have borne out the fact that the moon is depleted of volatile elements relative to the refractory ones, an important fact which must be considered in any theory of the moon's formation and evolution.

Alpha-particle data taken during the Apollo 15 and 16 flights showed that the observed alpha activity was quite small, on the order of 10⁻³ counts/cm²-sec. The nature of the experiment was to seek three types of signals: alpha-particles having energies consistent with the decay of 222Rn and its daughter products, alpha-particles from 220Rn and the daughter products, and finally, alpha-particles from 210Po. The first two can be associated only with current activity (because of their short half-lives) and the last with events having occurred days to years ago. (210Po comes from the decay of ²¹⁰Pb with a half-life of 21 years.) Two features were observed in the Apollo 15 data. There appeared to be a general but small increase in count rate over Oceanus Proceilarum and Mare Imbrium. The trend appears to parallel the U and Th observed by the gamma-ray experiment. One of the most dramatic features was the increase in 210Po at the edge of some of the maria. An additional correlation was the finding of heightened activity in the Aristarchus region where transient lunar phenomena had been observed. This last observation is particularly interesting because these transient glows which have been observed telescopically in the past have been attributed by some investigators to solar excitation of escaping gases.

Summary

The results obtained from the remote analysis of the moon by spectroscopic techniques have contributed substantially to a unified view of the chemistry of the lunar surface. Further important principles have been established for future planetary studies. The lunar investigations give us reason to believe that such studies can be done on other surfaces many millions of miles from Earth.

Literature Cited

- Turkevich, A. L., Anderson, W. A., Economou, T. E., Franzgrote, E. J., Griffin, H. E., Grotch, S. L., Patterson, J. H., and Sowinski, K. P., The alpha-Scattering Chemical Analysis Experiment on the Surveyor Lunar Missions," NASA Tech. Report 32-1265, 1968.
- Rutherford, E., Chadwick, J., and Ellie C. D., "Radiation From Radioactive Substances," Cambridge University Press, 1949.
- (3) Vinogradov, A. P., Surkov, I. A., Chernov, G. M., and Kirnozov, F. F., "Measurements of Gamma Radiation of the Moon's Surface by the Cosmic Station Luna 10," Geochemistry No. 6, Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, USSR, 1966.
- Kraner, H. W., Schroeder, G. L., Davidson, G., and Carpenter, J. W., "Radioactivity of the Lunar Surface," Science, 152, 1235 (1966).
 Adier, I., Trombka, J., Gerard, J., Schmadebeck, R., Lowman, P., Blodgett, H., Yin, L.,
- (5) Adler, I., Trombka, J., Gerard, J., Schmadebeck, R., Lowman, P., Blodgett, H., Yin, L., Eller, E., Lamothe, R., Gorenstein, P., Bjorkholm, P., Harris, B., and Gursky, H., X-ray Fluorescence Experiment," Apollo 15 Preliminary Science Report, NASA Sp-289, 1972.

Goals

edited by:
DAVID A. PHILLIPS
Wabash College
Crawfordsville, IN 47933
PRUDENCE PHILLIPS
Crawfordsville High School
Crawfordsville, IN 47933

Introduction to "Goals"

In planning a chemistry course, some of the most important decisions a teacher must make involve the selection of material to be covered and the time to be devoted to each topic. For each column in this new series, a high school and a college teacher have been invited to discuss why they feel a particular topic is important and how it contributes to the students' understanding of chemistry.

About the Editors . . .

David A. Phillips received his BS in chemistry from the University of Redlands and his PhD from the University of Washington. After directing the General Chemistry program at Middle East Technical University in Ankara, Turkey for two years, he came to Wabash College, where his primary teaching interests are in general and inorganic chemistry.

Prudence K. Phillips received her AB in chemistry from Brown University and her MS from the University of Washington. She has been teaching high school chemistry for 11 years and is presently at Crawfordsville High School.

Both the Phillipses have participated in a variety of Division of Chemical Education and ACS activities.



Why Teach Kinetics to High School Students?

High school students often avoid chemistry because it demands mathematical reasoning. For that reason, high school teachers generally deemphasize math in first-year courses except where it is necessary for understanding. Nevertheless, I stress kinetics, a topic that demands at least a bit of math. Consequently, I must justify annually the time spent on kinetics at the expense of other topics in the curriculum.

We chemists do a great deal of theoretical hand-waving, and, after a while, chemical theory seems like fantasyland to most high school students. I stress kinetics because collision theory seems fairly easy for high school students to understand. In my course, they understand kinetic-molecular theory pretty well because it has been supported clearly by student experiments and instructor demonstrations, we have also thoroughly covered the behavior of solid spheres prior to the introduction of kinetics, which gives them all they need for a primitive understanding of the topic.

From their knowledge of theory, the students practice scientific reasoning by predicting the effects of concentration and temperature on reaction rate. They then have the exciting experience of confirming their predictions in lab. With this information and their prior grounding in theory, they can understand reaction mechanisms, rate laws, activation energy and catalysts. They have gone into the lab to answer real questions rather than to demonstrate some principle explained in advance. Is the acid a catalyst? If so, an extrapolation of the rate versus concentration graph to $\{H^+\}=0$ will show a finite reaction rate. Does the fast step in a reaction involve one molecule or two? Altering concentrations of reacting species will clearly indicate which is the case.

The lab work also helps the students to develop a host of important skills. Careful measurements of volumes, times, and

(Continued in col. 1, page 41)

Kinetics—Rates and Mechanisms

Probably 90% of chemistry teaching deals with chemical equations using an arrow or equal sign to connect the formulas of products and reactants. Without such highly informative (at least to some) equations, treatments of stoichiometry, equilibrium, thermodynamics, synthesis, and analysis would be quite impossible. However, there is one subject in which the equation for the net reaction has only a limited use. That subject is kinetics and its main sub-areas—rates and mechanisms of reaction.

Using only the equation for the net reaction and the formulas it contains, there is no way of confidently predicting either a reaction rate or a reaction mechanism. Even the effect of temperature on the rate cannot be told with certainty. Intelligent control of a reaction requires knowledge of the variables which affect its rate. A knowledge of reaction mechanisms is in turn essential to the understanding of reactions at the atomic-molecular level. Most introductory teaching of kinetics starts (and often stops) with a determination of the factors affecting the rate. So let's start there (but also let's not stop at the standard places).

Rates are most commonly discussed in terms of three variables: the nature of the system, its temperature, and the concentrations of the reactants. Even changes resulting from stirring, altering surface areas, or adding catalysts can be handled in terms of variations in systems, temperatures, and concentrations. Reasons cited for studying these effects include providing a deeper understanding of the nature of the reactions and an enhanced ability to control their rates. Yet few standard treatments really do either successfully.

Concentration Effects

Almost all chemical systems studied are found to involve first-and second-order reactants, most often with orders equal (Continued in col. 2, page 41)

temperatures must be made. Correct calculations of concentrations, logs, etc. must be made and the results accurately plotted. This piethora of calculations seems much more palatable to my students when they are using calculations to help solve a real lab problem, than when they are just manipulating math formulas. When the data from different lab groups from all classes are pooled, the necessity for replication is obvious; although individual runs often don't work well, the combined data always yield clear relationships.

The labs help the students to discover for themselves the idea that a reaction can have several plausible mechanisms. Before they do the experiments, I discuss nucleophilic substitution reactions and physically model first- and second-order mechanisms, being careful not to tip off the results to them. Consequently, the students develop a feeling for the role of physical models in predicting reactions.

Once a mechanism has been determined in lab, I introduce several reactions for which the mechanisms are unknown. I stress that this is a major field of chemistry in which the students might make contributions. In fact, many of them end up doing research projects in kinetics.

I also stress kinetics because I've found clear understanding of the effects of concentration on reaction rates helps my students understand dynamic equilibrium.

To summarize, my course includes an emphasis on kinetics because: (1) the theory is qualitatively simple; (2) students are able to practice their scientific reasoning in a meaningful way; (3) the experiments make palatable the repetitious practice of important lab, calculation, and graphing skills; (4) students develop a feel for the importance of molecular structure and action at the molecular level; (5) I can introduce the idea that there are still questions in chemistry which the students may be able to answer; and (6) the ideas developed in studying kinetics are important for understanding equilibrium.

Finally, I stress kinetics because the students and I enjoy clock reactions immensely. Teaching kinetics gives me lots of excuses for demonstrating these reactions while I lecture.

William G. Lamb

Oregon Episcopal School 6300 SW Alcol Road Portland, OR 97223

About the Authors

J. Arthur Campbell is Professor of Chemistry at Harvey Mudd College, where he teaches freshman and physical chemistry. He has an AB in Chemistry from Oberlin College, an MS from Purdue University, and a PhD from the University of California, Berkeley. He has had a long and illustrious cereer teaching and consulting at institutions around the world. He is a past chairman of the Division of Chamical Education and has served on many national and international committees. He has numerous honors including the Manufacturing Chemists' Award for the Teaching of Chemistry.

withern G. Lamb holds the Winningstad Chair of Physical Sciences at the Oregon Episcopal School, where he teaches chemistry and physics and serves as department head. He earned his MA and PhD in science education from the University of Texas at Austin and participated in the first Dreyfus institute on High School Chemistry. His recent activities include directing a state science fair, development of a descriptive physica course which will serve as a prerequisite for chemistry, and the initiation of a high school student research program in chemistry (for example, some of his students are doing projects on semiconductor photochemistry).

to the coefficients in the net equation. No matter how many admonitions (even in bold face) there may be against deducing orders from coefficients, the students note the correlations and remember them. Why not use examples where this apparent, but untrue, correlation does not exist?

Few treatments discuss the importance of zero-order reactants, which commonly occur. For example, most physiological reactions are zero-order with respect to the substrate, e.g., glucose. Consider the problems humans would have with their enting rates if this were not true. Any variation in local glucose concentration would cause a variation in physiological rates. Many living system reactions circumvent this problem hy operating with a simple first-order kinetics involving an enzyme concentration which they can control to give an appropriate rate of reaction. Similarly, many environmental problems have rates which are zero-order in certain possible reactants. Some bodies of water have algal growths which are first-order in nitrate, zero-order in phosphate. Other bodies have the orders reversed. Control is possible by regulating just one of the concentrations, but first it must be determined which concentration affects the rate. Seattle had a problem with this some years ago and initially tried controlling the zero-order reactant. Unsuccessful.

One of the most useful definitions of a catalyst (by R. Beli) is a reactant whose concentration appears in the rate equation with an exponent higher than its coefficient in the chemical equation. This is a highly operational definition which gives insight into why a catalyst affects a rate.

A most important, but seidom developed, reason for studying concentration effects is that the order of a reaction often gives direct insight into the formula of the activated complex formed in the rate-determining step. I know of no more powerful method for gaining perspective on how molecules actually interact than writing probable structural formulas of the activated complexes. Yet few treatments provide guidance here. The formula of the activated complex is usually just the sum of the formulas of the substances in the rate equation. If the rate equation is:

$$rate = h[X]^m[Y]^n$$

then the formula of the activated complex is $X_m Y_n$. It is often possible to write a reasonable structural formula for the complex and thus predict which molecules collide in the rate determining step, what bonds form, what bonds break, and what products result. This is a great deal of information and it provides excellent instruction as to what is actually concealed in that equal sign or arrow in the equation for the net reaction. The formula of the activated complex also gives insight into catalytic behavior.

Temperature Effects

Almost every treatment presents the Arrhenius equation and discusses activation energies, but there are often three serious deficiencies, all easy to remedy with a little additional theory. The most obvious is the failure to mention the minimum, but appreciable, effect due to the increased rate of molecular collisions with temperature, which the student learned about earlier in the course. True, this is a small effect compared to the exponential Arrhenius effect, but a clear discussion of their relative sizes clarifies the issue.

More serious is the error of telling the student that a catalyst operates by lowering the activation energy. This is just not true. A catalyst provides a new mechanism. The old mechanism continues with its activation energy unchanged. There must be an increase in rate simply because there are now at least two mechanisms operating, not just the one of the original reaction. The most fascinating problem here is that, for many systems (especially those involving enzymes), the catalyzed reaction may actually have a higher activation energy

(Continued in col. 1, page 42)

than the uncatalyzed one, yet its rate may be thousands of times faster at comparable concentrations of substrate. It seems a shame to include such an important point so late in an essay, but better late than never.

Of course, this problem of an increased rate despite the greater activation energy is solved by considering the free energy of activation, a decrease in which does increase the rate. Thus we make a marvelous tie between thermodynamics and kinetics and a most useful extension of the entropy principle to reaction mechanisms. If the activated state is less organized than reactants and products, the entropy of activation is high. This lowers the free energy of activation, even though the energy of activation may be larger.

$$\Delta G_a = \Delta E_a - T \Delta S_a$$

with $\Delta E_{\rm a} \simeq \Delta H_{\rm a}$ for most systems. Thus, the rate is increased. It is interesting that some organic texts are ahead of many physical chemistry texts in this area.

Why Teach Kinetics?

There are so many reasons for teaching kinetics early and often. If it is done just a bit more thoroughly than is now common, the students (with little extra effort) see that (1) the equal sign or arrow of the net equation conceals much of the most interesting part of chemistry, (2) control of a reacting system necessitates determination of reaction orders, (3) knowledge of reaction orders allows a good guess at the formula of the activated complex, (4) knowledge of this formula reveals a great deal about the rate determining step and the role of any catalyst involved, and (5) study of the temperature effect may be coupled with entropy of activation effects to provide deep insight into the energetics of reactions and a correlation of thermodynamic ideas with kinetics. Doesn't it seem short-sighted to stop with simple rate equations and leave mechanisms as dark secrets?

A knowledge of the factors affecting rates (as in the Arrhenius rate equation) allows engineering control of a chemical system. Knowledge of mechanisms (such as formulas of activated complexes and free energies of activation) allows insights into the chemistry at the molecular level. Shouldn't chemistry students achieve such insights?

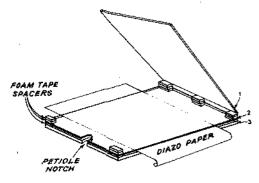
J. Arthur Campbell

Harvey Mudd College Claremont, CA 91711

Use of Photocopying for Non-Destructive Leaf Area Measurements

Planar measurements of area are frequently required for very diverse applications. General methods include planimetry, grids, dot counting, established correlation formulas, shadow or photographic prints, and various area meters. ^{1,2} In our work on plant growth and metabolism, it is often necessary to determine leaf shape as well as area. To study continuous growth and change in development, the method of measurement must be applicable to intact plants, non-destructive, and should provide a permanent record of linear dimensions. Preferably, the method should also be adaptable to fragile leaves of intricate shape and variable size, e.g., the compound leaf of tomato. A method combining general practices used in blueprinting and photocopying serves very well for this purpose.

The method consists of four steps. The first step utilizes a stage made from two Plexiglas® sheets separated at the corners by small squares of 1.3-mm thick foam mounting tape to hold a sheet of standard weight Diazo paper (8½ × 11 in, blueprint, rapid speed 11). An



additional Plexiglas sheet, hinged at one end to the other two and spaced appropriately with foam tape (3.9 mm), is placed over the undetached leaf. After the leaf is positioned, bayonet forceps (e.g., Lucae ear forceps) can be used to gently separate any overlapping or curled leaves. Diazo paper is inserted and suhsequently exposed with a photospot lamp (G.E. PH/RSP 2, 500 W) applied from a fixed distance of 12–15 in. above the stage for 10–15 s until the paper blanches. Second, the leaf print is developed in a hood by passing an inverted glass funnel connected with tubing to a tank of NH₃ gas over the exposed paper. If NH₃ gas is not available, a print may be held over a shallow dish of concentrated NH₄OH for development. Third, a photocopy (e.g., Kodak Ektaprint 150 copier-duplicator) is made of the leaf print to provide a clean, permanent record. From the photocopy, a final print is reproduced on a transparency (e.g., Kodak Ektaprint). Fourth, from the transparency print, area measurement is obtained by a grid, planimetry, or an area meter. In our use, measurements from the transparency prints by a LiCor 3000 area meter are within ±0.5% of compared direct measurements of detached leaves. The use of transparencies, which can be cut into strips, allows measurement of leaf sizes larger than can be accommodated by a portable area meter.

Since lamp intensity decreases with use, replacement of the lamp in the system will require adjustment of either the exposure time (decreased) and/or distance above the stage (increased) in order to maximize the clarity of the print and to avoid thermal damage to plant tissue due to the increased intensity. Our measurement of leaf temperature, under the described conditions, indicates a maximum expected increase of 5–6°C during exposure.

Reference to a company and/or product named by the Department is only for purposes of information and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

¹ Marshall, J. K., Photosynthetica, 2, 41 (1968).

² Kyet, J., and Marshall, J. K., "Plant Photosynthetic Production. Manual of Methods," (Editor: Sestak, Z.), Dr. W. Junk N.V. Publishers, The Hague, 1971, p. 517.

Marian L. Lyman Donald E. Campbell J. Corse

Western Regional Research Center Agricultural Research Service U.S. Department of Agriculture Berkeley, CA 94710

A High School Biochemistry Course



George B. Powers
Old Town High School, Old Town, ME 04468

The first-year chemistry courses at Old Town High School were described in a previous article in THIS JOURNAL¹. This article will describe a senior-level, advanced course in biochemistry. This biochemistry course was designed for students planning to pursue careers in nursing, engineering, and agriculture. The author, before he began teaching at the high school level, was a graduate assistant in the Biochemistry Department at the University of Maine at Orono where he assiated in the teaching of the biochemistry classes as well as their laboratories. This experience led to the conviction that high school students need to see what college courses are like. Therefore, the course is taught in a manner as close to the college course as possible. The students are given a syllabus at the start of the course containing all the reading assignments. Most general assignments are neither collected nor graded (as on the university level in biochemistry).

Course Description and Outline

Our second-year chemistry course includes general, organic, and biological chemistry. The prerequisites are first-year chemistry and instructor approval. The course is scheduled for three 42-min lecture periods and two 84-min laboratory periods per week. The student takes the course for a full year for 1 credit.

The format of the course is primarily lecture, but handouts are used liberally. Demonstrations and a few laboratory tests are also done during lecture. The laboratories have been chosen to follow the lecture topics. Many of the experiments are the same as those done on the college level, e.g., Isolation of Caffeine, Isolation of Cholesterol, Preparation of Aspirin and Preparation of Soap.

The textbook used for the course is "General, Organic and Biochemistry" by Rogers and Brown.² A college text must be chosen since, to my knowledge, no high school biochemistry textbooks are available. Therefore, some of the textbook material must be omitted or simplified. The course outline is given in the table.

Other Material

One of the favorite activities of the course is the seminars. Each student is required to present a 15-min seminar in a biological area of his or her choice. The students use the high school library, the University of Maine, or other sources to research their topics. Some of the topics covered are: Death and Dying, Bioluminescence, Sleep and Dream States, and Birth Control.

At several points in the course, professors from the University of Maine at Orono come and talk to the class. They cover such areas as nucleic acids, genetic engineering, biochemistry of aging, and photosynthesis.

The students also are given selected outside readings where they coincide with class materials; several are reprints from

Course Outline

Weeks	Торкс	Chapter	Laboratory
1	Matter and Measurement	1	None
1	Elements, Atoms, and Compounds	2	Worksheet
1	Atoms and their Elements	3	Worksheet
1	Compounds and Bonding	4	Worksheet
1	Chemical Reactions	5	Worksheet
*	Organic Chemistry	9	Carbon
1.5	Saturated Hydrocarbons	10	Hydrocarbona
2	Unsaturated Hydrocarbons	11	
1	Stereoisomerism and Optical Activity	12	None
1.5	Alcohols, Phenols, and Ethers	13	Alcohols and Ethers
‡	Aldehydes and Ketones	14	Aldehydes and Ketones
1	Carboxylic Acids	15	Preparation of Asperir
1	Functional Derivatives of Acids	16	None
1	Amines	†7	Isolation of Caffeine
0.5	Intermolecular Forces	None	None
1	Introduction to Biochemistry	7 (parts),	Acidity of Vinegar
		8	
2	Carbohydrates	18	Carbohydrates
			isolation of Starch
1.5	Lipids	19	Isolation of
			Choleater
3	Amino Acids and Proteins	20	Paper Chromatograph of Amino Acids
2	Enzymes	21	Enzyme Kit ^a Production of Cheese
2	Nucleic Acids (Protein Syn.)	22	Protein Synthesis Kit
0.5	Minerals	None	None
1	Vitamins and Coenzymes	None	None
1	Nutrition	None	None
1	Flow of Energy in Biol. World	23	None
3	Carbohydrate Metabolism	24	Metabolism Game
1	Lipid Metabolism	25	None
1	Amino Acid Metabolism	26	None
2	Integration of Metabolism	None	Worksheets

^{*} Experimental Enzymology Kit #20-2275 Carolina Biological Supply Company, Burlington, N.C. 27216

Scientific American. Carolina Biological Supply offers an outstanding series of short monographs on biochemical topics. Students also read and practice with a kit called "Elements of Protein Synthesis" by Thomas Peter Bennett.³

The best-liked and most utilized outside materialis a game, produced from an article in *The Biology Teacher*. ⁴ The article describes how to make and play the metabolism game, covering glycolysis, citric acid cycle, coenzymes, and the electron transport system. The students learn reactants, products, energies, and enzymes required for the major metabolic cycles.⁵

Conclusion

In general, the students who have taken this course have found it to be a great help. Not only do the college chemistry courses they eventually take cover many areas included in this biochemistry course, but the course also serves as an introduction to the college level approach to teaching.

Powers, George B., J. CHEM. EDUC., 58, 1015 (1981).
 Rogers, E. P. and Brown, W. H., "General, Organic and Biochemistry, Willard Grant Press, Boston, 1980.

³ Bennett, Thomas Peter, "Elements of Protein Synthesis," W. H. Freeman and Company, 1969.

⁴ Goodman, Richard E., The Biology Teacher, 34[2], 78 (February, 1972).

⁵ The game is now available from the Carolina Supply Company.



Implementation of the Thai High School Chemistry Curriculum

Nida Sapianchai and Thongchai Chewprecha

Institute for the Promotion of Teaching Science and Technology (IPST) 924 Sukhumvit Road, Bangkok 10110, Thailand

Thailand, with a population of 48 million, is one of the oldest countries in Southeast Asia. Before 1963, Thailand required four years of compulsory education. In 1978 the Thai government promulgated a new, 6-3-3 educational system (six years of elementary level, three years of lower secondary level, and three years of upper secondary level) with six years of compulsory education required for all children. Educational administration in Thailand is a centralized system; all schools throughout the country must use the same curriculum authorized by the Ministry of Education.

Since secondary education is not compulsory, study at that level depends on the parents' finaucial status and the student's own ability. In 1975, about 31% of the 14-16-year-old group was enrolled in the lower secondary level and about 12% of the 17-19-year-old group was enrolled in the upper secondary level. The number of students desiring to enroll in the public school exceeds space available; therefore, an entrance examination is required. Private schools can enroll some of the unadmitted students, but this still is not sufficient to accommodate all who desire secondary education. Education after the secondary level leads to one of two programs: the four-year bachelor degree program or the one-to-three year diploma program. There are 40 institutions which now offer the bachelor's degree, including 17 small teachers' colleges, 10 private colleges, 12 public universities, and I open university. Entrance to any public university is very competitive; only about 20-30% of the applicants can be accepted. In 1976, for example, the institutions of higher learning accepted only 12,502 applicants. An entrance examination is the main procedure used to select applicants. Private colleges also admit some students to limited areas of study but their enrollment is small since these institutions are expensive.

The one-to-three year programs of study, including training of technicians and skilled workers, are offered in over 100 technical institutions. These programs are, however, much less popular than the four-year bachelor degree programs.

Graduate programs are offered only in a few universities in limited areas. The enrollment of the graduate programs is small due to the limitations of subject specialists and facilities

Science Teaching in the Secondary Schools

The three years in the lower secondary education program, M.1, M.2, and M.3 are roughly equivalent to grades 7, 8, and 9 in the U.S. Science is studied in each of these grades, four periods a week. An integrated science program is presented rather than separate disciplines such as chemistry, biology, or physics.

Students at the upper secondary level who plan to further their education in science or science-related fields would be guided to take up to 60 semester credits in specific scientific courses such as chemistry, biology, and physics. They are also allowed to choose several elective courses. Nonscience students and those who plan to terminate their study upon graduation would be required to take only 12 semester credits of science. A new modular physical science course is recommended for this purpose.

The institute for the Promotion of Teaching Science and Technology

The nationwide chemistry curriculum at the upper secondary school level prior to 1976 in Thailand had been very traditional in comparison to many other countries. Theoretical chemistry and laboratory chemistry were taught separately with little relationship between them. Laboratory was not a required part of the course. Some topics were out of date; others, such as calculations and descriptive chemistry, were presented in too much detail. On the other hand, many important chemistry topics, such as bonding, rate of reaction, and equilibrium, were ignored.

Teaching strategies, emphasizing memorization, were based entirely upon a teacher's teaching rather than a student's learning. Teachers were not familiar with investigative or inquiry teaching techniques. High level questions were seldom asked. Students were not encouraged to ask questions, think, present ideas, or participate in a class discussion.

For a long time, this approach to chemistry had been criticized by many science teachers and science educators in Thailand. They agreed that new chemistry courses was needed for the upper secondary school. However, no attempt was made to do this until 1972, when the Institute for the Promotion of Teaching Science and Technology (IPST) was established through cooperative action of the Royal Thai Government, the United Nations Development Program (UNDP) and its executing agency, the United Nations Educational Scientific, and Cultural Organization (UNESCO). The main purpose of the Institute has been to develop modern science and mathematics curricula at every level below the university. Chemistry at the upper secondary school level was one of the first of the curricula to be developed, and its the nationwide implementation began in 1976 after three years of trial teaching from 1973 to 1975.

IPST Chemistry Curriculum

The IPST chemistry curriculum is very different from the earlier traditional chemistry curriculum. Theory and laboratory are integrated within the same course. Students are required to perform the experiments, observe, measure, gather data, organize data, interpret, make predictions, and draw conclusions from their own data. Inquiry and investigative teaching approaches were introduced to the teachers and they were encouraged to use these approaches in their teaching.

The unique characteristics of the IPST chemistry curriculum can be described as follows: It is inquiry-oriented (expecting students to think and to explain why), investigative (more doing chemistry), student-centered (stimulating their interests, ability, and ultimate use of chemistry), relevant (meaningful to everyday living), and innovative (new experiments, new equipment, new style of teaching, and new scheme of evaluation). Experiments play a large part, and the curiosity of the student is aroused. The student is placed in the role of discoverer, and the exciting, creative implications of this adventure encourage the student to become involved in his (her) own learning. Learning by inquiry, however, does

not necessarily mean that a whole curriculum will consist of experiments and problems. Curriculum developers in IPST science subjects have attempted to obtain a balance between factual content and inquiry activity. The criteria for selection of contents include the following:

Content selected should

- lead up to modern science and reflect the basic ideas and structures of the most recently accepted advances.
- 2) show continuity and follow a logical conceptual scheme.
- have a capacity for unifying and explaining the widest variety of phenomena and data.
- 4) be teachable within the time allocated and he suitable for the students' intellectual maturity and interests.
- be within the capability and experiences of the teachers and the adequacy of resources.
- contain examples of important applications to technology, agriculture, medicine, industry, and social science in Thailand.
- bring out the relationships to other fields of study, especially to the natural science and mathematics.
- 8) contribute to the growth and development of the individual as well as society and stimulate the proper utilization of natural resources and the preservation of the environment.

The IPST chemistry contents can be summarized as shown in Figure 1.

The iPST inservice Training Program

The teachers who would teach IPST chemistry were the same teachers who formerly had taught traditional chemistry. They were familiar with traditional chemistry topics and traditional teaching styles. This created the most difficult problem in implementing the new curriculum at IPST. Curriculum developers at IPST realized that the success of their work depended upon how well they could train these teachers. Thus an IPST inservice training program was developed with three main purposes: (1) to ensure that teachers have a sympathetic attitude to the new teaching approach; (2) to ensure that teachers understand the subject matter; (3) to ensure that teachers know how to use the new materials including the visual aids and new laboratory equipment.

Instructors of the inservice program used the techniques and methods which they wanted the teachers to use in their classroom. Although few special lectures on content or methology were given, through this role-playing technique teachers were exposed simultaneously to both. Teachers also had an opportunity to (1) perform all experiments which they would have to supervise in the classroom, (2) observe and use videotapes, audio slide-tapes, audio filmstrips, and programmed instruction booklets about the classroom management of experiments, laboratory safety, etc., and (3) discuss the IPST philosophy and objectives of chemistry teaching, and participate in its evaluation.

To date, over 90% of the chemistry teachers have completed at least two 90-hr IPST training sessions. In addition, elaborate teacher guides have been produced by the IPST to assist the trained teachers. In follow-up meetings, they report that these teacher guides have been of tremendous help.

Equipment and Chemicals

In addition to the need to train teachers in new techniques, school budgets for equipment and chemicals, teaching load, and class size pose other problems to the implementation of IPST. At the present time about 600 schools, 54,000 students, and 750 teachers are learning or teaching chemistry at the upper secondary school level. The average number of students in a class is 45. The average teaching load is 20 periods per week. Students study 3 periods of chemistry per week.

Because no laboratory assistants are available, teachers have to prepare all their own teaching aids needed for student experiments. Most schools do not have enough laboratory rooms; very often students have to do experiments in a regular classroom in which electricity and water are not installed. Students often have to carry a bowl of water and equipment from room to room. IPST has had to design experiments and equipment so that they can be used in such circumstances. Altogether, students have to perform about 90 experiments within 6 semesters; some representative examples of the experiments performed as listed below.

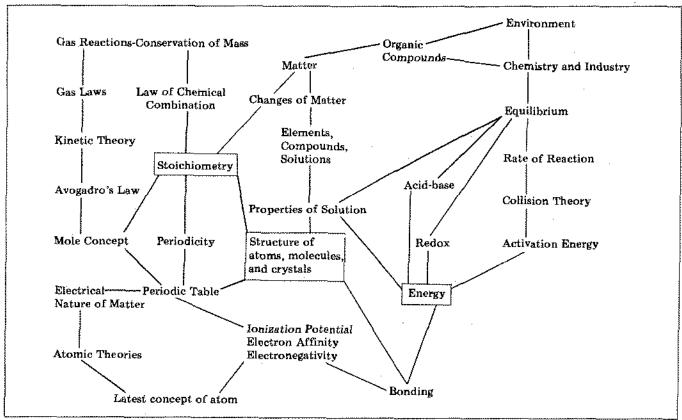


Figure 1. Conceptual scheme of the IPST chemistry course (six-semester course, three periods a week).

Matter and Changes: boiling of solutions and substances solvent extraction steam distillation extraction separation by chromatography energy and solubility energy and chemical reaction Stoichiometry (I): the study of mass in the system reactions between copper and sulphur mass ratio of elements in lead (II) iodide gas evolved from the reaction between oxygen and nitrogen monapproximation of molecular size of pleic acid Stoichiometry (II): preparation of solutions heat energy of chemical reaction

All the equipment used in chemistry courses at the upper secondary level except some glassware and balances has been designed by IPST and produced by local industries. Only some sophisticated equipment parts are imported; these are then assembled within the country. It is the IPST's goal to design low-cost equipment using local materials, thus encouraging

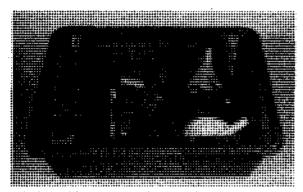


Figure 2. Kit containing student experimental equipment.

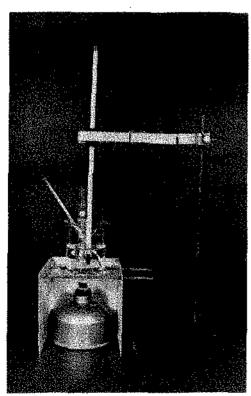


Figure 3. Apparatus for boiling-point determination.

development of local chemical and science equipment industries. Up to this point IPST equipment is lower in cost when compared with imported materials, and almost all equipment uses local material. Several privately-owned, small-scale factories for the production of equipment, and one science equipment plant has been organized by a commercial enterprise of the Teacher's Association.

The IPST equipment is classified into four groups: (1) the student's kit, (2) kits for special student experiments, (3) kits for teacher demonstration, (4) equipment for teacher preparation. The student's kit is shown on Figure 2, and selected examples of the equipment developed locally are illustrated in Figures 3-4.

1) The student's kit. This contains all the basic laboratory equipment needed by the student and should be all that he or she requires for at least 75% of the experiments in the course. There are two different kinds of storage: the wooden kit box and the open mesh plastic tray. The items in the kit are the same in both cases. The kit was designed so that experiments in the new curriculum could be performed in any room in the school where there was a table for the student to put the box on.

2) Kits for special student experiments. There are some pieces of equipment which are used several times during the course but not often enough to be included in the student's kit. This type of equipment includes that for the conductivity test, the electrolysis apparatus, and the insulated beaker (calorimeter). These will be supplied by the taacher when they are needed.

3) Kits for teacher demonstration. There is a small amount of equipment for teacher demonstration. It includes the ion migration set and the molecular and crystal models.

4) Equipment for teacher preparation. To assist the teacher in the task of preparing chemicals and solutions for the experimental work in the course, a set of additional equipment has been assembled. It includes additional glassware, storage bottles, volumetric flasks, pipet, and a buret.

Conclusion

Teachers are the most important link in the educational system. The training conducted to help these teachers acquire

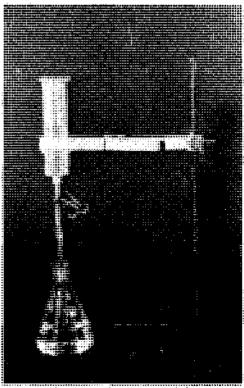


Figure 4. ilabilitaria manifica apprint par minga matingu

the necessary teaching skills and confidence is of utmost importance. In this connection, equipment and teaching materials must be readily available so that the schools can purchase them at reasonable prices. Even the best curriculum will not

achieve its goal, if the teachers are not provided with necessary materials to sustain their program. With the demands on their time being what they are, teachers can not expect to produce very much of their own equipment or materials.

thumbnail sketches

edited by MARY VIRGINIA ORNA, O.S.U Catlege of New Rocheile New Rocheile, NY 10801



Metal Substitutions in Wartime Coinages

Hugh A. Akers

Lamar University Beaumont, TX 77710

With the trend towards inclusion of more descriptive material in chemistry, many texts have, in addition to mentioning uses of specific elements, also included information on the sources and distribution of the appropriate raw materials. There are often comments on the effects of strategic supply interruptions, using the recent oil embargo as an example. For instructors interested in this area there are actual physical examples of the effects of supply interruptions preserved in the coinage of many countries. Current students are too young to remember that because of wartime metal demands, United States cents of 1943 were made of zinc-coated steel and five-cent pieces (called "five-cent peaces" in some circles) during World War II were made of a copper-silver-magnesium alloy.

Under normal circumstances a number of factors such as cost, inertness, availability, appearance, and hardness are involved in the selection of a metal or alloy used for coinage. During wartime, with supply interruptions and armament production taking precedence over domestic requirements, there was a redefining of the relative values of the various metals. Metal price changes often complicated the situation; however, in most instances the prices of domestically produced metals were "fixed" during wartime. The enclosed table lists some of the significant coinage changes brought about by World Wars I and II. Numerous other changes had a less significant effect of the circulating coinage as judged by mintage figures. In most of the examples listed, there was a return after the war to the pre-war coinage metal.

For many countries wartime adaptations included making smaller, thinner, or holed coins to save vital supplies, while in other cases there were no wartime coins minted or there was a shift to paper currency. Inflation was a major factor in the choice of coinage metal in several countries. Gradual debasement of the coinage did not occur during the World Wars; rather, there was a complete switch in metal content from the strategic and/or imported metals to less strategic, domestically produced metals. Significant debasement was often a postwar phenomenon, as in Great Britain in 1920 and 1947. During the World Wars there actually was an increase in mintage of silver coins in Canada, Great Britain, and the United States. Because of limited supplies, Sweden produced only a portion of its wartime coinage from silver (see table). Scrap material was frequently used for coinage: the United States produced one-cent pieces during 1944 and 1945 from salvaged shell

Prewar coinages were often produced from various combinations of copper, nickel, and tin. During wartime these elements also found increased importance as components of numerous steels and alloys used for shell casings. Central

Coinage Metal Changes Brought About by World Wars I and Il^a

			Coln	age Metal
Country	Denomination	War	Prior	During
Austria	2 Heller	‡	Cu	Fe
	20 Heller	1	Ni	Fe
Belgium	5, 10, 25 Centime	ł, 11	Cu-Ni	Zn
	50 Centime	}	Ag	Zn
	1 Franc	11	Ni	Zn
Bulgaria	10, 20 Stotinki	1	Cu-Ni	Zn
-	1 Lev	Ħ	Cu-Ni	Fe
Салада	5 Cent	B	Ni	Cu-Zn, Fe
Denmark	1, 2, 5 Ø re	1	bronze	Fe
	1, 2, 5 Øre	ß	bronze	Zn, Al
	10, 25 Ø re	11	Cu-Ni	Zn
France	(several)	B	(various)	Ai, Zn
Germany	1 Pfennig	- 1	Cu	Al
	5, 10 Pfennig	- 1	Cu-NI	Fe
	1 Pfennig	. #	bronze	Zπ
	5, 10 Plennig	ĸ	Al-bronze	Zn
Hungary	2 Filler	t	bronze	Fe
•	2 Filler	Ħ	bronze	Zn
	20 Filler	ł, II	Ni	Fe
Japan	1, 5, 10 Sen	II.	bronze	Al, Sn-Zn
Netherlande	1 Cent	Ħ	bronze	Zn
	5 Cent	H	Cu-Ni	Zn
	10, 25 Cent	ŧ	Ag	Zn
Norway	1, 2, 5 Ore	ŧ, 11	bronze	Fe
•	10, 25, 50 Ore	Ħ	Cu-Ni	Zn
Romania	2 Lei	Ħ	Cu-Ni	Zn
	20 Let	fl	Ni-brass	Zn
Sweden	1, 2, 5 Öre	1, H	bronze	Fe
	10, 25, 50 Öre	1, 11	Ag	N⊩bronze, Ag
Switzerland	1, 2 Centime	Ħ	bronze	Zn

^a Deta and metal descriptions from: Harris, R. P., "A Guide Book of Modern European Coins," Whitman Publ. Co., Racine, Wi, 1965; Krause, C. L. and Mishler, C., "Standard Cetatog of World Coins," Krause Publications, Iola, WI, 1972.

Europe produces some copper while most of the world's nickel comes from Canada. Iron is readily available in Central Europe, as is zinc from deposits in Poland and Germany. Consequently, areas dominated by the Central and Axis powers had iron and zinc coinages during the World Wars. These changes were suitable for emergency coinages only. Many of the iron alloys used for World War I coinages oxidized readily, while zinc coins were rather soft. World War II created tin shortages in much of the world, but because Japan controlled the major tin sources in southeast Asia this metal was less strategic to the Japanese, who used it as a major component in alloys for wartime coinage.

Brief descriptions of phenomena, topics, facts, etc., which chemical educators have found to be of interest in their teaching, are presented in this column in a "note type" format.

edited by: TAMAR Y. SUSSKIND Oakland Community College Aubum Heights, MI 48057

A Note from the Chair of 2YC₃

Today, more than ever before, the two-year college with its unprecedented growth and its highly diversified program has become an extremely important segment of higher education. Although two-year colleges in their transfer programs provide academic preparation comparable to that offered in the first two years of four-year institutions, there are many aspects of two-year college chemistry teaching that are unique.

This new column, The 2YC₃ Viewpoint, hopes to address issues, problems, and points of view that are of particular interest

to two-year college chemistry teachers and of general interest to all chemistry educators.

The following paper was presented to a group of community college teachers from Delta College, Michigan, at their Spring Professional Growth Development Conference. The theme of the conference was "Striving for Excellence" and the special topic was "Coping with Shifting Student Expectations." The point of view expressed here may be a provocative one, at least in the context of the two-year college.

Coping with Shifting Student Expectations

Tamar Y. Susskind

Oakland Community College, Auburn Heights, MI 48057

The title, "Coping with Shifting Student Expectations" implies that students now in higher education have expectations different from previous students. Do we have evidence of this? Is it an impression that we have? Could it be that our expectations of the students is what has changed? We can assess ourselves but in the absence of adequate data we cannot presume to assess the students. If for a moment we turn this topic around, we may get a little perspective, at least, on ourselves.

Everyone who has been teaching for more than five years is aware that, for a variety of reasons, the way we feel ahout our students begins to change. We often feel about our students the way we feel about ourselves. When we are young, new in the profession, vigorous and enthusiastic we demand a great deal of ourselves and assume that we can also demand a great deal of our students. As we continue to teach is it possible that we put out less energy and that our students therefore achieve less? Because of that, we ascribe to our students a lowering of expectations. If we mean the opposite, I have yet to hear it. Are the student expectations shifting upward or downward?

If the shift of expectation occurs in what is expected of us as instructors that is one issue and a big one. But if the shift is one that includes the goal of an entire college education then we have yet another issue. Judging from the flurry of students taking business courses, data processing, computer courses, and robotics one would think that the ultimate goal of education was to enable a person to enter the job market competitively. The students seem to look upon education more vocationally and to be more goal-oriented than ever before. We are expected as teachers to show them how to "make it"—that is, have a marketable skill. The question I would like to pose is; how do I (and maybe some of you) having been raised in a tradition of knowledge for its own sake face students who are not interested in the very values that drove me to find my own education? How do I hridge the gap between the value systems: vocational skills versus pursuit of knowledge? Thomas Lounsbury, that great turn-of-the-century Yale

educator once commented on "the infinite capacity of the undergraduate to resist the intrusion of knowledge." This infinite resistance to knowledge applies more than ever now, especially to the fields of science and, in particular, chemistry. I have spoken with students who take pride in telling me that they have never had a chemistry course, and furthermore hoped they never would. Other students who have had one disastrous chemistry course in high school tell me they would never consider taking another. When I meet a class for the first time I'm apologetic. I try to convince them that chemistry is not something dreadful; that it can be exciting, challenging, and even stimulating. I tell them that learning itself is a chemical process and although taking the course may not lead directly to immediate employment or a "pot of gold," it may come in handy some day when they least expect it. It may help them make informed choices on scientific and technological issues facing our society.

We are caught in the compromising position of having to teach skills without abandoning the development of the kind of mind that can think logically and reason effectively. Somewhere in my education I've come to believe in learning, in questioning, and in the human spirit. I owe it to my students to let them know how much there is which goes beyond immediate gratification. In coping with these waves of dualistic tension—pragmatism versus theory, vocation versus academies, experience versus homework, now versus yesterday or tomorrow—I feel that the teacher must have the pervasive conviction that learning is in and of itself a highly valuable activity; a goal worthy of everyone's pursuit and one that draws a variety of rewards.

The economic climate of the 80's, in which teachers must worry about enrollment, combined with our egalitarian open door policy has forced us to make certain adjustments. I'm aware, for example, that it has become increasingly important for me not to fail too many students. Because of that, our demands are lowered and there is an erosion of student expectations. It is known that people perform at a level at which you assume they are going to perform. Perhaps we tend to sell our

students short by descending to a lower level of expectation. Before long, they inevitably come to share our expectation of them. We know that students never, or hardly ever expect enough of themselves. Don't you think they know where the easy A's are? They can get by with a minimum of work, but in so doing they deprive themselves of an education. It is our job to expect the best of them and I suspect we can get it. It is the only way the students will find the best in themselves. Teachers must find their own way of expecting the best of their students. Most of us don't even know how little we expect of them. Getting back to my earlier point: do I find myself expecting less of my students as a trade-off so that they will expect less of me? After all, I can pay them off fairly well. Haven't we all been a little guilty of grade inflation? The result seems to be that students want better grades for less input.

The question we face is shall we continue to acquiesce in the lowering of expectations by accepting the diminished demands of our students, a reflection of our own lowered estimate of their abilities? I believe we have permitted it to happen and we have the ability to turn it around. Although we are involved in a crisis where headcount in the classroom looms large and some of our jobs may be at stake, I feel that we must do a balancing job. We must offer courses with substance and reward excellence and not mediocrity. A faculty member's enthusiasm and commitment to his or her subject will have the greatest impact on students and they will in turn be motivated to dig in.

Further, how do we cope with behavioral patterns that go

along with students' shifting expectations, e.g., the increased demand for make-up tests, extra help sessions, extra credit requests, the resistance to write anything except check-off multiple-guess answers, the apparent lack of discipline? These are real problems and coping with them is not easy.

My experience has taught me to try to communicate, verbally and in writing, realistic goals with realistic demands to my students from the start. I explain my policies regarding grading system, make-ups, absences, etc. With this strategy the student hardly ever tries to make a special plea. And special pleas have to be very special indeed. In this balancing act (and there always seems to be one), I try to be student-centered but I also maintain a firm directiveness.

Although student evaluations are not terribly reliable, I have found them to be helpful in improving my interactions with students. They are suprisingly candid and I believe we ought to consider themes repeatedly expressed therein.

In conclusion, I must admit that this topic is an enormous one. It can be viewed in various ways. We must consider teacher responsibility as well as students'. They are intricately intertwined. I would like to leave you with two general conclusions:

- Be realistic—make reasonable demands on yourself and your students.
- Acknowledge the fact that students are job oriented, but do not in the process lose sight of the great value of learning in and of itself

safety tips

edited by MIRIAM C. NAGEL Avon High School Avon, CT 06001

Risk Assessment

Miriam C. Nagel

Avon High School Avon, CT 06001

"Zero Risk 'Unattainable,' CMA Says" is the thought-provoking title of an article in the March 1982 issue of ChemEcology, published by the Chemical Manufacturers Association (1). The article opens with the statement, "One challenge now facing scientists and regulators is to assess the significance that small quantities of contaminants may have for human health and to steer the necessary course that protects society's health while meeting society's needs." It further states, "Today, advances in analytical skills and toxicology have improved detection and identification. Substances that pose potential human health hazards in higher concentrations can now be detected in parts per hillion."

With these improved methods of detection, lists of potentially toxic chemicals and carcinogens are growing longer. Strange and previously unknown substances lurk even in a beaker of laboratory tap water. "For example, in s recent analysis of water taken from a tap in Cincinnati, Ohio, over 700 separate compounds were found, of which only 460 or so could be identified. Of those identified, few had ever been reported before in raw or treated water supplies. Many are known or suspected carcinogens, though probably not at the extremely low concentrations reported in the study" (2).

The ChemEcology article (1) poses the question, "Even though human experience tells us that low-level exposures need not be harmful, does this lead to the conclusion that such

"Safety Tipe" is a source of safety information and practical suggesstions to meet the special needs of high achool chemistry teachers, it is also intended to be a forum for teachers to share their experiences and seek solutions to safety related problems. exposures are totally risk free?" It quotes from a Supreme Court decision which said that "safe" is not the equivalent of "risk free." Additional comments on the decision were, "Some risks are plainly acceptable and others plainly unacceptable. If, for example, the odds are one in a billion that a person will die from cancer by taking a drink of chlorinated water, the risk could not be considered significant. On the other hand, if the odds are one in a thousand that regular inhalation of gasoline vapors that are two percent benzene will be fatal, a reasonable person might well consider the risk significant and take appropriate stepa to decrease or eliminate it."

Let us look at the two chemicals cited in the quoted comments from the Supreme Court decision. The risks associated with the use of chlorine in water are "plainly acceptable" by the Court's definition of the term. On the other hand, benzene is unacceptable in high school labs and storerooms. It is highly toxic and a suspected carcinogen. The Permissible Exposure Limit (PEL), the maximum time-weighted average level for an 8-hr exposure, is 1 ppm with a ceiling of 5 ppm, according to the NIOSH/OSHA Pocket Guide to Chemical Hazards. The Immediately Dangerous to Life or Health (IDHL) concentration, representing a maximum level for a 30-min exposure, is 2000 ppm (3).

Benzene is also a flammable liquid, having a flash point of 12°F (~11°C). Vapors form explosive mixtures in air. The explosive limits are 1.3-7.1%. Liquid benzene has a specific gravity of 0.8 and is insoluble in water. The vapor is heavier than air and may travel considerable distances to a heat source resulting in a flash back, adding to the hazards.

Although benzene should not be found in the high school lab, teachers and students may be exposed to the toxic fumes of benzene when they patronize the nearest self-service gas station. Benzene is often used as a substitute for lead in unleaded gasoline. "In the general public, benzene exposures rarely exceed the parts-per-billion level, and are ordinarily



not risky. However, some health authorities note that the benzene fumes that collect at the top of a car's gas tank are often released in a whoosh when the cap is removed for a fillup, and that ambient benzene levels as high as 250 ppb have been recorded at gas stations" (4). It is to be hoped that owners and attendants at busy full-service gas stations are aware of the possible health hazard.

The safety of food additives come under the jurisdiction of the Food and Drug Administration (FDA) in much the same way that the Environmental Protection Agency (EPA) is responsible for enforcing laws passed by Congress to protect the environment from toxic substances. Food additives are rarely encounted in high school chemistry lahs, but a brief survey of saccharin, an artificial sweetener, will show how possible risks from its use have been evaluated by the FDA, Congress and the public.

Saccharin was discovered accidentally in a chemistry lab in 1879. It is noncaloric and, in dilute aqueous solutions, it is 300-500 times as sweet as sugar. Since 1900 it has been used as a sugar substitute by diabetics and in weight-control diets.

Amendments to the 1938 Food, Drug and Cosmetic Act brought food additives under regulation by the FDA in 1958 and 1960. Before 1958, it was the responsibility of the FDA to prove that a food product was potentially dangerous. Afterwards it became the responsibility of the manufacturer to prove that a new product was free of risk to the public. In regard to carcinogens, the Delaney Clause (part of the 1958 and 1960 amendments) states that "... no additive shall be deemed to be safe if it is found to induce cancer when ingested by man or animal, or if it is found, after tests which are appropriate for the evaluation of the safety of food additives, to induce cancer in man or animal..." (1).

The ChemEcology article on zero risk states (1),

Animal testing is an important step in assessing the potential carcinogenic risk of a substance... Although uncertainties exist with the animal feeding studies and the mathematical extrapolation of the dose-responses, the greatest uncertainty lies with the direct translation of animal response to human response. Risk assessment is the only means available to quantify the probable risk associated with a specific food or food additive. It also permits comparison to other societal risks.

Which brings us to the saccharin controversy.

Responding to a Canadian study which indicated that saccharin causes malignant bladder tumors in rats, the FDA in March 1977 proposed a ban on the use of saccharin. There was immediate and continuing public outcry against the ban from users of the product. The president of the Calorie Control Council maintained that saccharin had been used for 80 years with no evidence that it had produced cancer in humans. Some manufacturers of products containing saccharin claimed that the FDA han was based on "flimsy scientific evidence" and would destroy the diet beverage industry and deprive diabetics of sweets. Producers of soft drinks and other low-calorie products began using substitute sweetners to lessen the economic impact of the ban. A Congressman announced plans to introduce legislation to stop the FDA action and to modernize the Delaney Clause. Within the month the FDA considered classifying saccharin as a drug instead of a food additive so doctors could prescribe it for diabetics and weight disorders.

Opponents of the ban in April 1977 included the president of the American Cancer Society. The FDA said it would con-

tinue to permit bulk sales of saccharin in tablet and powder form, but would ban its use in prepared food and beverages. Later in the month, the FDA announced a two-month delay in enforcing the ban to evaluate new data linking saccharin to bladder cancer. In May the New Jersey Medical Society opposed the ban on saccharin, and a World Health Organization report indicated that saccharin does not increase risk of bladder cancer.

Proponents of the FDA stand were vastly outnumbered by opponents of the ban who continued their efforts through the summer and fall. The Congressional Technical Office which had begun a study of the risks of saccharin and the adequacy of animal testing reported in November that it is one of the weakest cancer causing agents ever detected. After months of hearings and legislative maneuvering, Congress passed and President Carter signed the Saccharin Study and Labelling Act late in November 1977.

Under terms of the act, the National Academy of Sciences would review the data on which the proposed saccharin ban was based, and the FDA would develop procedures and regulations for warning labels on saccharin products about the risk of cancer. In November 1978 the National Academy reported to Congress that saccharin must be considered a danger to humans, both because it is a weak carcinogen and it may be a promoter of other cancers. Despite the Academy's warning, opposition to the FDA's proposed ban on saccharin did not diminish. As far as its opponents were concerned, it was an "acceptable" risk to use saccharin. In 1979 and again in 1981, Congress voted to forbid the FDA to impose the ban for successive two-year periods.

In 1983 the FDA announced approval of the use of aspartame, a new low-calorie sweetener. The newspaper story (5) about the announcement reported that before the approval of aspartame, saccharin had had a monopoly in the soft drink market which accounted for 70% of its sales, or about \$115 million a year. Not bad for a product which nearly came under ban in 1977.

A new publication, "Risk Assessment in the Federal Government," is now available from the Committee on the Institutional Means for Assessment of Risk to Public Health, National Research Council (6). The text, prepared at the request of Congress, evaluates past efforts to develop and use guidelines and proposals for changes in risk assessment procedures for carcinogens in the environment. The authors recognize there are no quick answers, but do present an objective analysis of the problems. Another new publication, "Identifying and Estimating the Genetic Impact of Chemical Mutagens," from the Committee on Chemical Environmental Mutagens, Board on Toxicology and Environmental Health Hazards, National Research Council (6), provides information on assessing genetic risks.

Literature Cited

- ChemEcology, Chemical Manufacturers' Association, 2501 M Street NW, Washington, DC 20037, March 1982.
- (2) Skjei, E., and Whorton, M. D., "Of Mice and Molecules," The Dial Press, New York, 1983, p. 132. (Data credit: W. E. Coleman et el., "Identification of Organic Compounds in a Mutagenic Extract of a Surface Drinking Water by a Computerized Gas Chromatography/Mass Spectrometry System (GC/MS/COM)," Environmental Science and Technology, 14, 576, May 1980.)
- (3) DHEW (NIOSH) Publication No. 78-210, Superintendent of Documents, U. S. Government Printing Office, Washington, DC 20402
- (4) Ref. (2), p. 103.
- (5) Hollie, Pamela G., "Searle Sweetner Wins Approval for Soft Drinks," New York Times, July 2, 1983, p. 31.
- (6) National Academy Press, 201 Constitution Avenue NW, Washington, DC 20418.

Single-Pan Balances, Buoyancy, and Gravity or "A Mass of Confusion"

Rubin Battino

Wright State University, Dayton, OH 45435

Arthur G. Williamson

Department of Chemical Engineering, University of Canterbury, Christchurch, 1, New Zealand

The advertising literature on single-pan balances (both mechanical and electronic) is a commentary on the gullibility of consumers and the apparently confused ideas many manufacturers have about weighing. For example, one manufacturer of single-pan electronic balance lists for a dual weighing range of 1500/150 g, "readabilities" of 0.1/0.01 g, "precisions" of 0.05/0.007 g, and "linearities" of 0.1/0.01 g. The readout displays five digits which accounts for the readability. We certainly hope the linearity is of the same order. As to how they determine precisions which are better than the "readability" or "linearity" we can only guess.

Most single-pan electronic balances display five digits, some show six, and one company even offers eight (0.1 mg for the 1-kg range). The single-pan mechanical balances of the analytical type (load 160–200 g, "readability" of 0.1 mg and "precision" of 0.05 mg) generally deliver seven significant figures. This wealth of "readabilities, precisions, and linearities" is offered along with oodies of significant figures despite the fact that (we fondly hope) any sophomore taking quantitative analysis could tell the manufacturers that due to buoyancy effects (if, indeed, this arcane topic is still discussed) the accuracy is often of the order of one part per thousand or 0.1%. If an accuracy of 0.1 mg is required in a mass of 100 g then buoyancy corrections must be made to 0.1%!

Being mightily intrigued by the foregoing and the manufacturers' literature, we sent out a brief questionnaire to all companies which we could identify as manufacturers of single-pan balances. We asked the following questions of their research directors

- A. Single-Pan Mechanical Balances
 - What are your "weights" made of and what is their density?
 - 2. Do you have a set of instructions for calibrating the "weights", or must this check be done by you?
 - 3. Do you have a set of instructions applying to buoyancy corrections?
- B. Single-Pan Electronic Balances
 - Do you have a set of instructions for calibrating the accuracy of your balance over its full range?
 - 2. Since your balances will only read correctly when weighing objects of a certain density, what is the density of the standard weights against which your balances were calibrated?
 - 3. Do you have a set of instructions applying to buoyancy corrections?

The responses to these queries were most disheartening since almost all of the manufacturers just sent us more literature in return. Moreover, it was quite evident from the responses that most manufacturers either do not understand the idea of buoyancy corrections or believe them to be irrelevant (which they sometimes are). This ignorance of buoyancy corrections is not limited to manufacturers—one of us recently heard a colleague complaining that the top loading single-pan balance in his laboratory had had a "systematic" error of approximately 1 g/kg ever since it had been bought.

The manufacturers of single-pan mechanical balances expect you to accept their original calibrations indefinitely

(perhaps, because the weights are protected, i.e., untouched by human hands), or to consult them in case of trouble. None supplied directions for calibration. The calibration of the weights in such a balance is fully described by a publication of the American Society for Testing Methods (1). An alternative approach which examines the internal consistency of the weights but does it without checking their absolute values and which has been used as a laboratory exercise by one of us is described in the Appendix.

Most manufacturers of single-pan electronic balances included directions for calibration. The procedure was to put a "standard" weight, usually unspecified as to density or NBS class (2), on the balance pan and then turn a calibrating screw until the read-out gave the nominal weight. The Mettler Instrument Corporation supplies a calibrator weight with its balances and also sells them. The Sartorius balance has a built-in calibration weight. To calibrate any electronic balance one needs to use a standard weight of adequate accuracy. For a 100-g weight (a typical calibration weight) the class S tolerance is 0.25 mg, the class S-1 tolerance is 1.0 mg, and the class P tolerance is 2.0 mg. Thus, strictly from the viewpoint of accuracy, it is difficult to understand the extra digits these balances display. How can an analytical balance be accurate to 0.1 mg when a class S weight is only accurate to 0.25 mg? (The tolerance of a class M 100 mg weight is 0.50 mg.)

Let us now turn to the interesting problem of the density of the weights used inside single-pan mechanical balances. A standard for weights used in analytical balances was promulgated in 1973 by the Organisation Internationale de Metrologie Legale. Their recommendation is to use weights of density 8.0 g cm⁻³ at 20°C. All of the Mettler balances built since 1973 have weights made of stainless steel with a density of 7.96 g cm⁻³ but "adjusted" to 8.0 g cm⁻³ for a standard air density of 1.2000 g cm⁻³. Earlier Mettler balances used stainless steel weights of 8.4 g cm⁻³. We do not know how Mettler accomplishes this "adjustment". Ainsworth uses nickel-plated brass weights of density 8.4 g cm⁻³ in some balances and stainless steel ones of density 7.8 g cm⁻³ in others. Sartorius balances use weights of 7.88 g cm⁻³ density. Whatever the original reasons for this multiplicity of weights of different densities, there can be no real excuse for not standardizing on weights of a density of 8 g cm⁻³.

Recently an entire new technology of weighing has been developed in the form of the all-electronic balance. (A transition period included mechanical/electronic hybrid balances.) With these devices we have in effect returned to the spring balance. The object to be weighed is placed on a pan and downward force is given by

$$mg\left(1-\frac{\sigma_{\rm air}}{\sigma_{\rm object}}\right)$$

where m is the mass of the object, g, the acceleration of gravity, and σ is the density ($\sigma_{\rm air} \simeq 0.0012~{\rm g~cm^{-3}}$). This downward force is automatically balanced exactly by the interaction of the magnetic field from a coil and that of a permanent magnet. The current in the coil is converted electronically to a weight reading and then displayed digitally. It is possible to make the

scale much more linear than that of a mechanical spring balance, and precisions of a few parts per million or better are possible. For measurements where only relative masses are important (and using the same balance in the same place for all weighings) no calibration point is necessary (within the "linearity" of the balance!). The apparent mass scale is obviously a function of the local gravitational field. Although Portland, Oregon and Charleston, South Carolina have essentially the same altitude, g differs by 0.11%; between New York, New York and Denver, Colorado this difference is 0.07%.

When one calibrates single-pan electronic balances one is, in effect, determining the force constant of the electromagnetic nulling system against a standard weight of a particular density. If one knows that density (or the one the manufacturer used), then one can reasonably apply buoyancy corrections and also calibrate the balance for the density of weights the manufacturer designed it for. Mettler supplies a standard weight of 8.0 g cm⁻³ density with its instruments (and also sells them separately). Sartorius calibrates all of their balances against weights with a specific gravity of 7.88 g cm⁻³. All of the other manufacturers we contacted gave no information on this matter. Basically, they tell you where the calibration screw is and to use it in conjunction with a "standard" weight.

Buoyancy corrections for single-pan mechanical balances have been dealt with before in THIS JOURNAL (3-5). The most complete analysis was given by Winward, Woolley, and Butler, But, no matter how one approaches it, if one weighs an object of density 10 g cm⁻³, the buoyancy corrections are of the order of 0.1% or one part per thousand. Mettler gives charts on how to handle this for their mechanical balances, and Sartorius gives directions in their instruction manuals.

Air buoyancy corrections for single-pan electronic balances are the same as for two-pan equal-arm mechanical balances or

$$W_0 = W_{\text{wt}} \left(1 - \frac{\rho_{\text{air}}}{\rho_{\text{wt}}} \right) \left(1 - \frac{\rho_{\text{air}}}{\rho_0} \right)^{-1}$$

where W_0 is the *in vacuu* weight of the object, $W_{\rm wt}$ is the weight read on the read-out device, and $\rho_{\rm air}$, ρ_0 , and $\rho_{\rm wt}$ are, respectively, the densities of air, the object, and the weights used to calibrate the balance. The buoyancy correction for weighing 1 kg of water is about 1 g!

While the manufacturers of balances are to be congratulated on their achievements in providing both very high precision and great convenience in the use of their products, it is unfortunate that these advances have not been accompanied by corresponding advances in the education of balance users, particularly with respect to the precautions necessary to use these fine devices. A standard 100-g weight is of such small cost relative to the cost of a balance that they should be supplied with the balance.

Beware of being bedazzled by all of those bright red digits. If all else fails, re-read the section in a good quantitative analysis book on balances and their errors, or even choose to work with the slower equal-arm balances where one can easily calibrate the weights and tare with real objects. Of course, if you never work beyond precisions of 1 ppt, feel free to ignore this paper. But, then, why are you using such an expensive balance?

Literature Cited

- (1) A.N.S.I., E 319-68, Standard Method of Testing SINGLE ARM BALANCES.
- (2) AN51/ASTM, E 617-78, Standard Specification for Laboratory Weights and Precision Mass Standards; National Bureau of Standards, Circular 647, Precision Laboratory Standards of Mass and Laboratory Weights, Leshof, T. W., and Macurdy, L. B., 1984.
- (3) Burg, W. R., and Veith, D. A., J. CHEM. EDUC., 47, 192 (1970).
- (4) Lewis, J. E., and Woolf, L. A., J. CHEM. EDUC., 48, 639 (1971).
 (5) Winward, M. R., Woolley, E. M., and Butler, E. A., Anal. Chem., 49, 2128 (1977).

Appendix: Intercalibration of Weights on a Single-Pan Weight Loading Salance Using Dummy Weights of Approximately Known Mass Only

- 1) Set balance level
- 2) Release beam
- Set optical scale zero (this is useful but not necessary)
- 4) Read optical scale: S_o
- Arrest beam
- 6) Dial up 1 unit: M1
- 7) Release beam
- 8) Read optical scale: S1

$$M_1 = (S_1 - S_0)$$
 (optical scale units)

- 9) Arrest beam
- 10) Add external weight: $W_a (\simeq M_1)$
- 11) Release beam
- Read optical scale: S_s

$$W_a = S_a - S_o$$

- 13) Arrest beam
- 14) Dial M_1
- 15) Release beam
- 16) Read scale: S_s

17)
$$W_a = S_{a'} - S_{b}$$

 $W_a = M_1 + (S_{a'} - S)$

- 18) Arrest beam
- 19) Remove M₃
- 20) Remove W_a and add W_b ($\simeq M_1$)
- 21) Release beam
- 22) Read S_b

$$W_{\rm b} = (S_{\rm b} - S_{\rm o})$$

- 23) Arrest beam
- 24) Add M₁
- Release beam
- 26) Read S_b'

$$W_{\rm b} = M_1 + (S_{\rm b}' - S_{\rm o})$$

- 27) Arrest beam
- 28) Add Wa
- 29) Dial up $M_2(\simeq 2M_1)$
- 30) Release beam
- 31) Read S_c

$$W_{\rm a} + W_{\rm b} = M_2 + (S_{\rm c} - S_{\rm b})$$

32) Now:

$$M_2 = (S_c - S_o)$$

$$W_a = M_1 + (S_a' - S_o)$$

$$W_b = M_1 + (S_b' - S_o)$$

$$M_2 + (S_c - S_o) = W_a + W_b = 2M_1 + (S_a' + S_b' - 2S_o)$$

and hence

$$M_2 = 2M_1 + (S_a' + S_b' - S_c - S_c)$$

It is always necessary to examine the way in which the removal of interval weights from the beam is related to the dial readings. For example the Mettler H5 balance has the weights: 1, 1, 2, 5, 10, 20, 40, 80 g. The Mettler H10 has 1, 2, 3, 6, 10, 10, 20, 40, 80. It is important to order the measurements so that the proper intercomparisons are made. By the careful choice of dummy weights and their combinations all the weights can be expressed in terms of each other and some (small) term in optical scale units. This latter can, of course, in its turn be expressed in terms of M_1 if desired. Usually the error in the optical scale makes only a small contribution to the error in determining the relationship between the weights, but it can make a significant error in an actual weighing.

A logical extension of the procedure described in steps 1-32 is used to deal with all the other weights. Finally all weights can then, if desired, be expressed as fractions of the largest weight in the set which is the one likely to have the smallest percentage error.

As has been pointed out in the text, if all weighings for a chemical experiment are done on the same halance there is usually no case for requiring anything other than a linear mass scale because gravimetric chemical experiments are concerned with the ratios of masses at various stages of the experiment.

Qualitative Analysis, with Periodicity, for "Real" Solutions

Ronald L. Rich

Bluffton College, Bluffton, OH 45817

The outline of group separations for a non-H₂S analytical scheme applicable to all metallic elements is presented here, along with an outline of an abbreviated and otherwise modified version designed for some emphasis on nutritionally important metals, with special attention to 10 cations. The more complete scheme will be referred to as the Bromide Scheme and the shorter one as the Iodide Scheme. A survey of the relevant literature from about the last 50 years is included.

Major Features

One problem in basing teaching on systems of qualitative analysis is the incomplete correlation between membership of an element in an analytical group and its position in the periodic table. As stated by Sorum and Lagowski (1),"... since the periodic table provides the best available organized picture of the properties of the elements and their compounds, we should expect the periodic table to serve as a useful guide in many phases of qualitative analysis." The Bromide Scheme is partly the result of a long effort to accentuate that usefulness.

Another problem with qualitative analysis has been the interference of various organic and inorganic substances. Even phosphate causes the calcium (carbonate) group, in standard systems, to precipitate too early. Citrate, sugar, EDTA, and polyphosphates are a few of the common ligands that can prevent precipitation of the aluminum (hydroxide) and other groups. Bromide and iodide can prevent precipitation of some sulfides, even that of mercury. As a result we either dispense artificial unknowns without these important substances, or include tedious ways of dealing with them. Students can still learn a great deal, perhaps even because of this, but one value of the Bromide and Iodide Schemes is that each can overcome most, though not quite all, of these difficulties.

Presented at the 6th International Conference on Chemical Education, College Park, MD, August 9–14, 1981, and at the 7th Biennial Conference on Chemical Education, Stillwater, OK, August 8–12, 1982. Many basic ligands, such as carbonate, coordinate to metallic cations, just as water does, through oxygen atoms. It is therefore not surprising that nonchelating oxy-ligands that can displace water from some cations will probably react with most of them. This leads to poor selectivity for initial separations. We do well to start, consequently, with reagents acting through (nonmetallic) atoms far from oxygen in the periodic chart and correspondingly different chemically. (Even nearby chloride, in the standard procedures, removes several of the few metals in the first group quite incompletely.) A good general strategy, then, is to use oxy-ligands, and perhaps fluoride, only after many metals have been removed from unknowns by means of more polarizable and selective reagents, such as bromide and iodide.

Figure 1 outlines the main Bromide Scheme separations. Figure 2 shows the resulting organization of the periodic chart. The numbers are analytical group numbers. Mn, Fe, Co, and Ni, for example, are in Group 2. The numbers with asterisks designate the nonmetals that coordinate directly to the cations in the corresponding groups. The 2* over N, for example, shows that the N atoms in cyanocobaltate are directly attached to the precipitated cations in Group 2. The Iodide Scheme outline is in Figure 3. We note that the simplified procedures of Figure 3, without solvent extraction, put Zn into analytical Group 2 rather than Group 1.

Any specific set of directions raises the question of using a cookbook approach. This author also preaches and claims to practice a strong emphasis on thinking. We should certainly recognize, though, that students need the most help at the beginning of any systematic analysis, partly because they then have to work with the largest number of potentially present metals. Readers will see some of our ways of dealing with this. We may add that the proper and improper use of fixed instructions is not confined to qualitative analysis.

Additional comments and procedural details are available. Expensive reagents have been avoided, but information on costs per unknown is also available. (See summary.)

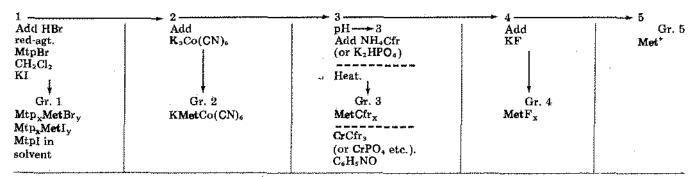


Figure 1. Group separations in the Bromide Scheme.

After each group precipitation (or solvent extraction) the remaining aqueous solution is treated by the next procedure to the right. The resulting precipitates and extracts are shown below the corresponding procedures.

Notes: The reducing agent, red-agt., can be ascorbic acid. Mtp is methyltriphenylphosphonium. Met is a metal in the group. Of is cupferrate

Bromides of Ge, As, and Se can be distilled out (2) as Subgroup 1a before extraction of the bromo-complexes in Group 1 (or 1b), for which the [HBr] is made 3

The Role of Organic Reagents

One notable feature of Figure 1 is its inclusion of some organic reagents. Does this mean that the student is overwhelmed with rote procedures and "incomprehensible" reactions? By no means! Since that may be a misleading first impression, however, let us briefly discuss the role of organic reagents in this work before we go further.

Dimethylglyoxime and aluminon are accepted almost universally in confirmatory tests. More recently thioacetamide and benzoate (3) also have been accepted as group reagents. One criterion for adopting each group reagent in the present case has been that it can be interpreted to students.

A reducing agent is needed in procedure 1, especially for Fe(III) and Cu(II). Ascorbic acid works well and is widely known. Its structure is a bit complicated, but the active part is quite comprehensible. Its formula is easily remembered if written as $H_2C_6H_6O_6$. Mercaptoacetic acid is also effective, very simple structurally, and not too malodorous. The inorganic reductants sulfite and hypophosphite could be used, in fact, but the oxidized products could then precipitate some metallic ions from later groups. (The original presence of sulfate and phosphate in unknown solutions is perfectly acceptable, however, since incompatible cations obviously cannot also be present.)

To help extract the bromo-complexes into methylene chloride we can use a large cation (Cat⁺ in Table 5) in a moderately priced salt. Methyltriphenylphosphonium (Mtp⁺, $CH_3(C_6H_5)_3P^+$) can be viewed as an analog of ammonium ion. Unlike some specific organic reagents, but like the reductants just mentioned, its effectiveness is largely independent of any mysterious details of structure. The students should already have encountered the benzene ring.

Cyanocobaltate is similar to the well-known cyanoferrates and is scarcely organic. It also lacks the toxicity of cyanide (4). Cupferrate, C_6H_5 — N_2O_2 — (not quite a nitrosamine), should be considered as simply a phenyl derivative of the hypomitrite ion, $N_2O_2^{2-}$. Moreover, students can benefit here from learning about a reagent important in practical analysis. Phosphate, however, can be substituted for cupferrate for most, hut not all, members of this group (not vanadium). It also is used at a pH of 3 (hot) but is somewhat less effective in competing against interfering chelating agents.

For separations within the groups we have used a great variety of procedures, but always with few organic reagents. Both thioacetamide, widely used in sulfide systems, and cupferrate are suspected as possible mild carcinogens. We might note that zinc salts (required nutrients) also have been so classified (5). Whether methylene chloride poses any similar significant health hazard at all is disputed, but it certainly does so less than chloroform (6). In any case, we can probably use other cationic extractants with other solvents. Our remaining reagents appear to call for no unusual concern.

Periodicity

Figure 4 shows the distribution of elements in a common form of the bydrogen-sulfide analytical scheme. This reveals clearly the problems of explaining the relationships among the traditional analytical groups. We must also recall that even the inter-group boundaries shown are further drastically modified if unknowns contain various common interfering substances.

Several points in partial defense of the sulfide scheme, however, are needed for a full and fair appraisal. The HCl precipitation of Ag, W, Hg, Tl, and Pb could be omitted, especially since the last three are not completely removed anyway, and these metals would then be well-behaved members of the acid sulfide group (7-9). The lodide Scheme produces a somewhat similar first group, but it does remove Tl and Pb essentially completely from solution, and it puts Cu, Ag, and Au together. This scheme is not ready at present, however, to handle all the metals in the periodic table.

We can illustrate the pedagogical value of periodicity with one condensed interpretation: The heavy-metal cations on the right side of the periodic chart, compared to the cations on the left, have large nuclear charges, and large effective (poorly shielded) nuclear charges. These act on the loosely held, easily polarizable electron clouds of large negatively charged atoms such as Br⁻ and I⁻, and bind them relatively strongly (10). In our analytical Group 1 we thus have such reactions as:

$$Cd^{2+} + 4 Br^{-} \rightarrow CdBr_{4}^{2-}$$
(or $Cd[H_{2}O]_{n}^{2+} + 4 Br^{-} \rightarrow CdBr_{4}^{2-} + n H_{2}O$)
$$CdBr_{4}^{2-} + 4 T^{-} \rightarrow CdI_{4}^{2-} + 4 Br^{-}$$

Such qualitative considerations, taken alone, are sometimes fallible and they may at times have to serve only as rationalizations. Yet they connect us with fundamental causes in a way that is possible neither with the more precise language of thermodynamics, which demands the prior measurement of quantities similar to those to be predicted, nor with the upper reaches of quantum mechanics, which would elude most beginning students.

A discussion of this sort, deepened, qualified, and broadened, can give the student an idea of what to expect for any element, without a detailed study of each one. When, on the

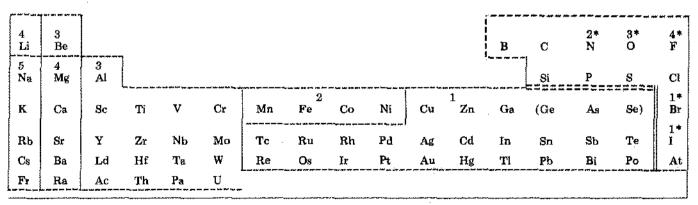


Figure 2. Groups in the Bromide Scheme.

Ld = tanthanoids or rare earths.
Groups separated:

2. Cyanocobaltates, approx. KMet[Co(CN)_e]

- 3. Cupferrates: MetCfr_x; MetO_yCfr_x. (Or phosphates.) Cfr \equiv C₆H₅ \rightarrow -N₂O₂.
- 4. Fluorides, MetFx.
- 5. (Soluble).

¹ Methyltrioctylammonium ion, i.e. CH₃(C₈H₁₇)₃N⁺, appears at this writing to be at least as effective if used es an extractant in CH₃CCl₃ or disobutyl ketone. However, it has not yet been tested thoroughly. Hexadecyltrimethylammonium appears likewise to be an excellent precipitant. The author would welcome collaboration on further testing.

Mainly bromo-complexes, MetBr_x^{y--}; Metl_x^{y--}; Met.

other hand, the membership of several analytical groups appears to be distributed somewhat randomly around the periodic table, even in the absence of interfering agents, useful correlations may seem less convincing to students.

Soon enough, of course, we must introduce the other part of the real world, the exceptions. But this may be more effective if we can show first that some generalizations do work fairly well in practice.

In the present schemes Mn, of the "common" elements, is slightly exceptional. Small amounts of it, less than millimolar, remain after separating Group 2. These do not interfere subsequently, and they are much less than the amounts of Tl, Pb, and Hg(II) left after the usual chloride group, but they might justify assigning Mn partly to our Group 5. At that point they could be removed with Fe(CN)₆⁴⁻⁻. In the Iodide Scheme, Zn behaves similarly.

No tests have been done with Po, Fr, Ra, Ac, Pa, the trans-uranium elements, or some rare earths. The other rare metals including Tc, however, have been checked experimentally at least to a limited extent. The general literature contributes to confidence about the unchecked group classifications.

Interference

Interfering species can be classified as basic and non-basic (with respect to H⁺). Bromide and iodide ions, which can prevent the precipitation of various sulfides, are non-basic. High levels of acidity, such as required for separation of the first sulfide group from the others, therefore do not inhibit this interference. One thing we can do, however, is to follow the rule, "If you can't lick 'em, join 'em," as we have done here by

using both bromide and iodide. (Cyanocobaltate is also non-basic, but does not interfere in the sulfide schemes.)

Various interfering, basic, organic and inorganic ligands, on the other hand, can be inactivated with high concentrations of hydrogen ion. Unfortunately, however, some desirable precipitants are also inactive in acidic solution. Still, we can exploit some basic reagents, such as cupferrate and fluoride (3), for which the metal ions remaining in solution can nevertheless compete against high or moderate acidities. The net result is that we can use acidic conditions throughout our schemes to eliminate most sources of interference. (Oxalate can still precipitate calcium prematurely in Group 3. Bromate can be added, however, to oxidize some HBr to bromine, which, when hot, destroys oxalate.)

We tested the effectiveness of this approach. Half of a class of 36 students (at International Christian University in Tokyo) received the usual variety of unknowns. The other half received the same unknowns, but with half the water consisting of filtered orange juice. There was no difference at all in the accuracy of results.

This was the only test of this sort, however, partly because the possible variety of such unknowns is limitless. It seems preferable to continue the exploratory checking of many potential improvements than to concentrate too much on any one version, which we expect to supersede anyway. Students benefit by knowing that this is not a finished science. We have nevertheless done great numbers of tests on synthetic mixtures, checking each of a large variety of "interfering" substances with metals that might be problematic. Difficulties that arose in earlier versions appear to be largely solved.

How does the students' accuracy, using "realistic" un-

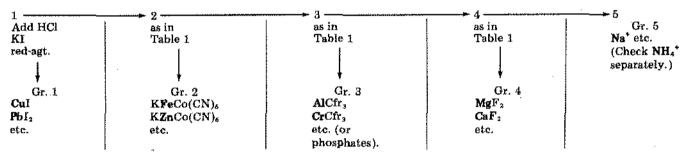


Figure 3. Group separations in the lodide Scheme.

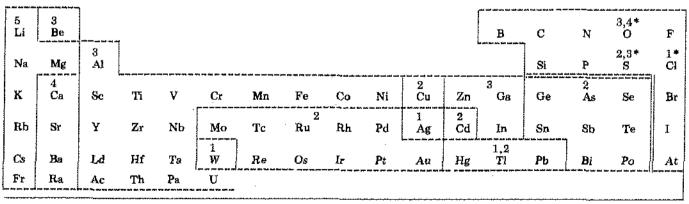


Figure 4. Groups in the H₂S Scheme.

Ld = lanthanoids or rare earths.Groups separated:

- Chlorides; tungstic acid.
- Sulfides.
- 3. Sulfides; hydroxides.
- Carbonates.
- 5. (Soluble).

Ci-a		.	^b H₂S¢			d NH3	HS	-c	HCO,	- e	Cl	assical Schen	ne, Modern Fortns
HBr distill e	tc. Br		H ₂ S			NH ₃	нѕ	-	нсо,	-e			(2)
C1-	Cl-		H₂S			NH ₃ H	PO42-	HS-	CH,C	O ₂ H C ₂ O ₄	?-a		(11, 12)
Cl-	CH ₃ C	0,-	H₂S¢	SO ₄ 2-	C2O42-	NH ₃ H	PO ₄ 2-						$(13)^f$
H' ^g HSO ₄	Ag+g	C1	H,8						CO3 2-8				(14)
CI-			CO ₃ ²⁻		OH-	S2	HCI		CO32-	нсі сн₃с	O2-	.HCO3 etc.	(15)
C1-			NH₃/HC	O3-4	•	HS"/S _x	2 C		SO ₄ 2-	oxy-anto			(16-18), (19)
Cl.			SO ₄ 2-a	S ₂ O	32-	NH ₃ HCO ₃ - OH-			(20, 21)				
Ci-	I- Ag		H8O₄-e	H₂S		NH ₃ et	e. HS	-					(22)
Cl.			HSOe	H₂S	c	NH ₃ /ox	y-an ⁱ /	OH-					(23-25), (26)/
Cl ⁻			HSO4	H₂E	DTA ^{2-k}	H₂PO.	Он	- S2-	Н⁺ Ң₂	Sc			(27) ^f
HNO₃-evapo	ratea	CI-	HSO₄ ^{−a}			NH ₃ oxy-an ⁱ /OH-				(28-32)			
CI HNO3-6	aporate	,a	HSO₄ ^{−e} ,	a		он- с	O ₃ 2-a	H' N	H ₃ ox	y-ani/HS-e			(33-39), (40-42)f
NaNO, NaO fuse!	H Na₂C	0,	н• сн₃с	O ₂ ~		NH ₃			нсо,	-	OH.		(43)m
Cl-			СН₃СНО	НСО₁Н Н₂	PO₄-	NH3			SCN-	C₅H₅N (pyı	idine	1)	(45)
Cl~			CH₃CO₂	_		80 ₄ 2- <i>e</i>			OH-				(46)
Ct-	I · (47)		RCO, ""	······································		F-			он-				(3, 47, 48), (49)
HBr-Cat	p,a ₁ -	Co(C	CN) ₆ 3- C	6H5N2O2H/	H₂PO₄-	HF				В	romic	de, lodide ^j S	chemes

Figure 5. Actual key reagents in various major-group separations.

knowns, compare with the results, for conventional unknowns, from the sulfide scheme? The last class, 35 students, using the Bromide Scheme had perfect results for 6 out of the 8 metals studied. (Group 5 was omitted.) Any judgment is difficult, however, because we haven't made extensive comparative studies, because there are many varieties of the sulfide scheme, because the Bromide Scheme also is still being improved, and because the interest generated by any novelty may provide a temporary advantage.

Optimization of the Bromide Scheme, incidentally, ought to take longer than that of traditional ones, and provide more opportunities for student research, while possibly yielding technically better results, because there are more variables in the most crucial group separation. Corresponding to the former choices of precipitant (sulfide) and pH (to control its concentration), we have the choices of ligand (bromide), cationic extractant, solvent, and concentrations of the first two.

The lodide Scheme

Most American schools allow limited time, if any, for qualitative analysis. Some extra attention will therefore be given now to a short version, recently devised, which focuses on 10 cations (in Figure 3). In each of the five groups just two cations are selected for possible use in students' unknowns. (The selections can be varied occasionally, or from student to student.) This obviously shortens separations within the groups. In fact, we can give the students some information on chemical properties and let them devise separations and identifications for each pair. One way is to give a list of chemical equations (available from the author) as a starter. The absence of the unpleasant hydrogen sulfide in group separations, incidentally, is no reason to exclude completely sodium sulfide, for example, from every later separation.

Our list of 10 ions was chosen to emphasize somewhat those which are important in our nutrition. Na, Mg, Ca, Cr(III), Fe,

^a Omitted in some cases.

b : represents a phase separation omitted in some schemes.

 $^{^{\}circ}$ Or CH₃CSNH₂, C₂H₅OCS₂ $^{+}$ (24), or S²⁺ + H⁺, etc.

^d Various oxidants and reductants used here and elsewhere are omitted for simplicity.

^{*} Plus C₂H₅OH in some cases.

^f Give(s) considerably less interference.

With removal and analysis of volatile acids (initially) or other anions.

h X/Y means X and/or Y, sometimes with phase separation(s).

¹ Basic oxy-anions: HCO₃**/CO₃^{2**}/H₂PO₄**/HPO₄^{2**}.

For only 10 or fewer metals.

 $[^]k\,C_2H_4\big[\text{NH}^+(\text{CH}_2\text{CO}_2^-)_2\big]_2.$

Fusion destroys organics well but vaporizes Hg; several separations are incomplete; uses CH₃CSNH₂ on the fusion solution, Or fuse KNO₃ KOH K₂CO₃ (44).

^m Claims to perjodicity are questioned.

[&]quot; C6H6CO2"/CH3CO2"/0-C6H4(CO2")2 (48).

O HBr distill (only for Ge, As, Se); normally omitted.

P See text.

Cu, and Zn are essential metals. Pb, and potentially Cr(VI), is included as a poison. Even with our environmental concerns, or because of them, students ought to have some scientific acquaintance with toxic elements, especially one that they meet every day on the streets. The Bromide and Iodide Schemes can handle low concentrations of the dangerous heavy metals, and it is recommended to dispense them at the millimolar level. In this way the dangers of handling them, which may have induced some professors to omit qualitative analysis entirely, are greatly reduced. The solvent extraction in the Bromide Scheme could, unlike ordinary precipitation. separate even individual hazardous atoms from the aqueous solution for possible detection by special methods.

To study some other toxic elements, e.g. cadmium, we can simply precipitate (or extract) Mtp₂CdI₄, for example.

Other Schemes

We are at last seeing in this country a resurgent recognition of the teaching potential in qualitative analysis, and various systems are proposed. Sometimes, however, the wheel is reinvented, and too frequently without acknowledgment of the earlier contributions. (Normally, of course, some modifications are made.) Also, a look at the relationships of the present schemes to the others may help put all of them into perspective. Figure 5 is therefore presented as a condensed survey, mainly of the last 50 years, and mainly of non-H₂S systems unless other features have special interest. Some schemes are omitted where later improvements by the same authors are included. Also omitted are many non-H2S schemes using other sulfur compounds with rather similar results. Systems showing substantially improved periodicity are rare, but various approaches toward somewhat less interference are available as listed, even without the tedious classical procedures.

The order of listing in Figure 5 depends more on similarity than on chronology. The main reagents for the separation of each major group, usually as precipitates but sometimes as a solution, are shown in successive boxes from left to right,

Generally, only the predominant species of a reagent in solution is shown here, partly to reveal essential similarities. Thus, in acidic and sometimes alcoholic solutions where some writers call for H₂SO₄, others call for (NH₄)₂SO₄; both, represented here as HSO₄-, actually yield mainly HSO₄- (or SO₄²⁻, depending on the exact conditions). And in solution the usual "(NH₄)₂CO₃" is really mostly NH₃, NH₄+, HCO₃-, and CO₂NH₂- with HCO₃- actually providing most of the carbonate ions used for precipitation. The representation chosen here also gives useful information about pH; H₂PO₄-, for example, is known to predominate at pH's from 2 to 7.

Many fascinating papers depend heavily on spot tests, various sorts of chromatography, etc., but these sometimes bypass pedagogically valuable chemistry and they are slighted here, though several such techniques can well be presented as parts of any broader system. Some of the most original ideas listed in Figure 5, by the way, have appeared in relatively obscure journals.

A few additional papers, excluded from Figure 5, will be mentioned here. Cr₂O₇²⁻ has been used to separate the elements of sulfide groups II and III (50). Reducing agents may also be used to precipitate members of the sulfide groups, as with reagent Mg (51), Al or Zn (52, 53), or with the product of the reaction of $S_2O_4^{2-}$ and HCO_2H (54); also see (22). Another interesting non-H2S approach uses a separate portion of unknown solution for each group of cations, but sometimes with separate preliminary removal of the same (non-member) cations from the various portions (55).

A survey of methods applied to the alkaline earths is one article (56) in a valuable series especially on classical qualitative analysis. A Dutch book (57) includes a detailed summary of four non-H2S methods (for cations), two of which are outside the scope of this article. The others (15, 52) have been touched on here.

Three of the many papers on solvent extraction seem particularly interesting and/or useful: one on inorganic complexers plus quaternary ammonium extractants (58), one on halides and organic chelons for separating 18 groups (59), and one on 5 chelons for 8 groups (60). Separations can be done in acetic acid instead of water, with, for example, CH₃COCl to precipitate an enlarged group of metallic chlorides (61).

Finally, we should note some cautions about the reliability of published qualitative analytical data (62).

The Bromide Scheme now proposed begins with the solvent extraction of a group of bromo-complexes from a highly acidic solution, with several major and minor advantages. Teaching is promoted because the analytical groups make sense in the periodic table. Realistic unknowns can be used because most organic and inorganic "interfering" substances no longer interfere. The need to look for some elements in two different groups is reduced, and H2S is not needed. Some attention is given to handling small amounts of the more toxic elements. Students have good exposure to complexation, solvent extraction, and such a practical analytical reagent as cupferron. They may also have more opportunity to make significant improvements in the scheme.

The goals pursued here have been under exploration for several decades, but their expression in the Bromide Scheme is only about 10 years old, and this lack of experience is a disadvantage. Also, some reagents are currently unfamiliar to beginning students. Of the few organic compounds used in group separations, however, none is specifically required and none depends for its essential function on any impenetrable structural complexities.

The Iodide Scheme is a more recent, somewhat simplified form, without initial solvent extraction, and not developed for all the metals. Students may be asked to work out separations for a pair of elements within each of the five groups. Elements important in nutrition may be emphasized.

Some further information is available from the author. Please send \$2 for expenses.

Acknowledgment

Special recognition for major contributions must go to the late Charles Kauffman and to John Buhr and Yung-Kuo Chao, former students at Bethel College, North Newton, Kansas, as well as to Albert Sun-Chi Chan and Tai-Wai David Chan, former students at International Christian University, Mitaka, Tokyo, Japan. The author also carried out parts of this work at the Universities of Kansas and Illinois, at Harvard and Stanford Universities, and at home and Bluffton College. H. W. Berky at Bluffton suggested the original project.

Literature Cited

- Sorum, C. H., and Lagowski, J. J., "Introduction to Semimicro Qualitative Analysis,"
 5th ed., Prentice-Hall, Englewood Cliffs, NJ, 1977, p. 121.
 Noyes, A. A., and Bray, W. C., "Qualitative Analysis for the Rare Elements," Macmilian, New York, 1948, pp. 8, 12, 16-17, 37-39.
 West, P. W., and Vick, M. M., "Qualitative Analysis and Analytical Chemical Separations," Macmilian, New York, 1959, p. 18.
- (4) Rich, R., J. CHRM. EDUC., 39, 403 (1962).
- Melnikow, J., Keeffe, J. R., and Bernstein, R. L., J. CHEM. EDUC., 58, A12 (1981); NIOSH, "Suspected Carcinogens," 2nd ed., Pub. #77-149, US Dept. HEW, Washington, 1976.
- (6) Carlton, T. S., J. CHEM. EDUC., 59, 530 (1982).
- (7) Gelbach, R. W., J. CHEM. EDUC., 10, 621 (1933).
- (8) Scherer, G. A., School Sci. Math., 59, 540 (1980).
 (9) Swift, E. H., "A System of Chemical Analysis," Prentice-Hall, Englewood Cliffs, NJ,
- 1939, p. 197.
 (10) Rich, R., "Periodic Correlations," W. A. Benjamin, New York, 1965, Chapter 8.
- (11) Scheinkmann, A., Z. anal. Chem., 91, 415 (1983).
 (12) Kreshkov, A. P., J. Gen. Chem. (USSR), 2, 593 (1932).
- (13) Cornog, J., "Semimicro Qualitative Analysis," Houghton Mifflin, Boston, 1948.
 (14) Saredo, J. F., Anales asoc. gaim. farm. Uruguay, 51, no. 2, 58 (1951); Anales fac. gaim. y farm., 4, 123 (1955).
- (15) Vortmann, G., see Chem. Abstr., 16, 2458 (1922).
- (16) Serbinovskaya, E. L., see Chem. Abstr., 49, 3731b (1955).
 (17) Mesnard, P., Colleter, J. C., and Bernard, H., Butt. Soc. Pharm. Bordeaux, 109, 185

- (18) Baudot, P., Monal, J. L., Lejaille, M. F., and Martin, J. A., Sci. Pharm. Biol. Lorraine, 1, 121 (1973).
- (19) Rathnamma, D. V., J. CHEM. EDUC., 57, 287 (1980).
- (20) Defrance, E., J. pharm. Belg., 13, 771 (1931).
 (21) Tougarinoff, B., J. pharm. Belg., 15, 223 + preced. (1933).
- Henry, A. J., Analyst, 89, 255 (1964).
- (23) Chao, T. P., and Hwang, S. C., J. Chinese Chem. Soc., 8, 21 (1941).
 (24) Wenger, P., Duckert, R., and Ankajdi, E., Helv. Chim. Acta, 28, 1592 (1945).
- (25) Galmés, P. J., Afinidad, 28, 154 (1951).
 (26) Poonia, N. S., and Bhagwat, V. W., Mikrochim. Acta, 1969, 1008.
- (27) Arribas Jimeno, S., and Alvarez Bartolomé, M. L., Inform. Quim. Anal., 17, 145
- (28) Eichlet, H., Oesterr. Chem.-Ztg., 39, 185 (1936).

- (28) Bictitet, H., Oesterr. Chem.-Leg., og., 180 (1800).
 (29) Petraschenj, W. J., Z. and. Chem., 106, 330 (1936).
 (80) Rane, M. B., and Kondaiah, K., J. Indian Chem. Soc., 14, 46 (1937).
 (81) Khoroshkin, M. N., Acta Univ. Voroneg., 10, no. 4, Sect. Chem., 95 (1939).
 (82) Okáč, A., Pubs. faculté sci. univ. Masaryk, no. 311, 25 pp. (1948).
 (83) Brockman, C. J., "Qualitative Analysis," Ginn, Boston, 1930.
 (84) V. J. J. D. J. J. J. L. B. 202 (1908).
- (34) Lewin, A. B., Z. anal. Chem., 105, 328 (1936).
- (35) Valente de Couto, A., Quim. e ind. (São Paulo), 8, 1601 (1940).
- (36) Beskov, S. D., and Slizkovskaya, O. A., see Chem. Abstr., 46, 1911g (1952). (37) Cornog, J., "Semimicro Qualitative Analysis," Houghton Mifflin, Boston, 1961.
- (38) Handler, B. L., Cook, R., and Siemiencow, G., J. CHEM. EDUC., 59, 333 (1982).
 (39) Matsuoka, K., J. Nippon Univ. School Dentistry, 5, 157 (1963).
 (40) Gerstenzang, E. M., J. CHEM. EDUC., 11, 369 (1934).
- (41) Zelada, F., Anales asoc. quim. argentina, 30, 29 (1942).

- (42) Bianchi, F., Arch. farm. bioquim. Tucumán, 5, 263 (1951).
 (43) Swift, E. H., and Schaefer, W. P., "Qualitative Elemental Analysis," Freeman, San Francisco, 1962.
- (44) Nagami, S., and Kato, T., J. Chem. Soc. Japan, 53, 237 (1932).
 (45) Dobbins, J. T., and Gilreath, E. S., J. CHEM. EDUC., 22, 119 (1945).
 (46) Prokopov, T. S., Mihrochim. Acta, 1976, 694.
- (47) Johar, G. S., Sci. Res. News., 1, 135 (1979).
 (48) Lumme, P., and Tummavuori, J., Acta Chem. Scand., 27, 851 (1973).
- Lambert, J. L., and Meloan, C. E., J. CHEM. EDUC., 54, 249 (1977)
- (50) Efros, S. M., and Golynko, N. Z., see Chem. Abstr., 49, 5210g (1955).
 (51) Rosenthaler, L., Pharm. Acta Helv., 19, 95 (1944).
- (52) Schoori, "Qualitatieve Analyse der Metalen zonder Toepassing van Zwavelwaterstof," D. B. Centen's, Amsterdam, 1941, (53) Kiba, T., J. Chem. Soc. Japan, 70, 323 (1949).

- (64) Virgilio, G., Izv. Akad, Nauk SSSR, Ser. Khim., 1964, 2245.
 (55) Lipchinski, A. P., Godishnik Khim. Tekhnol. Inst. (Sofia), 1, 59 (1954); oversized flow charts facing p. 126; Russ. summary, p. 128.
- (56) Jones, W. F., Mikrochim. Acta, 1967, 1004. (57) Van Nieuwenburg, C. J., and Van Ligten, J. W. L., "Kwalitatieve Chemische Analyse," D. B. Centen's, Amsterdam, 1951.
- (58) Maeck, W. J., Booman, G. L., Kussy, M. E., and Rein, J. E., Anal. Chem., 33, 1775
- Toolg, G., Z. anal. Chem., 190, 161 (1982).
- (50) Chalmers, R. A., and Dick, D. M., Anal. Chim. Acta, 31, 520 (1964).
 (61) Hardt, H. D., and Eckle, M., Z. anat. Chem., 197, 160 (1963).
- (62) Belcher, R., Analyst, 99, 802 (1974).

profiles in chemistry

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School of Education, Box U-33 The University of Connecticut Storrs, CT 06268

Jean Rey: Unsung Prophet?

Sidney Rosen

341 Astronomy Department University of Illinois Urbana, IL 61801

In January 1775, Antoine Lavoisier sent to the Academie des Sciences in Paris his now-famous memoir on the calcination of metals that was to reduce the phlogiston theory to ashes in the history of science. Two months later, another chemist wrote a letter to the Academie, pointing out that Lavoisier's solution to the question of what happens when a heated metal becomes a calx had already been suggested some 145 years earlier (1).

That second chemist was Pierre Bayen, Apothecary to the King's Army; the person to whom he referred was a 17thcentury French physician named Jean Rey. On the first of January 1630, a little book, privately printed, had appeared in the Bordeaux area of southwest France. The title was rather long: "Essays by Jean Rey, Doctor of Medicine, on the Search for the Cause of the Increase in Weight of Tin and Lead when they are Calcined." Within its 144 pages were 28 short es-

Not much is known about Jean Rey's life. He was born about 1582 in the little town of Le Bugue, the son of a greffier (one who collected taxes from lands put in his name and farmed). Jean's parents died when he was a boy, and he was raised by his elder brother. In 1609 he graduated from the University of Montpellier with an M.D. degree and set up a medical practice in his home town. Rev was, apparently, considered an excellent physician; there is a record of his having been requested to visit a noble patient at Toulouse, about a hundred miles away. It is supposed that Rey died in 1645, but the year is not certain (1).

While there is little evidence that Rey was a practicing alchemist, he was most certainly acquainted with the language

"Profiles in Chemistry" is a biographical feature, highlighting the contributions of distinguished chemists in the context of their lives. The column is designed for curriculum enrichment, allowing the secondary school teacher to enhance the vitality of chemistry with the sense of scholarship and adventure shared by chemists throughout history.

and arcana of that profession. By 1600, alchemy in Europe was almost completely under the influence of the followers of Paracelsus. The abstract concepts of Salt, Sulfur, and Mercury had been added to the original Aristotelian elements: Earth, Wøter, Air, and Fire.

Nowhere in his book does Rey admit to doing the actual experiments of calcining tin and lead and measuring changes in weight. The essays are introduced by a letter to Rey from Monsieur Brun, an apothecary from Bergerac, who had done the experiments and who essentially challenged Rey to provide an explanation of the results. Brun heated 2 lbs 6 oz of the purest English tin (from Cornwall) in an iron container for 6 hr; upon weighing the resulting white calx, he found 2 lbs 13 oz. Doing the same experiment with 6 lbs of lead, Brun found the calx diminished in weight. "I beg of you in all affection," Brun ends his letter, "to go to work on the cause of such a rare effect; and I will be wholly obligated if, by your means, this marvelous result is made clear to me" (1).

The first 15 essays are devoted to proving that the element Air has weight. The basic argument used by Rey is that Air is composed of parts of different densities. Upon heating Air, the lighter densities are driven off, leaving the denser parts of the element around the metal which is being transformed into a calx by the same heat. Rey's arguments tell us that he was quite familiar with alchemical equipment, procedures, and language (2).

The point of this discussion becomes clear in Essay 16, where Rey points out that the reason the calx is heavier than the original tin metal is that during the heating process, the denser, and therefore heavier, air in the alchemical furnace adheres physically to the already formed calx. He uses the analogy of water making sand heavier by moistening and clinging to each grain (2). While Rey's explanation is made in physical terms, rather than chemical, it was close enough to the truth to interest a famous contemporary French intellectual, Father Marin Mersenne, and later to influence Lavoisier.

In his first paper presented to the Academie, Lavoisier made no mention of Rey. However, after her husband's death, Mme. Lavoisier published a memoir in which Lavoisier writes that the discovery and reading of Jean Rey's sixteenth essay had some influence upon his thinking (1). It seems amazing that Rey's book should have been ignored for so many years; however, it was published without the privilege du roi and apparently in small quantity. Thus, even though Professor Spielman, a chemist at the University of Strasbourg in 1770, recommended Rey's book to his students, the chances are that they were unable to find a copy available (1). Another reason for the eclipsing of Rey's work may have been the publication in 1673 of Sir Robert Boyle's "Essays of Effluvium." In this work, Boyle proposed that the gain in weight of a calx was caused by the absorption of "corpuscles of fire" passing through the walls of the sealed container in which the calx was formed. Boyle's explanation became widely accepted; undoubtedly, the popularity of Isaac Newton's view of both light and matter as "corpuscles" helped.

In his last essay, Rey makes it quite clear that Brun's result (in which the calx was lighter) is inaccurate (as the book title indicated). Rey declares that the experiments of other well-known alchemists (he names Cardan, Scaliger, and Caesalpinus) bear out the conclusion that the calx of lead gains weight just like that of tin (2). Rey proposes that M. Brun made the error of using impure lead and that the loss of weight was caused by vaporization of the impurities (2).

There are extant two letters to Jean Rey from Father Marin Mersenne, the intellectual priest who gathered scientific pen-pals like flowers from a garden. In the first letter, dated 1631, Merseene mentions having read the "Essays" and goes off on a wide tangent, discussing Copernicus and Giordano Bruno. Eventually he gets around to discussing the idea of Air having parts of different densities. Rey answered Mersenne the following year (hut six months later); in his letter, Rey describes a thermoscope he had invented to measure temperature (Galileo was inventing one in Italy, too). Rey's thermoscope consisted of a glass bulb with a long hollow neck. The bulb was filled with water and the temperature of a substance was measured by observing the expansion of the water.

Rey's thermoscope was closer to the modern thermometer than Galileo's, which used a column of air.

Mersenne replied to Rey's letter a few months later, but Rey did not answer until March of 1643, eleven years later! His letter apologized for the delay, which he blamed on domestic troubles. Mersenne had already published in 1632 an approval of Rey's essays in a book entitled, "Les Questions Theologiques, Physiques, Morales, et Mathematiques" (1).

Looking back, it seems amazing that the hypothesis of phlogiston, proposed by George Stahl in his "Fundamenta Chymiae" (1700), should have gained such popularity. Stahl got the idea of a principle of burning from his teacher, Joachim Becher, who invented the term, terra pinguis—the combustible element. But the evidence that was to give the phlogiston theory the kiss of death was already available! Yet the major chemists of the 18th century tended to ignore that evidence for over 75 years, even after Pierre Bayen brought Rey's essays to their attention in 1775. Of course, the path to the formulation and acceptance of oxygen theory was a long and difficult one. Even Lavoisier's tight-knit evidence was not immediately accepted by all chemists. Joseph Priestly died in 1804, a self-exile in America, still believing in phlogiston and still calling oxygen "de-phlogisticated air."

In his classic "History of Chemistry," F. J. Moore mentions Jean Rey in a footnote that concludes: "No one who reads this charmingly written and amazing paper]... will be likely to believe the author capable of making any serious discovery" (3). While Moore's evaluation of Rey may be well-founded, Jean Rey's work remains as a reminder of how easily clues to scientific truths can be overlooked.

Literature Cited

- (I) McKie, Douglas, "The Essays of Jean Rey," Edward Arnold, London, 1951.
- (2) Rey, Jean, "The Increase in Weight of Tin and Lead on Calcination," Alembic Club Reprints, No. 11, Edinburgh, 1953.
- (3) Moore, F. J., "A History of Chemistry," McGraw-Hill, New York, 1918.

The History of Science in China: A Summer Science History Tour

Temple University in Philadelphia and Tianjin Normal University in the People's Republic of China are again offering their summer study tour on The History of Science in China in 1984.

The 21-day prigram will cost approximately \$3,000, including air fare to and from San Francisco, all food and lodgings, and travel to historically important sites within China. Graduate credit is available, and side trips to Hong Kong, Japan, and Hawaii can be arranged.

Participauts will receive a current bibliography for background use well in advance of departure.

The last summer history tour of China was described by Benfey and others in a report in THIS JOURNAL [60, 371 (1983)]. The article is an excellent documentary of the 1982 exchange between Temple and the host institution, Tianjin Normal University.

For futher details, contact: Dr. Joseph S. Schmuckler, 452 Ritter Hall, Temple University, Philadelphia, PA 19122, Office: (215) 787-6137, Home (215) 649-3607.

Qualitative Determination of Nitrate with Triphenylbenzylphosphonium Chloride

Donna A. Berry

Shaker Heights H.S., Shaker Heights, OH 44120

Jerry J. Cole

Ashland College, Ashland, OH 44805

The general procedure for the identification of nitrate is the anion group separation which is made with barium and silver solutions (1), or by division into three main groups: AgNO₃ group, BaCl2 group, and the soluble group (which are the anions that do not precipitate with AgNO₃ or BaCl₂), NO₃⁻ is in this group (2). The separation procedures are then followed by the individual tests for the anions.

The standard test for nitrate will be referred to as the "Brown Ring" test. Since the dependability of the Brown Ring" test is questionable, a new qualitative scheme was written using the reagent, triphenylbenzylphosphonium chloride (TPBPC).

Triphenylbenzylphosphonium chloride is a slightly crystalline solid that is soluble in alcohol, but only slightly soluble in water and acetone. It is soluble in aliphatic and aromatic hydrocarbons. It has a molecular weight of 388.9, minimum purity of 95% as supplied, and a melting point of 325-333°C (3). When added to a solution containing nitrate, the triphenylbenzylphosphonium chloride forms triphenylbenzylphosphonium nitrate, a white crystalline solid.

Standard Qualitative Test for Nitrale (4)

The "Brown Ring" test for nitrate is made by adding ferrous sulfate to the unknown in a test tube and then carefully adding concentrated sulfuric acid in such a manner that it does not mix but forms a separate layer at the bottom of the tube. If nitrate is present, a fine, brown ring will be formed at the junction of the acid and the solution.

$$NO_3 + 3Fe^{2+} + 4H \rightarrow 3Fe^{3+} + NO + 2H_2O$$

 $Fe^{2+} + NO \rightarrow [Fe(NO)]^{2+}$

In the first reaction the nitrate ion is reduced to nitric oxide by the ferrous sulfate. The nitric oxide then combines with excess ferrous ion to form a brown complex, [Fe(NO)]2+.

Interferences in the Brown Ring Test

The reaction only occurs at the junction of the solution and the H₂SO₄, where the acidity is high. If the solution is mixed, no test is obtained.

Bromides and iodides react with the concentrated H₂SO₄ to liberate free iodine or bromine.

Sulfides, sulfites, and other reducing agents interfere with the reaction or ferrous sulfate and nitric acid (5).

Chromates are reduced by ferrous sulfate to chromium sulfate, which will appear as a green layer at the place where the brown ring should form.

Permanganates interfere because of their color.

The triphenylbenzylphosphonium chloride (TPBPC) reagent was tested to see if it precipitated any anions other than nitrate, or would interfere with the standard qualitative tests (6), (7), for anions other than nitrate. As a result of the tests, a new qualitative scheme had to be written, since TPBPC precipitated the anions: Br-, NO2-, I-, and MnO4-.

New Qualitative Procedure

(This Procedure follows the laboratory manual by Hered and Nebergall) (8):

Procedure 6

Identification of NO_8^- in the absence of NO_2^- , Br^- , and I^- . To 1 ml of the prepared solution add 5-8 drops of the prepared reagent (TPBPC). A white crystalline precipitate confirms the presence of NO_3^- .

Procedure 7

Identification of NO_3^- in the presence of NO_2^+ .

If the NO_3 is between 0.3 and 0.1 M there is no interference with TPBPC.

Removal of NO₂"

To 6 drops of the prepared solution add 4 M H₂SO₄ until acidic, and then add 4 drops of $1 M (NH_4)_2SO_4$ solution. Place the mixture in a casserole and slowly evaporate to a moist residue (not dryness). Add 4 drops of H₂SO₄ and evaporate to a moist residue a second time. Dissolve the residue in 10 drops of H₂O and transfer the mixture to a small test tube. Repeat the test for the confirmation of NO₂" (as described in Procedure 6 with the TPBPC reagent) on the sample resulting from the removal of NO_2^- .

Three different trials were run to see if the elimination process interfered with nitrate samples.

- Sample of NO₂⁻: removed NO₂⁻; no precipitate with reagent TPBPC when testad for NO_3 .
- Sample of NO₂⁻ and NO₃⁻: removed NO₂⁻; tested positive with reagent TPBPC for NO3-
- Sample of NO₃⁻: followed procedure to remove NO₂⁻; tested positive for NO₃- with reagent TPBPC.

Thus, the method of eliminating NO₂⁻ and testing for NO₃⁻ with the reagent TPBPC was successful.

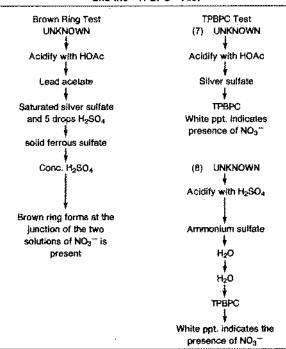
Procedure 8

Identification of NO_3^- in the presence of Br^- and I^- . Removal of Br^- and I^- . To a test tube containing 6 drops of the prepared solution, add 10 drops of H2O. Acidify the solution with 4 M HOAc and then 80 mg of powdered Ag₂SO₄ (NO₃⁻⁻ free). Stir and grind the mixture in the test tube for 2-3 min. Separate and transfer the solution to a test tube. Repeat the test as described in Procedure 6 on the solution obtained from the removal of Br and I ...

Or follow procedures 13 and 14 as follows:

Dilute 6 drops of the prepared solution with 12 drops of H₂O. Add HOAc until the solution is acidic and then add 2 drops in excess. Add 1 ml of CCl₄ and 5-10 drops of prepared chlorine water to the prepared solution. If Br and I are present, they must be removed by separating the aqueous and CC34 layers and repeating the process of adding CCl₄ and chlurine water until the sulution is colorless.

Table 1. Comparison of the "Brown Ring" Test and the "TPBPC" Test



After all of the Br- and I- are removed, add the TPBPC reagent, and if there is a white precipitate, NO₃⁺ is present. If no precipitate forms, the NO₃ is absent.

Note

- 1) A saturated solution of TPBPC was used.
- 2) In the preparation of the chlorine water—test the solution with the TPBPC reagent. If there is a precipitate, the chlorine water must be diluted until no precipitate forms.
- 3) When making a solution acidic or putting a solid into solution-do not use HNO3 to acidify it.
- 4) In Procedure 8, if the bromide and iodide are not removed completely there will be a cloudiness or even a white precipitate when the TPBPC reagent is added. Be sure to remove all of the

A comparison of the "Brown Ring" and the "TPBPC" methods is shown in the flow charts in Table 1. The flow charts indicate the similarity of the two methods, with the exception of the sulfuric addition being replaced by the direct addition of the TPBPC reagent.

For the last few years samples of college students proceeded to run the qualitative tests (9), (10). Solid and liquid unknowns were prepared, each containing two anions (NO₃⁻⁻ and another anion (some interfering ones: Br⁻, NO₂⁻, and I⁻)). After following the procedure for qualitative identity, the unknown solutions were divided into two portions and the students ran both the "Brown Ring" and the "TPBPC" test for nitrate.

The data concerning these tests is listed in Table 2. It was found that the "Brown Ring" test gave positive results only 42% of the time, while the "TPBPC" test gave positive results everytime.

Determination of the Limits of TPBPC

Dilutions were made from a solution of 0.1 M KNO₃ and placed in 100-ml volumetric flasks. A saturated solution of triphenylbenzylphosphonium chloride was prepared with

Table 2. Summary of Test Results

	"Brown Ring" Test	"TPBPC" Test
positive	42%	100%
negative	58%	0%

n = 100 students (College---general chemistry)

Table 3. Limits of TPBPC

KNO ₃		TPBPC (Saturated Solution)	Final Concentration of nitrate ion
1.0	М	ppt.	0.1 M
0.1	М	ppt.	0.01 M
0.05	М	ppt.	0.025 M
0.025	М	ppt.	0.00625 M
0.0125	М	stight ppt.	1.5625 × 10 ⁻⁴ M
0.010	M.	slight ppt.	$1.0 \times 10^{-4} M$
0.001	M	no ppt.	
0.0001	м	no. ppt.	

- 1. A seturated solution of TPBPC was made with 95% alcohol to see if the solution could increase the limits and it was found that there was no precipitation with even 0.1 M KNO₈.
- 2. A saturated solution of TPBPC was also made with acetone and there was no precipitate with 0.1 M KNOs.

distilled water. Two milliliters of each dilution was pipeted into a test tube and then 2 ml of TPBPC was added (pipeted also). The precipitation of triphenylbenzylphosphonium nitrate denotes the limits that the reagent possessed. The data from the determination is found in Table 3. The limit of detection was determined to be $1.0 \times 10^{-4} M$ in nitrate ion in the total solution; and for best results a saturated solution of TPBPC should be used.

Summary

Triphenylbenzylphosphonium chloride (TPBPC) forms a slightly soluble salt with nitrate ion. A satisfactory method was found using TPBPC for the qualitative analysis of mitrate ion, but certain precautions had to be observed, since the reagent also reacted with Br-, I-, MnO₄-, and NO₂-.

One hundred general chemistry college students performed both the standard "Brown Ring" test and the "TPBPC" test for nitrate. Comparison of the two methods shows no major differences in procedure, and from the students' results the TPBPC method proved to be more sensitive and accurate. It is easier to identify a white precipitate than a brown ring, for the "Brown Ring" test gave positive results only 42% of the time, and the TPBPC worked every time. The good detection capability of $1.0 \times 10^{-4} M$ nitrate ion in total solution also leads to selection of the TPBPC method especially for high school and general chemistry college students.

Literature Cited

- Maldrom, William B., Flosdorf, Earl W., and Daggett, Albert F., "Semimicro Qualitative Analysis of Inorganic Material," American Book Company, NY, 1938, p. 253.
 Barker, John W., and Glao, Paul K., "Laboratory Manual for First Year College
- Chemistry," McGraw-Hill Book Company, Inc., NY, 1951, p. 177.

 (3) Carlisle Chemical Works, Inc., "Data Sheets on Phosphonium Salte," 1968.

 (4) Hahn, Richard B., and Welcher, Frank J., "Inorganic Qualitative Analysis," D. Van
- Nostrand Company, Inc., New Jersey, 1968, pp. 181, 188.
 (5) "Inorganic Qualitative Analysis," p. 181.
 (6) Cheronis, Nicholas D., and Stein, Herman, "Bemimicro Experiments in General Chemistry and Qualitative Analysis," John De Graff, Inc., NY, 1959.

 (7) "Inorganic Qualitative Analysis," p. 188.

 (8) Hered, William, and Nebergall, William H., "Basic Laboratory Studies in College
- Chemistry," 3rd Ed., Raytheon Education Company, NY, 1968.
- (9) "Basic Laboratory Studies in College Chemistry.
- (10) "Inorganic Qualitative Analysis," p. 188

Qualitative Analysis by Gas Chromatography

GC versus the Nose in Formulating Artificial Fruit Flavors

P. W. Rasmussen¹

Universiti Kebangsaan Malaysia, Bangi, Malaysia

It is sometimes forgotten that, besides being a very powerful technique of quantitative analysis, GC can also be used qualitatively (1). This is especially true if, as is often the case, considerable information is already available on the sample to be identified. Examples would be in monitoring environmental samples for a suspected contaminant, or the identification of one or more of a restricted set of compounds such as drugs in a biological sample, or volatile compounds in an artifical flavoring. In these cases, a direct coupling of the GC with other instrumentation, especially MS, gives good qualitative and quantitative results but such expensive and dedicated instrumentation is often not necessary for nearly unambiguous identification. At the very least, proper use of the GC alone can limit the use that needs to be made of other instrumentation.

The following experiment is intended for the undergraduate laboratory as an illustration of the use of GC retention indexes for the identification of unknown compounds, specifically, the identification of the volatile compounds responsible for the odor of the banana. This complex sample was chosen to show the limitations as well as the usefulness of identification by retention index only, and because of student interest in such a sample. In addition, other common laboratory procedures are illustrated: preparation of the sample illustrates steam distillation and solvent extraction, and the preparation of standards requires an ester synthesis. The experiment can be extended so that individual components of banana are isolated and their identity confirmed by infrared, nuclear magnetic resonance, and/or mass spectrometry. Finally, from the results of the GC analysis, an artificial banana flavor can be prepared and compared (by GC and hy nose) to the natural flavor and to a commercially available artificial banana flavor.

Extraction of the Volatile Compounds from Banana

There are two main problems in the analysis of any fruit by GC: large amounts of non-volatile material are present and can clog the injector port and column; and the main volatile component is water, which obliterates the very small quantities of other volatile compounds present. The usual methods of dealing with these problems are distillation to separate the non-volatile material and solvent extraction to separate the water (2). These two methods can be carried out in either order, but the extraction-distillation sequence involves extracting a pulpy mass with the attendant difficulties of non-separating immiscible layers and distillation of very small amounts of volatile material. Thus, the distillation-extraction sequence is easier.

A quantity of banana pulp is liquefied in a blender with approximately twice its weight of distilled water and is steam distilled. (The slurry will rapidly turn to a greyish-brown color due to oxidation.) The best extract is obtained if the co-distillation is carried out at reduced pressure to avoid the possibility of a "cooked" flavor developing. Under aspirator pressure, the banana slurry need only be heated to 40-50°C and about ½ of it should he distilled. The distillate is saturated with NaCl and extracted four times with small portions of

CH₂Cl₂. The combined CH₂Cl₂ extracts are dried over NaCl and distilled to a small volume.

Although banana is a fruit that contains a relatively high percentage of volatile flavoring compounds, still only about 20 ppm is normally present (3). This means that if a kilogram of fruit is used in the distillation, the final extract will contain only about 20 mg of volatile material. This will be sufficient if the volume of the extract is reduced to $100-200~\mu l$ and if a GC with flame ionization detectors is used. It will probably not be enough if a thermal conductivity instrument is to be used, and it may then be necessary to combine the extracts of several students; in fact, it would be an advantage to have a small group of students do the experiment as a project and use a pooled extract. The extract should have an odor similar to the original bananas; the residual CH_2Cl_2 does not contribute significantly to the odor.

Preparation of Standards

Although it is possible to look up retention indices in the literature (4), not very satisfactory results are obtained since the GC columns used will probably differ considerably from those in the literature. Therefore, it is necessary to prepare standards. This is made easier by the fact that by far the majority of volatile compounds present in hanana are low-molecular-weight alcohols, esters, and ketones (5). In fact, the C_2 - C_6 alcohols (including isobutyl and isoamyl), esters of these alcohols with C_2 - C_6 acids (including isobutyric and isovaleric), and the C_4 - C_6 2-alkanones are those most commonly found in most fruits (6). In banana, 2-pentanol and esters of 2-pentanol are also common, while propanoates are rare and can be omitted. The propyl esters can be omitted as well, but to include them requires no extra time, and it helps in the assignment of GC peaks (vide infra). Later they may be deleted.

Thus, 59 standards must be measured, but they may be run as only nine samples by combining them in series that will give

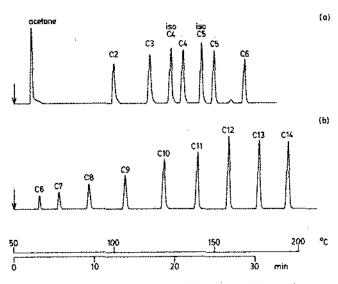


Figure 1. Gas chromatograms on Aplezon L figuid phase. (a) Mixture of valerate esters. (b) Mixture of n-alkanes.

¹ Present address: Department of Chemistry, University of Calgary, 2500 University Drive, NW, Calgary, Alberta, Canada T2N 1N4.

separate peaks on the GC. All other things being equal, retention time on any GC column will increase with molecular weight and decrease with chain branching (7). Therefore, a mixture of the C_2 - C_6 straight chain alcohols plus 2-methyl-1-propanol (isobutyl alcohol) and 3-methyl-1-butanol (isoamyl alcohol) will give separate peaks on any GC column, and esters prepared from this mixture and a carboxylic acid will also give separate peaks. This is illustrated in Figure 1(a), which shows a regular series of n-alkyl compounds, interspersed with a two-member isoalkyl series. The regularity of the series makes assignment of peaks easy, and it was for that reason that the propyl group was included. Figure 1(a) actually shows the mixture of valerate (pentanoate) esters, which is prepared as follows:

About 0.1 ml of the mixture of alcohols mentioned above, 0.2 ml of valeric (pentanoic) acid and 2 drops of concentrated sulfuric acid are mixed in a small test tube or vial and the test tube put in a water bath at 75°C. After about 1 min, when the tube contents have warmed up, the tube is stoppered with a cork to prevent evaporation of the more volatile alcohols and esters. Heating is continued, with occasional shaking, for about one hour, then the tube is cooled and the contents shaken with two 1-ml portions of 10% NaOH and then dried over a small quantity of Na₂SO₄ or NaCl. The supernatant liquid can be decanted and used directly or diluted with a vólatile solvent such as acetone.

The esters of the other acids can be prepared in the same way. The esters of 2-pentanol can be included in the same mixtures by adding 2-pentanol to the mixture of alcohols, but it may be difficult to interpret the GC. It is better to combine 0.1 ml of 2-pentanol with 0.2 ml of a mixture of acids (C₂, C₄-C₆, including isobutyric and isovaleric acids) and 2 drops of concentrated H₂SO₄ and react as above to get a mixture of 2-pentyl esters. The final standard mixture consists of 2-pentanol combined with the 2-alkanones (C₄-C₆).

Gas Chromatography of Standards

The nine standard mixtures (alcohols, acetates, isobutyrates, butyrates, isovalerates, valerates, hexanoates, 2-pentyl esters, 2-alkanones plus 2-pentanol) and the banana extract must be run on at least two different GC columns in order to obtain reliable identification. These columns should be chosen so that they have widely differing characteristics. If two columns are used, the most logical choice is a column with a non-polar liquid phase and one with a polar liquid phase or one which has a special affinity for esters. Apiezon, squalane, and silicone are examples of the former, and Carbowax, FFAP, and DEGS are examples of the latter (8). A listing of the McReynold constants for liquid phases is useful in choosing columns (9). The actual choice will probably depend mainly on availability in the individual laboratory, and it is not critical, The two columns chosen here are Apiezon L and Carbowax 1540, both 3 mm \times 2.5 m stainless steel with 10% loading on Chromosorb W. The GC is dual column with flame ionization detectors and is oven-temperature-programmed from 50°C at 4°/min. This gives excellent separation of the major constituents of the banana extract, but the analysis can be carried out isothermally with slightly less good separations. In fact, isothermal operation may give better reproducibility of retention times, unless the temperature programming is carried out carefully and is reproducible.

It is possible to do qualitative analysis by using retention times only, but it is more meaningful to use one of the calculated retention indices which appear in the literature since a retention time is characteristic of an individual instrument and set of operating conditions while a retention index is independent of instrument variables and essentially characteristic only of the compound being measured. Any retention index may be used (7) but the commonest, and the one used here, is the Kovats Index (10), which is the retention time relative to the retention times of the n-alkanes. For a GC peak

(X) which falls between the peaks for the n-alkane with N carbons and the n-alkane with M carbons (M > N), the Kovats Index (K_X) is given by (7):

$$K_{\rm X} = 100N + 100(M - N) \left(\frac{\log V_{\rm X} - \log V_{N}}{\log V_{M} - \log V_{N}} \right)$$
 (1)

for isothermal operation, where V is the retention volume (or corrected retention time) for the three peaks.

For linear-temperature-programmed operation, the Kovats Index can be approximated by (11):

$$K_{\rm X} = 100N = 100(M - N) \left\{ \frac{t_{\rm X} - t_{N}}{t_{M} - t_{N}} \right\}$$
 (2)

where t is the uncorrected retention time.

The usual method for calculating Kovats Indices is to combine a mixture of n-alkanes with the compounds to be measured, but this can be difficult with complex mixtures such as fruit extracts because of the extensive overlapping of peaks (vide infra). A faster and only slightly less accurate method is to run the unknown compounds and mixture of alkanes separately, and keep conditions as nearly as possible the same during the two chromatograms. Thus, alkanes need not be mixed with any sample, and only 11 samples need be run on each column (9 standard solutions, the alkane mixture, and the banana extract). The stability of isothermal conditions or the reproducibility of temperature programming must be checked by comparing two runs of the n-alkanes. Isothermal operation should present no problems, but programming may or may not be acceptable. For instance, in our laboratory, a Hewlett-Packard 5710A GC with the 5702A oven temperature programmer is reproducible to within ± 2 Kovats Units; a HP5840A-microprocessor-controlled GC gives unacceptable results (up to ±20 Kovats Units), when they are programmed from 50-170°C at 4°/min. The data given here were obtained on the former instrument.

When reproducible GC conditions cannot be attained, the alkane mixture must be combined with a portion of each of the samples to be run. Then, in any chromatogram where overlapping occurs between sample peaks and alkane peaks, the clearly separated alkane peaks are used to calculate the indices for the clearly separated sample peaks, using eqns. 1 or 2. A chromatogram of the sample without alkanes is then obtained, and the sample peaks with already calculated indices are used as references to calculate the indices for the rest of the peaks, using slightly modified forms of eqns. 1 or 2:

$$K_{\mathbf{X}} = K_{8} + (K_{L} - K_{S}) \left(\frac{\log V_{\mathbf{X}} - \log V_{S}}{\log V_{L} - \log V_{S}} \right)$$
(3)

$$K_{X} = K_{S} + (K_{L} - K_{S}) \left(\frac{t_{X} - t_{S}}{t_{L} - t_{S}} \right)$$
 (4)

where S and L are the reference peaks (sample peaks with known indices) nearest to, and on either side of, the peak to be measured $(K_{\rm L} > K_{\rm X} > K_{\rm S})$ (11). Thus, whenever alkane peaks overlap with sample peaks, two chromatograms are necessary for complete assignment of indices. A mixture of alkanes with the banana extract will have overlapping peaks, but many of the standard solutions may not. For instance, a mixture of the valerates with alkanes will not have any overlapping peaks on either the Apiezon or the Carbowax liquid phases (see Fig. 1).

For the banana extract and the standards used here, a mixture of C_6 - C_{14} n-alkanes is sufficient for the Apiezon L column. This is shown in Figure 1(h). For the polar column (Carbowax 1540), C_9 - C_{17} alkanes will cover the desired range.

The Kovats Indices for the 52 standards (the seven n-propyl compounds were omitted) are measured on both GC columns (Apiezon and Carbowax), and are listed in Table 1. The table is arranged in order of increasing Apiezon index; this facilitates matching unknown indices with the series of known values.

Table 1. Koyats Indices of Standard Compounds

Kovats Index						Kova	ts Index
No.	Compound	Apiezon	Carbowax	No.	Compound	Apiezon	Carbowax
1	ethanol	<600	957	27	isobutyl isovalerate	965	1214
2	2-butanona	<600	926	28	iscemy! isobutyrate	968	1215
3	isobutyl aicohol	637	1105	29	hexyl acetate	974	1290
4	ethyl acetate	645	905	30	2-pentyl butyrate	978	1232
5	2-pentanone	668	1005	31	amyl isobutyrate	1003	1261
6	n-butyl atcohol	680	1162	32	bulyl isovalerate	1005	1272
7	2-pentanot	712	1133	33	isobutyl valerate	1012	1275
8	ethyl isobutyrate	716	979	34	isoamyi butyrate	1015	1286
9	isobutyl acetate	732	1029	35	2-pentyl isovalerate	1029	1263
10	isoamyi alcohol	747	1224	36	butyl valerate	1054	1334
11	ethyl butyrate	764	1052	37	arnyl butyrate	1057	1338
12	2-hexanone	768	1110	38	isoamyl isovalerate	1067	1318
13	butyl acetate	775	1088	39	2-pentyl valerate	1073	1328
14	amyl alcohol	761	1269	40	amyl isovalerate	1101	1370
15	2-pentyl acetate	808	1090	41	hexyl isobutyrate	1101	1359
16	ethyl isovalerate	818	1090	42	feobuty/ hexanoate	1108	1372
17	isoamyl acetale	836	1140	43	Isoamyi valerate	†11 5	1385
18	ethyi valerate	859	1153	44	arnyl valerate	1150	1432
19	isobutyl isobutyrate	868	1108	45	butyl hexanoate	1152	1434
20	arnyl scetale	874	1190	48	hexyl butyrate	1155	1436
21	n-hexyl alcohol	878	1370	47	2-pentyl hexancate	1168	1423
22	butyl isobutyrate	905	1165	48	hexyl isovalerate	1199	1467
23	isobutyl butyrate	916	1176	49	isoamyl hexanoate	1211	1482
24	2-pentyl isobutyrate	926	1152	50	amyl hexanoate	1246	1535
26	butyl butyrate	958	1236	51	hexyl vaterate	1252	1534
26	ethyl hexanoste	959	1254	52	hexyl hexanoate	1347	1631

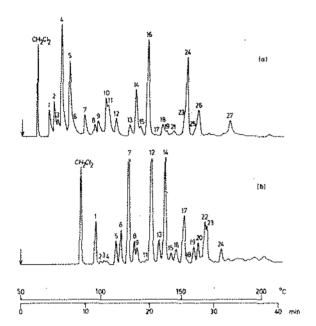


Figure 2. Gas chromatograms of natural banana extract. (A) Aplezon L column. (B) Carbowax 1540 column.

Identification of the Compounds in Natural Banana Extract

The gas chromatograms of the natural banana extract on the Apiezon and Carbowax columns are shown in Figure 2. The major peaks are numbered in both chromatograms so that each peak can be identified with a letter (A or C for the two columns) and a number. Also, for each chromatogram, the heights of all peaks are measured and normalized to a sum of 1000. The listing of peak number, Kovats Index and relative peak height for both chromatograms is given in Table 2. The components of the banana extract can now be identified as follows:

(1) For each peak in the Apiezon chromatogram, write its number, Kovats Index and relative peak height in columns

Table 2. Retention Data and Relative Peak Heights for the Gas Chromatograms of Natural Banana Extract

Peak	Aplezon Chromatograd Kovats	Peak	Peak	Carbowax Chromatogra Kovats	Peak ·
No.	Index	Height	No.	Index	Height
A1	638	34	C1	1007	54
A2	672	46	C2	1029	4
A3	684	22	C3	1046	6
Α4	711	143	C4	1051	4
A5	743	98	C5	1088	30
A6	761	18	C6	1105	43
A7	806	28	C7	1136	174
A6	641	16	CB	1162	29
A9	653	20	C9	1176	21
A10	676	50	C10	1195	3
A11	888	40	C11	1215	6
A12	915	25	C12	1230	160
A13	957	16	C13	1268	30
A14	979	61	C14	1288	133
A 15	987	13	C15	1317	14
A16	1010	124	C16	1332	18
A17	1042	3	C17	1370	100
A 18	1065	16	C18	1386	4
A19	1077	9	C19	1418	21
A20	1092	3	C20	1436	26
A21	1106	9	C21	1451	4
A22	1137	4	C22	1489	52
A23	1153	30	C23	1479	47
A24	1163	103	C24	1545	17
A25	1196	13			
A26	1209	34			
A27	1347	22			

1, 2, and 3 of Table 3. Write in column 4 all of the standards that have an Apiezon Kovats Index that matches the Kovats Index of the peak. A match is taken to be within 6 Kovats Index Units. This range reflects the reproducibility of the gas chromatograph used and is chosen large enough so that no possible match will be missed. Include in columns 5 and 6 the two Kovats Indices of the standard compounds (taken from Table 1).

Table 3. Identification of the Major Components of Natural Banana Extract

,	Apiezon Chromatogram		Refer	ence Compounds		Carbo	wax Chromatog	ram
Peak	Kovats	Peak		Kova	ts Index	Peak	Kovats	Peak
No.	₹ndex	Height	Name	Apiezon	Carbowax	No.	{ndex	Heigh
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
A1	636	34	isobutyl alcohol	637	1105	C6	1105	43
A2	672	46	2-pentanone	6 66	1005	C1	1007	54
A3	684	22	1-butanol	680	1162	C8	1162	29
A4	711	143	∮ 2-pentanol	712	1133	C7	1138	174
			ethyl isobutyrate	716	979			
A5	743	98	isoamyl alcohol	747	1224	C12	1230	160
A6	761	16	fethyl butyrate	764	1052	C4	1051	4
			2-hexanone	768	1110	C6	1105	43
A7	806	26	2-pentyl acetate	808	1090	- C5	1068	30
A8	841	16	isoamył acetate	838	1140	C7	1136	174
A9	653	20	ethyl valerate	859	1153			
A10	876	50	famyl acetate	874	1190	C10	1195	3
			1-hexanol	678	1370	C17	1370	100
A1†	668	40	·					
A 12	915	25	isobutyl butyrate	916	1176	C9	1176	21
A 13	957	16	f butyl butyrate	958	1236	C12	1230	160
~ 10	557	10	ethyt hexanoate	959	1254			
A14	979	61	∫hexyl acetate	974	1290	C14	1286	133
A 14	318	Q I	2-pentyl butyrate	978	1232	C12	1230	160
A 15	987	13						
			butyl isovalerate	1005	1272	C13	1266	30
A 16	1010	124	isobutyl valerate	1012	1275			
			liosamyl butyrate	1015	1266	C14	1288	133
A17	1042	3						
A 16	1065	16	isoamyl isovalerate	1067	1316	C15	1317	14
A 19	1077	9	2-pentyl valerate	1073	1326	C16	1332	18
A20	1092	3						
			(amyl isovalerate	1101	1370	C17	1370	100
A21	1108	9	hexyl isobutyrate	1101	1359			
			(isobuty) hexanoate	1108	1372	C17	1370	100
A22	1137	4						
			[amyl valerate	1150	1432	C20	1436	26
A23	1153	30	butyl hexanoate	1152	1434	C20	1436	26
			hexyi butyrate	1155	1436	C20	1438	26
A24	1163	103	2-pentyl hexanoate	1168	1423	C19	1418	21
A25	1196	13	hexyl isovalerate	1199	1467	C22	1469	52
A26	1209	34	isoamyi hexanoate	1211	1482	C23	1479	47
A27	1347	22	hexyl hexancale	1347	1631			

Table 4. Major Volatile Components of Natural Banana Extract

	Da	eak	P	eak	Average	Synthetic
Compound		nber		eight	Percent	Mixture
isobutyl alcohel	A 1	C6	34	43	4	4
2-pentanone	A2	C1	46	54	5	9
1-butanol	A3	C6	22	29	3	1
2-pertanol	A4	C7	143	174a	15	18
isoamyl atcohol	A5	C12	98	160 ^b	10	10
ethyl butyrate	Аβ	C4	16	4	1	1
2-pentyl acetate	A7	C5	26	30	3	
isoamyl acetate	A8	C7	16	174ª	2	2
1-hexanol	A10	C17	50	100°	5	3
isobuty! butyrate	A12	C9	25	21	2	2
buty! butyrate	E1A	C12	16	160₽	2	2
2-pentyl butyrate	A 34	C12	61	160 ⁵	6	6
leoamy! butyrate	A 16	C14	124	133	13	12
isoamy! isovalerate	A18	G15	16	14	2	1
2-pernyl valerate	A19	C16	9	18	1	
isoamyl hexanoate	A26	C23	34	47	4	_

a Contains 2-pentanol and isoamyl acetate.

(2) Compare the Carbowax Kovats Indices in column 6 with the listing of the peaks for the Carbowax chromatogram of banana extract (Table 2). Write in columns 7, 8, and 9 the peak number, Kovats Index and relative peak height of each peak with a matching Index (±6 units).

(3) Finally, for each row in Table 3, compare the relative peak heights in columns 3 and 9. They should match to within experimental error.

Using this procedure, a number of the volatile constituents of banana can be identified. The reliability of the identification will of course differ for the various peaks. For instance, the presence of isobutyl alcohol is quite unambiguous; peaks A1 and C6 match in peak height (within experimental error) and closely match the two known Kovats Indices. However, there may be room in the C6 peak for a small amount of something else (C6 has a slightly higher peak height than A1). This leads to ambiguity when peak A6 is examined, because the peak height of 18 for A6 may be made up of a height of 4 from ethyl butyrate (peak C4) and a height of 14 from 2-hexanone (peak C6). Thus, peaks A1 and A6 may contain a total of three components (total height 52) which appear in a different combination at peaks C4 and C6 (total height 47) in the Carbowax cbromatogram; on the other hand, 2-hexanone may not be present at all.

It must be remembered that the simplicity of the results in Table 3 is mainly due to a judicious choosing of the reference compounds, but such a choice is normal practice in solving most analytical problems. Furthermore, in general, the use of an expanded set of known indices usually does not lead to incorrect assignments, rather it leads to greater complexity and therefore fewer unambiguous assignments.

Table 4 summarizes the major compounds in banana extract which can be identified with reasonable confidence using Table 3. The percent of each component is calculated from the

b Contains Isoamyl alcohol, butyl butyrate, and 2-pentyl butyrate.

^c May contain small amounts of other compounds.

Table 5. Major Components of Commercial Banana Flavor Extract

	Apeizon Chromatogram Carbowax Chro				gram	Reference	Reference Compounds		
Peak	Kovats	Peak	Peak	Kovats	Peak		Kovata	Indices	
No.	Index	Height	N o.	Index	Height	Name	Apeizon	Carbowax	
1	718	12	1	975	14	ethyl isobutyrate	716	979	
2	754	2	2	1031	5				
3	787	48	3	1055	48	ethyl butryate	764	1052	
4	840	590	4	1148	654	iscamyl acetate	836	1140	
-	4000	0.47	e	1323	270	(Isoamyl isovalerate	1067	1318	
0	1068	347		,323	210	2-pentyl valerate	1073	1328	

two relative peak heights (which are in parts per thousand of the total mixture).

Synthetic Banana Flavor

Using the peak height data in Table 4 a synthetic banana flavor is constructed. Most of the compounds identified in banana fall into three groups: butyrates, isoamyl esters, and non-esters. The esters are synthesized using the above procedure.

A 1:3:3:17:8 mixture (by volume) of ethyl, isobutyl, butyl, isoamyl, and 2-pentyl alcohols is reacted with excess butyric acid to form the butyrates (solution A), and a 5:2 mixture of acetic and isovaleric acids is reacted with excess isoamyl alcohol to form the isoamyl esters (solution B). Isobutyl, butyl, isoamyl, hexyl and 2-pentyl alcohols, and 2-pentanone are mixed in a 3:1:7:2:1:6 volume ratio (solution C). Then solutions A, B, and C are combined in a 8:1:15 volume ratio to give a synthetic banana flavor with the composition given in the last column of Table 4 (the percentages were adjusted to a total of 70 to match the total percentage of the compounds in the natural banana extract). A little dichloromethane is added to match that present in the original banana extract.

The GC (on the Carbowax column) of the synthetic mixture is compared to banana extract in Figure 3. It shows a fairly good match for the major components present in banana; a similarly good match is obtained on the Apiezon column. However, the odor of the synthetic mixture is not a good imitation of banana odor, thus indicating that there is more to the synthesis of srtificial extracts than the identification of the major components present in the natural extract. In fact, the very minor components often play a disproportionately large role in fruit aromas (12), and this makes it very difficult to construct a satisfactory artificial extract by reproducing the natural composition. Therefore commercially available extracts are not usually made in this way; rather the nose is used instead of the GC (13).

A highly trained nose is of course necessary. Such a nose (for instance, one belonging to a flavorist who constructs commercial artificial extracts) can identify various "notes" present in an odor and then suggest certain compounds that will reproduce these "notes." For example, banana odor has a prominent "fruity" note, and fruity notes can be provided by esters, and the particular quality of the banana fruity note can be approximated by isoamyl acetate (13). As most chemists know, isoamyl acetate does not quite smell like banana, so the flavorist will add small quantities of other compounds to modify the odor slightly, until he has a product which will be acceptable as a banana substitute, when used in the intended manner. This last qualification is important because the flavorist will usually design a flavor for its ultimate use, so that a banana flavor in the bottle may not smell at all like banana but may given an excellent flavor in a banana cake.

A commercial artificial extract can be examined easily by GC, but first it should be extracted into dichloromethane to leave behind any non-volatile insoluble material (which, of course, also contributes to the overall flavor). Dilute 10 ml of extract with 5 ml water, extract 3 times with 10-ml portions of CH₂Cl₂, wash the combined extracts three times with 10-ml

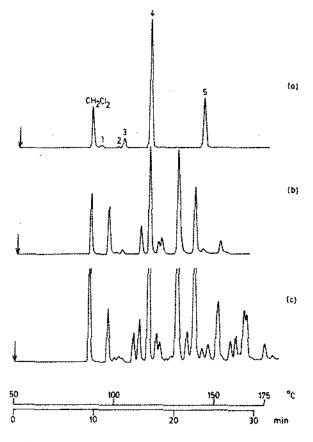


Figure 3. Gas chromatograms on Carbowax 1540 liquid phase. (a) Commercial banana flavor. (b) Mixture of volatile compounds identified in natural banana extract. (c) Natural banana extract.

portions of saturated NaCl, dry over NaCl or Na2SO4, and reduce in volume to about 1 ml. It is best to use a non-alcoholic extract or the final solution will contain a large quantity of alcohol. In any case, a GC of this extract can be run at the same time as the standards and natural extract. A British-made brand available worldwide, and a Malaysian-made brand both gave the same GC, and an example of a GC on Carbowax is shown in Figure 3. The Kovats Indices for the peaks in this GC and those obtained on the Apiezon column are given in Table 5, along with the identifications that can be made using the standards listed in Table 1. As predicted, isoamyl acetate is the major component, and all three major components are only minor components of the natural extract (see Table 3). Thus, the commercial extract is much simpler than the one constructed to imitate the GC of natural flavor. On the other hand, neither is a very faitbful imitation of the natural flavor.

Conclusions

A detailed report on the preparation of a banana extract by vacuum distillation-solvent extraction, and the identification

of the major volatile components by GC/MS, has appeared elsewhere (14). The author will be glad to supply a copy of the paper to anyone interested, although it is not concerned with identification by GC retention index. The banana used was a variety found in Malaysia, "pisang emas" of Musa acuminata (Colla), var. Sucrier. However, any banana should give equivalent results, and in fact would be easier to check in the literature, since most published work has been on the common varieties found in the markets of North America and Europe

It should be emphasized that due to the complexity of the natural banana extract, all identifications by retention data are tentative only. Nevertheless, with the help of relative peak heights for identifying the position of a compound in the GC's on both columns, results are quite reliable and would be even more reliable on a less complex mixture. In fact most of the identifications listed in Tables 4 and 5 are correct, as checked by GC/MS and comparison with mass spectra of the reference compounds (14).

This experiment would take a single student quite a number of laboratory sessions to complete and is best used as an extended laboratory project which would include synthesis of the standards, extraction of the samples, and identification by GC. In addition, the student could trap sufficient of the major components of banana to obtain MS and perhaps also IR and NMR spectra, although the small quantities of extract obtained may preclude the latter two. However, mass spectra are easy to obtain by inserting a short length of glass tubing packed with a suitable absorbent in the GC exit (2) and then putting the tube directly into the solid-liquid inlet port of the mass spectrometer. Some of the likely standard compounds also could be trapped and the mass spectra compared. Mass spectra in the literature also could be consulted (15)

On the other hand, the time required to carry out this experiment could be reduced considerably by reducing the most time consuming step—the obtaining of the reference Kovats Indices. The 52 reference compounds used here are probably a minimal set for demonstration purposes (restriction to this set can be justified on a priori grounds), so the time required can be reduced by having several students each do one or two of the nine standard mixtures along with the banana extract and the alkane mixture, using either or both of the GC columns. All reference data can then be pooled and each student can carry out his own analysis. Alternatively, the reference values listed in Table 1 or found in the literature can be used (4). If Table 1 is used the columns must be Apiezon L and Carbowax 1540. If the literature is used, appropriate columns must be selected. Neither alternative is very satisfactory, because Kovats Indices will differ sufficiently between laboratories so that a peak in the banana extract may match a reference peak to within ±15 or 20 Kovats Index Units, and this difference may lead to great confusion in assigning peaks of a mixture as complex as the banana extract.

Finally, two difficulties arise in this experiment. First, because a dilute organic extract is reduced to a very small volume containing the banana volatiles, the purity of the extracting solvent is important. This is one reason for using dichloromethane. Reagent grade probably can be used directly or after a simple distillation. However, this should be checked: the reagent grade CH2Cl2 available in Malaysia shows considerable amounts of two impurities identified by MS as a trichloroethylene (Kovats Indices 721 and 1005) and tetrachloroethylene (Kovats Indices 842 and 1041). These two could not be removed by distillation and are present in the banana extract. The former is quite small and is under peak C1 in Figure 2, while the latter is peak C3 in Figure 2. Second, Kovata Indices may change slightly with time and if the same values are to be used for longer than a few weeks, they should be checked by running one of the ester mixtures and the alcohol mixture. If there is significant difference, the average difference in the ester values can be used to correct all of the other ester values (and probably the ketone values as well) since all will change to the same degree. As an example: over a six-month period, the Kovats Indices of all the esters in Table 1 increased from 6 to 13 units (average 9) on the Apiezon column, and 36 to 44 units (average 39) on the Carbowax column. During the same time interval, the alcohols increased an average of 40 units on both columns. These changes were probably due to gradual deterioration of the columns, since they were used continuously during the six months.

Acknowledgment

I thank the Universiti Kebangsaan Malaysia for financial support as grant No. 10/77.

Literature Cited

- (1) (a) Kováts, E., Advan. Chromatogr., 1, 229 (1965).
 (b) Schomburg, G., and Dielmann. G., J. Chromatogr. Sci., 11, 151 (1973).
- Teranishi, R., Issenberg, P., Hornstein, I., and Wick, E. L., "Flavor Research: Principles and Techniques," Marcel Dekker, Inc., New York, 1971, pp. 37, 233.
 Issenberg, P., and Wick, E. L., J. Agric. Food Chem., 11, 2 (1963).
- (4) (a) McReynolds, W. O., "Gas Chromatographic Retention Data," Preston Technical Abstracts Co., Evanston, IL, 1966. (b) Schupp, O. E., III, and Levis, J. S., Res./Devel., 21 (5), 24 (1970).
- (5) (a) Wick, E. L., Yamanishi, T., Kobayashi, A., Valenzuela, S., and Issenberg, P., J. Agric.
- Food Chem., 17, 751 (1969). (b) Dupaigne, P., Fruits, 30, 783 (1975).

 (6) See, for example: Silverstein R. M., in Schultz, H. W., Day, E. A., and Libbey, L. M., (Editors), "Symposium on Foods: The Chemistry and Physiology of Flavors," AVI.
- Westport, CT, 1967, p. 450.
 (7) Haken, J. K., Advan. Chromatogr., 14, 367 (1976).
 (8) Baiulescu, G. E., and Ilie, V. A., "Stationary Phases in Gas Chromatography," Pergamon, Oxford, 1975.
- (9) (a) McReynolds, W. O., J. Chromatogr. Sci., 8, 685 (1970). (b) Zweig, G., and Sherma, J., (Editors), "Handbook of Chromatography," Vol. 2, CRC Press, Cleveland, 1972.
- (10) Kováts, E., Helv, Chim. Acta, 41, 1915 (1958).
- (11) van den Dool, H., and Kratz, P. D., J. Chromatogr., 11, 463 (1963)
- (12) See, for example: Parliment, T. H., and Scarpellino, R., J. Agric. Food Chem., 25, 97 (1977)
- (13) Broderick, J. J., Flavour Ind., 284 (1974).
 (14) Rasmussen, P., Nordin, Aziz, and Omar, Muhamet, Sains Malaysiana, in press.
- (15) (a) Stenhagen, E., Abrahamsson, S., and McLafferty, F. W., "Registry of Ma-Data," Wiley-Interscience, New York, 1974. (b) Cornu, A., and Massot, R., "Com-pilation of Mass Spectral Data," 2nd ed., Heyden and Son, Ltd., London, 1975. (c) National Bureau of Standards, "EPA/NIH Mass Spectral Data Bases," NBS National Standard Reference Data Service publications no. 63 (1978).

Royal Society Continuing Education Program

The Royal Society of Chemistry has organized a number of residential courses for practicing chemists who have a knowledge of the field being covered but are seeking a deeper understanding of the subject. Many courses are practically based to acquaint participants with the latest developments and techniques. The following residential schools are scheduled for 1984: March 26-30, Metallo-Organic Chemical Vapor Deposition; April 9-13, Inorganic Polymers; April 9-13, Equilibrium and Nonequilibrium Aspects of Food Structure and Behavior; July 2-6, Organometallic Reagents in Organic Synthesis; July 16-20, Water Soluble Polymers: Chemistry and Application Technology; September 10-14, High Performance Liquid Chromatography. Further details are available from Miss L. Hart, Royal Society of Chemistry, 30 Russell Square, London WCIB 5DT.



filtrates & residues

Mariborough School 250 S. Rossmore Avenue Los Angeles, CA 90004

Analysis of Alcohols

Brother Thomas McCullough

St. Edward's University Austin, TX 78704

This experiment presents a novel approach to identification of unknown alcohols using experimental measurements of boiling point and viscosity which are easily obtained without expensive equipment or instrumentation. Students or teachers can carry out the necessary glass bending. These procedures have been used quite successfully at the author's institution for over two decades.

Purpose

In this experiment unknown alcohols are identified by measurement of their boiling points and viscosities.

Equipment

test tube thermometer
ring stand 6-mm soft glass tubng
two rings string
wire gauze burner
clamp natural gas
boiling chip capillary viscometer

The capillary viscometer is prepared by pulling a section of 6-mm soft glass tubing; then a 30-cm length with a bore as uniform as possible is cut. A short right angle bend is made at each end of the capillary which is then taped to a small board having marks 15-20 cm apart inscribed on it. Both ends of the capillary should extend beyond the same side of the board (see figure).

The Experiment

Boiling Point

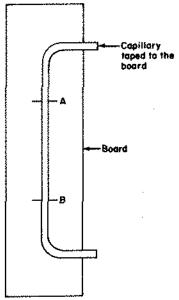
Place 1 mi of alcohol and a boiling chip in the test tube which is clamped to the ring stand. Clamp a ring and wire gauze immediately below the test tube and place a second ring above the test tube. Tie a string holding the thermometer to the ring so that the thermometer dangles in the test tube with the bulb about 20 mm above the liquid. The thermometer should not touch the sides of the test tube.

Heat the bottom of the test tube (through the wire gauze) gently so that the liquid boils slowly. When drops begin to fall from the bulb of the thermometer start to take temperature readings. Three or four readings, 10 or 15 s apart and with an agreement of ± 0.1 , should give the boiling point of the alcohol.

Viscosity

Introduce, by capillary action, a liquid sample, 15- or 20-mm long, into one open end of the viscometer and use gravity to force it to flow back and forth between the two marks in order to wet the inside surface. Move the sample above the marks. Hold the board vertically. Activate a stopwatch when the leading edge of the sample reaches the closer mark, A. Terminate the timing when the same leading edge passes the second mark, B.

New lectures and laboratory experiments and directions in teaching chemistry through the use of the laboratory are provided in this feature. Experiments will be fully detailed and will be field tested before they are published. Contributions should be sent to the feature editor.



The assembled capillary viscometer.

Sample Data

Alcohol	BP, °C	Flow Time, Seconds (Time to Flow 15 cm in a Capillary Tube)
Ethýl (95%)		8.1
lsopropyl	8181,4	10.5
t-Butyl	79~80	19.6
1-Propanol	97.0	10.6
2-Butanol	99.0	13.7
t-Pentyl	102	16.9

Results

Results for a typical set of experiments are given in the tables.

Pre-Laboratory Assignment

- 1) What is meant by boiling point?
- 2) What part of today's data can be found in a reference book?
- 3) What part of today's data will not be found in a handbnok? Why

Poat-Laboratory Assignment

- Draw the structures for the alcohols whose boiling points are similar to yours.
- 2) Is your thermometer accurate? How can you tell if it is or not? If it is not accurate (to within one or two degrees) should it be thrown away?
- 3) How closely can your thermometer be read?
- 4) Is there any correlation between structures of the alcohols and the flow times?

References

Boiling points of all common alcohols can be found in "Lange's Handbook of Chemistry," "CRC Handbook of

Chemistry and Physics," or any textbook of organic chemistry.

Special Notes

1) The glassware, including the thermometer, must be dry, as water and most alcohols form azeotropes that lower boiling points by 10-15°C. Is the alcohol being used free from water?

2) Temperatures can be taken only when drops of liquid are condensing and falling from the bulb of the thermometer. If the alcohol has been boiled away, a lowering of the temperature will be observed by your students. Increasing the amount of sample from 1 to 2 ml (or even more) should help eliminate this difficulty.

3) On the other hand, higher boiling points than warranted can be obtained if the sides of the test tube are heated too much. The vapors become superheated and, rather than condense on the bulb, heat it above the true boiling point. A low, low flame and a wire gauze usually prevent this phenomenon.

 The flame and test tube should be shielded from drafts and breezes during the BP determination.

5) Capillary tubing must be used, never 1, 5, 6 or larger ID (mm). The capillary is formed from 5 or 6 mm soft glass tubing and a very hot flame by gentle pulling.

6) In viscosity measurements, room temperature can be an important variable as a difference of several degrees Celsius will cause a significant change in the flow time. A more obvious variable is the angle at which the board and capillary are maintained during the flow. The fastest time will be obtained when the board is beld vertically. Smaller angles will increase the flow time and increase the sensitivity of the procedure.

7) The hest way to standardize the viscometer is to carry out the procedure using known alcohols. The actual length of the liquid sample in the capillary should be the same for all alcohols, knowns and unknowns alike.

An Addendum on Measuring the Entropy of Mixing of a Two-Ion System

J. D. Pulfer

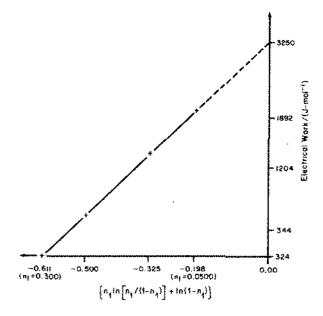
National University of Lesotho, Roma, Lesotho, South Africa

As Selley points out¹, concentration cells provide an accurate, direct method for measuring the entropy of mixing of a two ion system. The purpose of this note is to develop a relatively simple data handling procedure which has the effect of cutting experimental effort in half and making it considerably easier for students to obtain good results.

Observe¹ that a plot of the integral

$$I(n_1) = \int_{n_1}^{0.5} \mathcal{I}\mathcal{E}(n_1) dn_1$$
 (1)

¹ Selley, N. J., J. CHEM. EDUC., 49, 212 (1972).



Variation of maximum electrical work as a function of $\{n_1 \ln[n_1/(1-n_1)] + \ln(1-n_1)\}$.

against n_1 gives a nonlinear curve. This graph is then extrapolated to the origin to find the maximum amount of electrical work. Such an extrapolation gives rise to some uncertainty. There is no need for this ambiguity. Within Selley's assumptions, a theoretical plot of $I(n_1)$ versus $\{n_1 \ln[n_1/(1-n_1)] + \ln(1-n_1)\}$ will give a straight line with slope 2RT and intercept w_{\max} .

A plot which is supposed to be a straight line is easier to extrapolate and, in general, will be less prone to experimental inaccuracies. In addition, students need only find the potential $\mathscr E$ at four values of n_1 (Table 1) to achieve the same results as reported. For example, when the experimental integrals $I(n_1)$ (Table 2), evaluated by "counting squares" on a graph of $\mathscr E$ versus n_1 , were plotted in the suggested manner, w_{\max} was found to be 3250 J mol⁻¹. This was 6.9% lower than w_{\max} theoretical (3490 J mol⁻¹)—well within the range of Selley's values.

Table 1. Cell Potentials for 0,100 M Hexacyanoferrates (II) and (III) Mixtures

n ₁ /mol	Observed cell potential/abs V	Selley's observed cell potential/abs V
0.0500	0.145	0.148
0.100	0.108	0.104
0.200 0.069		0.073
0.300	0.034	0.046ª

a Total concentration of the cell was 0.025 M.

Table 2. Experimentally Estimated $^{\circ}$ integral Values of $I(n_1)$

rı ₁ /mot	/ (n ₁)/(J mol ⁻¹)
0.0500	2280
0.100	7670
0.200	818
0.300	324

^{*} Counting equares on a graph of $\mathcal E$ versus n_i .

Performance Characterization of an Instrument

Eric D. Salin

McGill University, Montreal, P.Q., Canada H3A 2K6

There is a tendency among certain students to have unquestioning faith in instrumentation. This is particularly true of modern instrumentation with digital readout. These students report data to a phenomenal number of significant figures while expecting a corresponding accuracy. An appreciation of the power of modern instrumentation must be tempered with an awareness of its limitations. Students should apply to instrumentation the same statistical awareness that is so conveniently and commonly applied to classical techniques. Propagation of error techniques can be used to pinpoint instrumental limitations and breakdowns as well as they can be used to demonstrate the canabilities and ultimate limitations of volumetric and gravimetric methods. With this in mind, an experiment has been developed for use in our second analytical chemistry course. We have used an atomic emission apparatus as the experimental vehicle; however, the techniques are generally applicable.

All instruments have limitations over their entire performance range. The experiment to be discussed introduces the student to the terms "detection limit," "signal-to-noise ratio," "dynamic range" and "linear dynamic range" as well as providing the student with a step-by-step procedure for the determination of experimental noise sources in the instrumental operating ranges. Flame atomic emission (FAE) was used due to the simplicity of the apparatus and data handling.

Experimental Procedures and Equipment

A FAE apparatus with a digital readout is most convenient for this experiment. A meter "needle" type of readout usually cannot provide the readout resolution required to quantize the experimental noise. A strip chart recorder is somewhat better if it has multiple ranges; however, we have found that an inexpensive 31/2-digit digital multimeter (DMM) is excellent, because it usually provides voltage ranges so that a change in amplifier settings is unnecessary throughout the entire experiment. We have found it convenient to use calcium (Ca) as an analyte for this experiment. It can be seen visually in the flame, has both elemental and molecular bands, is subject to the classic phosphate chemical interference, and provides good pérformance.

The student's first task is to adjust the spectrophotometer so that the 422.7-nm Ca atomic emission line is observed. The wavelength dial usually does not readout the wavelength precisely thus providing a convenient first contact with reality. While aspirating a high concentration (around 104 ppm) of Ca the student must set the gain of the instrument to provide a readout of 5.0 V on the DMM with appropriate initial operating parameters (gas flows, slit, etc.). This is the highest concentration that will he aspirated and the gain must be adjusted on our system to avoid saturation of our external

operational amplifiers.

The student is expected to determine the electronic time constant (1) of the entire apparatus by blocking a high-intensity signal and then quickly removing the block. Students use the guideline that 99% of the final value will be reached in 5 time constants (TC's). The students are then encouraged to use the general rule that digital observations should be made every 5 TC or farther apart so that the values will be statistically independent. It is best if the time constant of the system is from 0.1 to 1 s. This range normally will be available on both modern and old equipment. If the time constant exceeds 1 s then the students will spend inordinate amounts of Symbols and Terms

Symbol	Definition			
d	dark signal (no light falling on detector)			
m	stope of the analytical calibration curve in units of volts/concentration units			
п	number of measurements			
s	analytical signal ($E_s = E_{AEF}$) used in figures			
t	t statistic value from Student's t Test			
8	background			
С	concentration			
C Car	the concentration at the limit of detection			
Ε̈́	voltage			
N,z	riolse (RMS)			
S	signal			
AFE	analyte flame emission			
AS	total analytical emission signal			
BA	blank aspiration			
BE	total blank emission signal			
BFE	blank flame emission			

time recording their data and may introduce unnecessary long term drift (low-frequency noise) into their experiment. Time constants that are too small will allow unnecessary noise through the electronic bandpass.

Students are now ready to begin determination of instrumental noises. All noises are determined by acquiring 10 readings at 5 TC or greater intervals and taking the standard deviation, z, of those values. While it might be argued that 32 or some intermediate value is more appropriate, the inclusion of more values may introduce low-frequency noise contributions as well as student fatigue. For purposes of later reference we will refer to the following portions of the experiment as steps.

Step 1.

The first noise to be determined is the "dark" noise, z_d , E_d is measured by blocking the entrance to the spectrometer so that no light can pass in. E_d can be broken down further into other components, many of which can be predicted from fundamental principles and the reader is encouraged to examine the excellent series of papers by Ingle and Bower (2-7); however, this is not necessary at this educational level and would not necessarily even be implemented by a researcher interested in the evaluation of his or her apparatus. The dark noise, z_d , is the minimum noise that can appear in the apparatus.

Step 2.

The student must now optimize the spectrometer slit width and burner position. This is carried out by optimizing the signal-to-background (S/B) ratio. This is a common and sometimes fallacious technique popular in emission spectroscopy. The S/B is calculated by

$$S/B = \frac{E_{\rm AFE}}{E_{\rm BE}}$$

and $E_{\rm AFE}=E_{\rm AS}-E_{\rm BE}$ where $E_{\rm AFE}$ is the desired voltage such that $E_{\rm AFE}=m$ C, $E_{\rm AS}$ is the total voltage measured when aspirating a sample solution, and $E_{\rm BE}$ is the voltage of the blank solution. The table contains a list of terms and symbols.

Step 3.

The students are then required to make a calibration curve over four orders of magnitude. Solution concentrations range from 10^0 to 10^4 ppm Ca and there is one solution per order of magnitude. $E_{\rm AS}$ and $E_{\rm BE}$ are each recorded 10 times. The blank must be recorded so as to ensure that no memory effect is introduced by the use of high analyte concentrations. This calibration curve is called the gross calibration curve and extends well beyond the normal operating regions of FAE with Ca.

Step 4.

Another calibration curve called the fine calibration curve is recorded in what is normally the linear region, 1 to 20 ppm. To save time, only 5 readings each of $E_{\rm AS}$ and $E_{\rm BE}$ are made for the fine calibration curve. Students are given an unknown solution which is to be run immediately after the fine calibration curve. The concentration of the unknown should be between 5 and 20 ppm in our system, because the detection limit is around 0.1 ppm.

Step 5.

The final solutions analyzed are 5 ppm Ca, 5 ppm Ca with excess phosphate and 5 ppm Ca with excess phosphate and EDTA.

Experimental Report

Before writing up the experiment, students are instructed to scrutinize carefully a set of notes on signal-to-noise-ratio theory provided by J. D. Ingle, Jr. of the Chemistry Department of Oregon State University (8), From these notes, propagation of error theory (available in their text (9)) and lecture notes it is straightforward for them to derive the following expressions.

$$z_{\rm BE}^2 = z_{\rm d}^2 + z_{\rm BFE}^2 \tag{1}$$

$$z_{AS}^2 = z_{BE}^2 + z_{ASR}^2 \tag{2}$$

$$C_{dl} = \frac{(t) (2)^{1/2} (z_{BE})}{m(n)^{1/2}}$$
 (3)

$$S = E_{\rm AS} - E_{\rm BE} \tag{4}$$

$$N = (z_{\rm AS}^2 + z_{\rm RS}^2)^{1/2} \tag{5}$$

The information provided in Steps 1 and 3 provide the basis for determination of the variance of the other major noise contributors in the system. Using eqns. (1) and (2) as building blocks it is easy to estimate the magnitude of the blank flame emission noise, $z_{\rm BFE}$, and the noise due to the flame emission of the analyte, $z_{\rm AFE}$. The student is asked to carry out several graphing and writing exercises. We will discuss the more important of these.

Students are asked to plot the following data and label the curves A, B, C, D, and E, respectively.

S/N versus $\log C$ $E_{
m AFE}$ versus $\log C$ $\log E_{
m AFE}$ versus $\log C$ $E_{
m AFE}$ versus C $E_{
m AFE}$ versus C data

Exercise 1

The student is asked what the optimal height and slit settings were based on his data from Step 2. The important point here is that the students used S/B, which is very easy to determine, rather than the more demanding S/N ratio. Assuming that the noise in the blank, $z_{\rm BE}$, is the dominant noise in an analysis, this is the correct procedure; however, usually this is the case only when data is collected near the detection limit. When higher intensities are observed, other noise sources become dominant as S > B. Under these conditions the optimization procedure may not be valid.

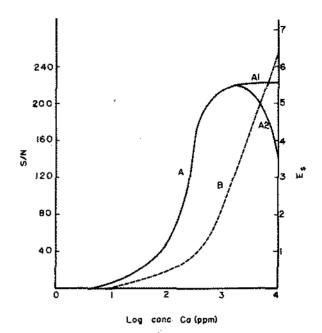


Figure 1. Typical student results plotted as S/N versus log C (curve A) and E_{AFE} versus log C (curve B).

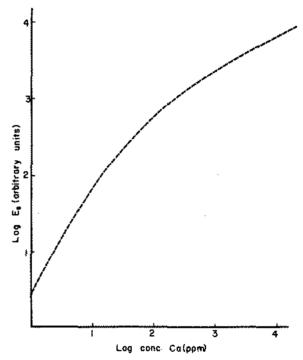


Figure 2. Typical plot of student results for $\log E_{\text{AFE}}$ versus $\log C$ (discussed as plot C in text).

Exercise 2

Plots A and B are made on the same graph. A typical graph is presented in Figure 1. Clearly the intensity of the radiation as measured by E_{AFE} (or by S/B) is constantly increasing; however, the actual performance of the instrument, as measured correctly by S/N, is not improving (A1) or degrading (A2). This is an important point; "bigger" is not necessarily "better." Indeed, in curve A it can be seen that under certain circumstances the S/N ratio degenerates at higher concentrations. This is due, in our case, to clogging of the nebulizer, a common malfunction with high sait solutions.

Plots C and D demonstrate the convenience of logarithmic plots for data that covers orders of magnitude. It becomes quite clear to the students that plot D is very difficult to use in any but the highest concentration range. The students are instructed to examine closely Plot C (Fig. 2). It is a log/log plot of a relationship which should, ideally, be linear and follow the general formula

then

$$\log E_{AFE} = \log m + \log C$$

Plot C should then have a slope of 1.00 in the region where this relationship holds and an intercept of $\log m$. Students are required to do a linear least-squeres regression analysis of the data using the procedures described in reference (10).

Exercise 3

The students have sufficient data provided in Steps 1 and 3 to calculate the magnitudes of the various noises in the system. This information can be combined with the graphical data provided in Plot A to provide an estimate of the type of noise and what might be done to improve the experiment. If the S/N improves directly with increase in S, then the system is "background noise limited." This should be confirmed by the student's calculated values of the magnitudes of the various noises. If the S/N ratio improves as $(S)^{1/2}$ then the system may he "shot noise limited," and one is then governed by Poisson counting statistics of the type commonly encountered in radiochemical photon counting experiments. If the S/N is independent of S, then one is usually "flicker noise limited."

The discovery of the limiting noise source is critical to system improvement. Close to the detection limit one is usually background noise limited and anything which will increase E_{AFE} without increasing E_{BE} will usually result in a direct improvement in performance. This could be an increase in emission caused by a change of fuels or a more efficient nebulization system. The total blank emission signal noise (z_{RE}) is the major source of noise, and anything which will lower this noise will also result in an improvement in the S/N ratio. If z_d is significant, then it is appropriate for the students to suggest that an improvement in the electronics or detector will enhance the performance in this concentration region. In the second concentration region, the performance improvement expected would be proportional to the square root of the S increase if one were shot noise limited; however, Plot A invariably goes through a concentration region where the slope would indicate a shot noise limited condition. This is to be expected as the conditions are changing toward a slope of 0 as a flicker noise limited situation is approached. An additional experiment would have to be performed to determine whether the instrument were indeed shot noise limited in this concentration region. A reduction of intensity can be achieved by partially blocking the beam from the flame or, preferably, the iosertion of neutral density filters. A reduction of intensity by a factor of 4 woold cause a degradation in the S/N by a factor of 2. The students have not done this, because they always process their data after the experiment. They cannot then state emphatically that they are shot noise limited in this situation, but simply that the slope of the S/N curve may imply that this is true. In the final case, the S/N cannot be improved by increasing S but must be improved by decreasing N. One must then examine the components of N. In the flicker noise dominated region the primary source of noise is z_{AFE} and only changes which improve the stability of E_{AFE} will have an enhancing effect. Stabilization of the flame by the use of sheathing or improvements in nebulizer design are reasonable improvements to suggest.

Plot A provides a final benefit in that it demonstrates the sometimes complex nature of reality. In the middle portion of the S/Ncurve, it is not trivial to state exactly what the situation is. Several noise sources may be significant and more experiments would be necessary for the students to state that the experimental precision was shot noise limited. While this might sound initially like "hand waving," instrumental evaluation can be a complex iterative process.

Exercise 4

Plot E, the fine calibration curve, is plotted using linear axes. The students must apply linear regression techniques (3) to this data. They are asked to use the linear regression data from both Plots D and E

to estimate the value of their unknown solution, provide confidence limits and detection limits. Usually the slopes and calculated unknown concentrations are significantly different using the two data sets. It then becomes apparent to the student that the data derived from the information collected in Step 3 is far more useful due to the close bracketing of the analyte signal by standards. The regression coefficient of the data from Plot D may be very close to 1.00; however, this is due in large part to the fact that the linear regression can be very deceptive when used with data values which extend over orders of magnitude. This serves as a valuable warning against mathematical "black box" solutions.

Exercise 5

Step 5 is a demonstration of a classical chemical (rather than spectral) interference. E_{AFE} with the phosphate solution is significantly lower (often 40%) than that of the original 5 ppm Ca solution. This is due to the creation of Ca₃(PO₄)₂, a very stable compound which is only partially decomposed in an air-acetylene flame of the type used in this laboratory. The EDTA/Ca/PO₄ solution E_{AFE} is usually 5 to 10% higher than the pure Ca solution. Students have been instructed that EDTA selectively complexes with the Ca and yet the complex is easily broken down in the flame. While this would justify a return to the original signal, it does not explain the significant increase in signal. The students are asked to explain any anomalies in their data, and how they would do an analysis for Ca which may be in a phosphate environment.

There are two reasonable explanations for the increase in $E_{
m AFR}$ in the final solution. The EDTA may act as a fuel, thereby increasing the flame temperature, or the EDTA may be emitting as it is burned in the flame. The good student will suggest one or both of these as possible solutions and will offer a simple experiment which might indicate which is the source of deviation. An EDTA solution could be aspirated after a water blank. If the intensity increased, then it would be due to EDTA combustion. An alternative would be to shift slightly off the Ca line. If the signal is due to EDTA combustion, it is most likely a broad bend molecular emission or stray light (from the Na in the Na-EDTA salt) and a shift to a slightly different wavelength should not reduce the signal back to the level of a water blank. In either case, the student should suggest the use of either the standard addition technique or standards and blanks with EDTA at the same concentration level for analyses of this type.

Conclusion

Using equipment available in many teaching labs, it is possible to provide students with a simplified but powerful introduction to Signal-to-Noise-Ratio Theory. The techniques are generally applicable and can be used for instrumental design and modification as well as day to day diagnostic performance analysis. The experiment described above provides an insight into some of the conveniences of logarithmic data presentation as well as some of the pitfalls. Basic principles of good data handling are encouraged throughout the experiment as they should be in all laboratories regardless of equipment or environment.

Literature Cited

- Malmstadt, H. V., Enke, C. G., and Crouch, S. R., "Electronics and Instrumentation for Scientists," The Benjamin/Cummings Publishing Co., Inc., 1981, pp. 142-145.
 Ingle, Jr., J. D., Anal. Chem., 46, 2161 (1974).
 Bower, N. W., and Ingle, Jr., J. D., Anal. Chem., 49, 574 (1977).
 Bower, W. W. and Logh, Jr., J. D., Anal. Chem., 49, 574 (1977).

- Sower, N. W., and Ingle, Jr., J. D., Anal. Chem., 48, 686 (1976).
 Bower, N. W., and Ingle, Jr., J. D., Anal. Chem., 50, 544 (1978).
 Bower, N. W., and Ingle, Jr., J. D., Anal. Chem., 51, 72 (1979).
 Bower, N. W., and Ingle, Jr., J. D., Anal. Chem., 51, 72 (1979).
 Bower, N. W., PhD Thesis, Oregon State University, Corvallis, Oregon, 1978.
- (8) Ingle, Jr., J. D., "Notes on Basics of Spectrometric Measurements," 1977.
 (9) Skoog, D. A., and West, D. M., "Principles of Instrumental Analysis," 2nd ed., Saunders
- (10) Peters, D. G., Hayes, J. M., and Hieftje, G., "Chemical Separations and Measurements—Theory and Practice of Analytical Chemistry," W.B. Saunders Co., 1974, Chapter 2.

romething new from the part

Gas Laws and Gas Behavior

Gas Laws and Syringes Revisited: Boyle's Law

In the December, 1980 issue of THIS JOURNAL, p. 885, the work of Derek A. Davenport involving the use of the hypodermic syringe to study gaseous behavior was reviewed. His work and similar demonstrations and experiments developed by others are wonderful sources for fun with gases in the classroom. Add to this collection Davenport's syringe experiments of Boyle's Law that appeared in "Tested Demonstrations," J. CHEM. EDUC., 56, p. 322 (May 1979). The experiments are easy to do, and typical data (all obtained in 5 minutes) are given.

Gauge Pressure and Absolute Pressure

On the same page as the Boyle's Law experiment mentioned above, Davenport describes some interesting (and fun) gas behavior using a standard tire pressure gauge and a side-arm test tube. Various pressure readings are made which show, "The sum of the gauge pressure and the residual pressure (in the same units) is sensibly constant." "When the test tube has been completely evacuated, the gauge reading will be found to have increased by an amount equal to the atmospheric pressure."

Who's Law?

"Boyle's/Hooke's/Towneley and Power's/Mariotte's Law," Robert M. Hawthorne, Jr., J. CHEM EDUC., 11, p. 741 (November 1979).

"Chemistry, like all the sciences, is filled with constants, principles, and mathematical laws, many of which have someone's name attached to them." The student of chemistry, knowing no better, is apt to assume that the person named is the person who actually produced the number or formula that's on the page before him, an assumption often far from the truth. Probably no great harm is done in this way, as the substance of the law is more important than its provenance. Nonetheless, there are some interesting anecdotes connected with the formulation of laws, or the determination of constants, that can be used to enliven classroom presentations. In some cases the background of these atories can lead to a deeper understanding of the principle itself.

A case in point is the gas pressure-volume relationship that we know as Boyle's Law, which has a very tangled origin indeed.

It is from articles such as this one that the "spice" of the story of chemistry comes. The significance of the priority of publication and of keeping a lab book is stressed by the author, read the entire article to get the rest of the story.

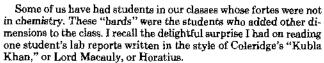
"The Fable: Laws are Mature Theories," Jack K. Horner and Peter A. Rubba, *The Science Teacher*, **46**, 31 (February 1979).

"At the heart of this fable is a fatal assumption about the relationship between laws and related theories: namely, that theories mature into laws by constant testing and confirmation." The authors present three familiar examples that show the fallacy of this common, naive misconception. Boyle's and Charles' laws are used as one of the examples showing "... that the relationship between theories and laws is an explanatory one—not, as the fable insists, a maturational one." One reading of this article and many of you will change your teaching, especially for your beginning chemistry classes.

"On Avogadro's Number: as Shakespeare's Prospero might write," S. R. Scholes, J. CHEM. EDUC., 42, 126 (March 1965).

Edited by: JOSEPH S. SCHMUCKLER Chairman of Science Education

Temple University 345 Ritter Half Philadelphia, PA 19122



Can you imagine yourself introducing Avogadro's number in the style of a Shakespearean thesbian? No? Try it. Both you and your classes might enjoy it.

"New Device for Determining Molecular Weight of a Gas," Howard Nechamkin. The Science Teacher, 35, 47-48 (April 1968).

With today's disposable butane lighters, this experiment is even easier to do than it was using the method suggested by Nechamkin.

"Reaction Kinetics" Brian Moar, The Science Teacher, 44, 48 (May 1977).

This is a "macro-demonstration" of kinetic molecular theory involving students as molecules in a confined volume (area).

"Kinetics Teaching Model," William W. Sadler, The Science Teacher, 38, 41 (November 1971).

In previous columns we have cited articles on physical models to demonstrate the effects of molecular activity. Sadler describes a simple inexpensive device that he has constructed from common items found in most high schools and which can be used with an overhead projector. It demonstrates random motion and transfer of energy as spheres "the size of basket balls" collide on the projection screen. It shows gaseous diffusion through a membrane, and effects of temperature changes and concentration changes.

"Analysis of the Upper Atmosphere," William B. Jensen, J. CHEM. EDUC., 54, 74 (February 1977).

I have reproduced this short article that can be used as an anecdote in your classes. You will have to go to the journal for the actual illustration.

"The illustration shows the balloon ascent made on August 20, 1804, by the French chemist, Gay-Lussac, and the French physicist, Biot, to test, among other things, an earlier Russian claim that the earth's magnetic field decreased with altitude. Their results indicated that it was constant. They also tested the atmosphere's chemical composition as a function of height and found it to be uniform. Gay-Lussac is at the left with the top hat, glasses, and air sample bottle.

"Gay-Lussac later made a second flight alone, reaching an altitude of 7016 meters. In order to gain height he threw several items out of the balloon, including the old white kitchen chair he was sitting on. It landed near a peasant girl who was minding sheep. The local villagers and the priest, after much debate, finally decided the incident was a miracle. They remained, however, puzzled as to why God owned such shabby furniture."

"Illustrating Principles of Kinetic Theory of Gases," Robert C. Plumb, J. CHEM. EDUC., 47, 175 (March 1970), 48, 119-120 (February 1971), and 50, 559 (August, 1973).

Sea-Lab Experiment

"The ocean floor is one of our unexplored geographical frontiers." To extend exploration of the ocean, scientists and engineers are developing hardware and procedures to permit people to live for days or weeks in chambers on the ocean floor. In these chambers oxygen and helium are used as an atmosphere. A strange physiological effact is noted when a person lives in an atmosphere in which nitrogen has been replaced by helium. If the temperature in the chamber is a normal, comfortable 70°F such as is used in buildings on the earth's surface, the aquanauts feel decidedly chilly. Why?



Space Vehicle Reentry and Thermal Effects of High Winds

"If a person is exposed to a cold wind, he loses body heat more rapidly than he does under circumstances where heat loss is controlled by diffusion—it may even lead to a tragedy such as on Mt. Washington in New Hampshire when two persons "froze to death" on July 20, 1959, even though the temperature did not go below 38°F, but the wind was as high as 65 mph.

"Why, then, does a space vehicle, in passing at high speed through the atmosphere, tend to get hotter than the gas? Why doesn't it get cooled to the temperature of the atmosphere? At what wind velocity would a person standing on a high mountain tend to heat up instead of cooling off, and why in terms of molecular behavior would this occur?"

Gas-Bubble Disease of Fish

vationist, then keeping fish alive and healthy is of concern to you. You will see in this exemplum how a simple chemical process is a common cause of fish kills; knowing the chemistry leads directly to solutions to the problem.

In each of the above examples of chemical principles you should read the articles in their entirety in order to answer the questions posed by the authors.

A Lab Experiment

"Does Pressure of a Gas Depend on the Number of Molecules?" James V. DeRose, Chemistry, 38, 26-28 (June 1965).

"The problem of counting molecules in a gas sample would seem to be insurmountable. However, it is not necessary actually to count molecules to conduct an investigation which provides data relative to this question." DeRose gives a detailed introduction and procedure to this "Lab Bench" experiment. He presents expected data and a series of good questions that will challenge the students to think.

The Density and Apparent Molecular Weight of Air

A Simple Introductory Experiment

Arlo D. Harris

California State College, San Bernardino, San Bernardino, CA 92407

Fundamental to a study of chemistry is an understanding of both extensive and intensive properties. Most inroductory courses utilize mass and volume as examples of the former. The ratio of mass to volume equalling density is most often used as an example of the latter. These concepts are quite easily defined and described in lecture materials, hence they require little effort on the part of the student for understanding.

Generally speaking, the first experiment done in most introductory laboratory courses deals with physical measurements. The aforementioned concepts and definitions lend themselves readily to simple measurements to confirm them as basic tenets of chemical science. A variety of measurements of mass and volume are used to demonstrate the density of solids and liquids, both pure and solutions. These can be found published in many commercially available laboratory manuals. Some institutions use modular units or use hand-out experiments of their own.

Few, if any, programs incorporate a measurement of the density of a gas at this early stage in a laboratory sequence. Possibly there is the idea of a need to include a discussion of gas laws which, of course, comes later in most courses. In fact, many experimental programs use the classical Dumas method later in the course to determine the molecular weight of a volatile liquid or even a gas itself.

The experiment described herein can be used by beginning students without the mention of gas laws. It relys solely on mass, volume, and temperature. The variables are mass and temperature while the volume of the system remains constant. Although this experiment uses the ideal gas law in deriving the working equation, students need not be hurdened with it. It is sufficient to instruct the student in simple concepts which are presented at the end of the derivation.

Apparatus (as shown in the figure)

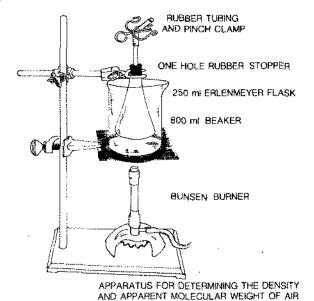
250-ml Erlenmeyer flask

1-hole rubber stopper

- 1 short piece of glass tubing (about 10 cm long)
- I short piece of rubber tubing (about 8 cm long)
- 1 pinch clamp
- 1 800-1000-ml beaker

Experimental Procedure

The glass tubing must go through the rubber stopper so that it is



Apparatus used to determine the density and apparent molecular weight of air.

flush with the bottom and will not extend into the flask. The rubber tubing slips over the extending end. The stopper is pushed very tightly into the mouth of the Erlenmeyer flask. The pinch clamp is placed anugly about the rubber tubing but not tightly closed, so that air can easily escape at the higher temperature. This apparatus is weighed to four decimal places at room temperature. The temperature must be measured to within 0.1°C.

The apparatus is then clamped in such a way that as much of the Erlenmeyer flask is inside the large beaker as is possible (see figure). The beaker is filled with water to the very top allowing only enough room for hubbling due to rapid boiling. The water is brought to a boil and allowed to boil vigorously for 10 min. The temperature of the water is recorded to within 0.1°C.

While the water is still boiling, the rubber tubing is folded over and the pinch clamp is clamped very tightly shut around it. The closed system is quickly removed from the boiling water, placed on a folded paper towel, and dried thoroughly with a second paper towel. After complete drying, the closed system is reweighed. Experience has shown that it need not be cooled to room temperature to do this. In fact, a lengthy cooling period may allow some air to seep into the system.

Remove the stopper and fill the flask with water. Push the stopper in, forcing water up to fill the glass and rubber tubing. Pour this into a graduate cylinder to measure the total volume of the system.

Derivation of the Working Equation

The experiment is performed using two temperatures. The lower will be designated by a subscript (1) while the higher will be designated by the subscript (2). The derivation is based upon the ideal gas equation in the form

$$PV = \frac{g}{M_*W_*}RT$$

for low temperature

$$P_1V_1 = \frac{g_1}{M_1W_1}RT_1$$

for high temperature

$$P_2V_2 = \frac{g_2}{M_*W_*}RT_2$$

Under the conditions of the experiment the molecular weight of air is unknown. However, the homogeneous concentrations of the mixture present will remain the same, and for this reason the apparent molecular weight will remain constant. Gathering together those parameters which remain constant in the above equations is shown as follows.

$$\frac{P_1V_1M.W.}{R} \approx g_1T_1$$

$$\frac{P_2V_2M.W.}{R} \approx g_2T_2$$

The left sides of hoth equations are equal, hence combining them yields:

$$g_1T_1 = g_2T_2$$

but $g_2 = (g_1 - x)$ where x is the mass of air driven out at the higher temperature. Substitution into the above equation yields

$$g_{1}T_{1} = (g_{1} - x)T_{2}$$

$$g_{1}T_{1} = g_{1}T_{2} - xT_{2}$$

$$g_{1}T_{1} - g_{1}T_{2} = -xT_{2}$$

$$g_{1}(T_{2} - T_{1}) = xT_{2}$$

$$g_{1} = \frac{xT_{2}}{T_{2} - T_{1}}$$
(1)

This equation is used to calculate the grams of air present at the lower temperature. Since

$$D = \frac{M}{V}$$

the density of air will be

$$D = \frac{g_1}{vol\ of\ system} \tag{2}$$

Equations (1) and (2) are the operant equations of this experiment.

Results and Calculations

The results of a typical experiment are as follows:

Weight of apparatus at
$$T_1$$
 138.2235 g
Weight of apparatus at T_2 138.1525 g
Weight loss ($\pm x$) 0.0710 g

$$T_1 = 20.5 ^{\circ}\text{C} \qquad T_2 = 100.5 ^{\circ}\text{C} \qquad Vol = 262 \text{ mi}$$

$$g_1 = \frac{(0.071)(373.65)}{80}$$

$$g_1 = 0.3316 \text{ g}$$

$$D = \frac{0.3316 \text{ g}}{262 \text{ ml}} = 12.66 \times 10^{-4} \text{ g/ml}$$

Discussion

The result obtained using this simple experimental procedure was 12.66×10^{-4} g/ml. The accepted value is 12.05×10^{-4} g/ml. The percent error is 5%. For this simple approach this is a reasonable error since no case was taken to assure a good seal of the closed system, the volume was estimated using a very large graduated cylinder, and the thermometers were not calibrated.

The procedure gives an answer well within an acceptable range of error for an introductory experiment. It allows the student to determine the density of air without relying on the gas law. The student need only realize that as the system is heated, the gas expands and some of it is lost. This physical fact is familiar to most students.

Using this experiment in conjunction with the determination of densities of solids and liquids gives students a hetter understanding of changes in intensive properties inherent in changes of physical phase.

Further Considerations

The experiment as presented here is directed toward the incoming first-year student. It is designed to be part of an experiment concerning physical measurements of mass, volume, and density. A student will be able to understand it with no reference being made to gas laws or the ideal gas equation.

The essential characteristic of the experiment is a combination of the Avogadro law and the Dumas method of determining the molecular weight of a gas. The experiment could therefore be used later in an introductory course when gas laws are being studied. Since the experiment presents a simple method of finding the mass of a gas in a discrete volume, measuring the prevailing atmospheric pressure will allow use of the ideal gas law

$$M.W. = g \frac{RT}{PV} = \frac{g}{V} \frac{RT}{P} = d \frac{RT}{P}$$

to obtain the apparent molecular weight of air.

The concept of an apparent molecular weight of a mixture of gases is useful and a brief discussion can be found in a recent textbook aimed at the introductory level.² It would be very instructive to the student to go through the derivation of the operant equation if the experiment is, in fact, used in conjunction with the study of gas laws. Very careful manipulation in the experimental procedure will yield an answer within $\pm 1-2\%$ of the accepted value of 28.96 g/app. M.W.

This experiment may be used to determine the density and molecular weight of a pure gas. The only change would be to flush completely the system with the gas whose density is to be determined and clamp the rubber tubing shut while weighing at room temperature. While heating the gas to the boiling point of water, the clamp would be opened. At the boiling point of water and after a 10-min period, the clamp would be tightly shut.

The same operant equations would be used and both the density and molecular weight may be calculated. This works well for gases such as nitrogen and carbon dioxide. Other gases would be used as long as they are not flammable since safety considerations would preclude these.

Note Added in Proof

David S. Moore of Dover College, Dover, England has successfully adapted this experiment by replacing the described stopper system with an appropriately prepared Bunsen Valve.³ The author is grateful for his suggested improvement.

¹ Norbert Adolph Lange (*Editor*), "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1956, p. 1411.

² Petrucci, R. H., "General Chemistry, Principles and Modern Applications," 3rd ed., Macmillan Publishing Co., Inc., New York, **1982**, p. 105

³ Linstead, R. P., Elvidge, J. A., and Whalley, M., "A Course in Modern Techniques of Organic Chemistry," Butterworths Scientific Publications, London, 1955, p. 143,

Solution Calorimetry in the Advanced Laboratory

A Study of Glycine Proton-Transfer Enthalpies

R. W. Ramette

Carleton College, Northfield, MN 55057

Heat effects accompanying chemical reactions are among the most fundamental and informative phenomena encountered by chemists, both in the classroom and in the laboratory. Yet, except for numerous general chemistry experiments, typically involving expanded-polystyrene-cup reaction vessels and relatively insensitive thermometers, students gain little experience with solution calorimetry. A major reason for this in the past has been the unavailability of reliable calorimetric equipment that is both reasonable in cost and high in accuracy. The introduction of a moderately priced solution calorimeter (1) has made it convenient to use this technique in the advanced laboratory. In our experience over a few years, the Parr Model 1451 calorimeter has performed reliably and in accord with its high specifications. The experiment described in this paper requires precise measurement of temperature changes of a few tenths of a degree. The Model 1451 generates a voltage output with a sensitivity of 100 mV per degree, and a strip chart recorder provides a convenient record.

In addition to a variety of acid-base reactions we have used powdered zinc metal in the rotating glass cell with copper perchlorate solution in the Dewar flask to determine the enthalpy change for the redox reaction. We have also measured the heat of complexation when a solution of ethylenediamine is added in excess to a solution of nickel chloride and the heat of reaction between permanganate and ferrous ion. A variation is to use the cell compartment as a titration vessel, using a dispensing pipet to add titrant. A plot of temperature versus volume added may be used to find the titration endpoint.

This paper discusses a fairly rigorous investigation of the heat effects accompanying the acid-base reactions of glycine. Adaptation to studies of other amino acids should be straightforward. A good reason for using glycine is that the calculated enthalpy values may readily be compared with those derived entirely from Gibhs free-energy measurements. This has the value of encouraging physical chemistry students to see key relationships in an integrated way. The entire experiment can be performed by a pair of students in one afternoon, and in our experience the results have been quite good.

Stock solutions of 0.300 M hydrochloric acid, sodium hydroxide, and sodium chloride are needed. Glycine, recrystallized from water and dried overnight at 80°C, is finely ground before use. What follows is an abridged version of the handout for students. Complete details on the experimental procedure are available from the author.

The purpose of this experiment is to determine the molar enthalpies for the two stages of glycine proton-transfer:

$$H_2Giy^+ = H^+ + HGiy^+$$
zwitter ion
(+HsNCH2COO-)
(1)

$$HGiv^{+-} = H^+ + Giv^- \tag{2}$$

The calorimeter will be used to find the quantities of heat absorbed or liberated when known amounts of glycine are mixed with sodium chloride, with hydrochloric acid, and with sodium hydroxide. The calculated enthalpy changes will not be the standard values because the experiments are carried out at electrolyte concentrations of about 0.3 M. However, the effect of ionic strength on the values is not large.

The equilibrium constant values for the above reactions were reported for a range of temperatures by King (2) who used precise measurements of galvanic cells based on the hydrogen electrode. Least-squares fits for results obtained at ionic strength 0.30 are as follows:

$$pK_1 = -46.7920 + 2378.22/T + 16.64 \log T$$
 (3)

$$pK_2 = -16.1083 + 3165.76/T + 6.09 \log T \tag{4}$$

Values for ΔH are readily inferred from these equations by using the thermodynamic relationship:

$$d \ln K/dt = \Delta H/RT^2 \tag{5}$$

Such values may then be compared with the calorimetric results of this experiment.

Experimental Procedure

This experiment requires three separate runs, using 0.300 M solutions of sodium chloride, hydrochloric acid, and sodium hydroxide. Step-by-step details for instrument operation are provided in a separate handout.

Study of Reaction (1)

Set up the calorimeter cell with 100 mL of 0.3 M hydrochloric acid in the Dewar compartment, and with about 20 mmol of glycine (HGly) in the solid sample compartment. Upon mixing, a temperature change will be observed because of the reaction:

$$HGly(s) + H^+ \rightarrow H_2Gly^+(aq)$$
 (6)

Note that reaction (6) is not simply the reverse of the desired reaction (1), because the glycine is added as a solid rather than being in the aqueous state. Therefore, it is necessary to make another calorimetric run, using 100 mL of 0.3 M sodium chloride. This will provide a similar ionic strength effect on the heat of solution of glycine, but there will be no proton-transfer reaction:

$$HGly(s) \rightarrow HGly(aq)$$
 (7)

If the observed molar enthalpy change for reaction (6) is subtracted from that for reaction (7), the result is the enthalpy change for reaction (1).

Study of Reaction (2)

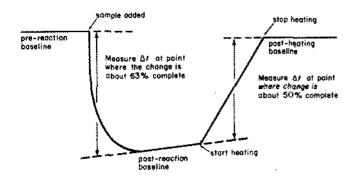
Set up the calorimeter cell with 100 mL of 0.3 M sodium hydroxide, and again add solid glycine. The reaction is

$$HGly(s) + OH^+ \rightarrow Gly^-(aq) + H_2O$$
 (8)

To obtain the enthalpy change for reaction (2) it is necessary not only to use the heat of solution determined for reaction (7), but also to introduce the heat of formation of water:

$$H^+ + OH^- \rightarrow H_2O \tag{9}$$

Note that $\Delta H_2 = \Delta H_8 - \Delta H_7 - \Delta H_9$. The enthalpy change for reaction (9) is -13,340 cal at zero ionic strength (3), and -13,550 cal at ionic strength 0.5 (4). An interpolated value of -13,465 may be used.



Typical thermogram for an endothermic reaction.

Interpretation of Data

Each thermogram has five parts: pre-reaction baseline, temperature change due to reaction, post-reaction baseline, temperature rise due to heating calibration, and post-heating baseline. To determine the precise temperature changes it is necessary to extrapolate the baselines as shown in the figure.

The purpose of the electrical heating is to determine the heat capacity, C_{α} , of the calorimeter under conditions identical to those used for the chemical reaction. The current and voltage through a heater is monitored to calibrate the calorimeter and its contents.

The heat change associated with the chemical reaction is calculated by using the temperature change Δt observed for the reaction thermogram:

$$Q = -C_D \Delta t \tag{10}$$

where the minus sign is used to satisfy the convention that heat evolved is given a negative sign.

Finally, to find the enthalpy change per mole of glycine

$$\dot{\Delta}H = Q/n \tag{11}$$

where n is the amount (moles) of solid glycine used for the run.

The Problem of Incomplete Protonation of Glycine

When solid glycine is added to a slight excess of hydrochloric acid the reaction HGlv + H+ → H₂Glv+ does not proceed quantitatively because the protonated species is not a very weak acid (p K_a about 2.3). This means that the heat change observed for reaction (6) should be interpreted as

$$Q_6 = Q_7 - Q_1$$

= $n \cdot \Delta H_7 - \alpha n \cdot \Delta H_1$ (12)

where α is the fraction of the glycine present as H_2Gly^+ in the equilibrium mixture,

Given the initial (pre-reaction) concentrations of hydrochloric acid and glycine, 0.300 and n/0.1, respectively, the value of α can be estimated from the stoichiometric/equilibrium relationship, which the reader should derive

$$K_1 = [H^+][HGly]/[H_2Gly^+]$$

$$= (0.3 - (\alpha n/0.1))((n/0.1) - (\alpha n/0.1))/(\alpha n/0.1)$$

$$= (0.3 - n/0.1)(1 - \alpha)/\alpha$$
(13)

The appropriate value for K_1 can be found from King's results (eqn. (3)), and then this expression can be simplified and solved by the quadratic formula. The value for ΔH_1 then follows from rearrangement of equation (12).

Report

Prepare a tabular summary of glycine masses, Δt values deduced from thermograms, values of Q, Q_h , C_p and ΔH . Calculate the enthalpy changes for the acid dissociation reactions (1) and (2), and compare your results with those inferred from the pK(T) studies by King. Look up the enthalpy of formation of solid glycine, and calculate the enthalpy of formation of glycine(aq). Calculate the entropy changes for reactions (1) and (2) and suggest an explanation for their algebraic signs. Make suggestions for improvement of the experiment.

Literature Cited

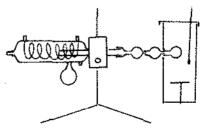
- (1) Bulletin 1451, Part Instrument Co., 211 Fifty-Third St., Moline, H. 61265.

- King, E. J., J. Amer. Chem. Soc., 73, 155 (1951).
 Glofisson, G., and Repler, L., J. Salution Chem., 4, 127 (1975).
 Christensen, J. J. Hansen, L. D. and Izatt, R. M., "Handbook of Proton Ionization Heats." John Wiley & Sons, New York, 1976.

A Kugelrohr Oven from a Rotary Evaporator

A simple modification of the rotary evaporator transforms it into a Kugelrohr oven, an extremely useful apparatns for distilling small volumes of high boiling compounds from bulb to bulb. Although this apparatus comes in different price ranges, the Aldrich version is simple and inexpensive; unfortunately, the motor has to be operated by vacuum or pressure and can be inconvenient at times

Here we report a simple method of converting the normal rotary evaporator bearing a 24/10 or 24/14 adapter. Moving the evaporator into a horizontal position transforms it into a simple Kugelrohr-oven-like device (see figure). Distillation is performed by operating the rotation at the lowest speed possible. With this setup we have been able to attain a pressure as low as I mm Hg.



R. Somananthan and L. Hellberg San Diego State University San Diego, CA 92182

Reactions of Thiocyanate lons with Acid

A Laboratory Experiment

Christopher Glidewell, James S. McKechnie, and Peter J. Pogorzelec

University of St. Andrews, St. Andrews, Fife KY16 9ST, U.K.

The reaction of solid ionic thiocyanates, such as KNCS and NH₄NCS, with concentrated sulfuric acid to produce carbonyl sulfide, OCS, along with $\rm CO_2$, $\rm SO_2$ and traces of HCN has been known for many years as a convenient small-scale preparation of OCS (1): of greater antiquity is the reaction of concentrated sulfuric acid with aqueous solutions of ionic thiocyanates to yield the solid product xanthan hydride (2) $\rm C_2H_2N_2S_3$, first prepared by Wöhler (3) as long ago as 1821. Xanthan hydride has been characterized in the solid state by X-ray analysis (4) as 5-amino-1,2,4-dithiazol-3-thione, (I), and this constitution persists in solution also (5).

The mechanism of formation of xanthan hydride from thiocyanate ions and acid has recently been elucidated by means of concurrent, and synergistic, experimental and theoretical investigations (5).

The reaction which forms carbonyl sulfide and other gaseous products is widely used as a safe introduction to vacuum line preparations in laboratory courses in inorganic chemistry (6). We have developed a more extended investigation of the reactions between ionic thiocyanates and sulfuric acid, which not only includes the usual vacuum line experiment, but also involves the elucidation of the structure of xanthan hydride from a combination of infrared, mass-spectral, and ¹³C and ¹⁵N NMR data, together with the testing of xanthan hydride as a possible intermediate in the formation of carbonyl sulfide. We use this exercise in our third (i.e., penultimate) year laboratory, where the emphasis throughout is on students learning the use of a wide range of techniques to solve real chemical problems (7,8). This laboratory represents the final stage of structured experimental work before the students undertake research projects during their final year.

The experiment falls into three parts. The students have no prior knowledge of the nature of any of the reaction products, all of which must be identified:

- (a) reaction of solid KNCS with sulfuric acid (identification of the reaction products);
- (b) reaction of aqueous KNCS solution with 96% sulfuric acid (isolation and identification of the involatile product);
- (c) reaction of the solid product from (b) with 96% sulfuric acid (identification of volatile products).

Experimental

For parts (a) and (c) the apparatus is a simple vacuum system (9) consisting of a rotary oil pump and cold-trap; a manifold equipped with a cold fluger, a take-off for an IR cell or molecular weight bulb, and a mercury manometer; and finally two U-traps to which reaction vessels can be connected.

(a) Reaction of solid KNCS with sulfuric acid

Attach a 250-ml two-necked flask equipped with an L-shaped sidearm to the end of the vacuum system, and place in it 5 ml of sulfuric acid: add 4 g of KNCS to the sidearm and evacuate the system. When the system is leak free, admit air to a pressure of 25 cm Hg to the apparatus, place a $-78^{\circ}\mathrm{C}$ hath (eithanol/CO₂) around the U-trap nearer the reaction vessel and a $-196^{\circ}\mathrm{C}$ bath (liquid N₂) around the further U-trap. Place a bath of ice water around the reaction flask and gradually add the KNCS to the sulfuric acid by rotating the sidearm. As the reaction proceeds, allow the reaction vessel to warm up gradually. Toward the end of the reaction, a warm water bath ($\approx 60^{\circ}\mathrm{C}$)

may be placed around the flask. After $\simeq 30$ min, replace the -78° C bath by liquid N₂, evacuate the system, and then pump away the contents of the further U-trap. Transfer the contents of the nearer trap to the cold finger. Record its vapor pressure at -78° C and its infrared spectrum and determine its molecular weight (6, 9).

Here we have followed the published procedure (\$\overline{6}\$) except that we run the reaction under a pressure of 25 cm Hg air since this generally gives an easier separation of CO₂ from the remainder of the volatile products, and use different concentrations of H₂SO₄ in the range of 60%–96%. Students are provided with vapor pressure data (-78°C) and infrared data, and they must identify the principal components of the reaction products from the IR spectrum and assign as many of the bands as possible to fundamentals and combination bands.

(b) Reaction of aqueous KNCS with 96 % H₂SO₄

(To be performed in a fume cupboard) Place in a 250-ml flask fitted with a dropping funnel and a magnetic stirrer, 9.7 g (0.1 mol) of KNCS dissolved in 50 ml water. Add 96% H₂SO₄ dropwise until a persistent yellow precipitate is produced: cool, filter off the product, denoted X, wash with water, and dry in vacuo. Note the yield and record an IR spectrum. (This product has no melting point: ¹³C and ¹⁵N NMR and mass spectral data are provided, together with the empirical formula, C₂H₂N₂S₃.)

Spectral Data

NMR; $\delta(^{13}\text{C})/\text{p.p.m.}$, +183.5, +208.6 (both quaternary) relative to TMS: $\delta(^{15}\text{N})/\text{p.p.m.}$, -116.9 (n.O.e. positive), -273.1 (n.O.e. negative) relative to CH₃¹⁵NO₂. Mass spectrum contains major ions at n/z: 150 (49%), 86 (17%), 85 (41%), 76 (96%), 74 (11%), 73 (100%), 64 (56%), 60 (52%), and 59 (97%). Infrared spectrum (KBr disc): ν/cm^{-1} ; 3220 s, 3040 s, 2915 m, 2700 w, 2340 ν w, 2175 ν w, 1630 s, 1515 ν s, 1335 ν s, 1320 ν s, 1155 ν , 1088 m, 1019 s, 1005 s, 750 w, 648 m, 630 m, 616 m, 538 w, 510 ν w, 410 w, 393 mw.

The infrared spectrum and the mass spectrum have been analyzed (10, 11).

(c) Reaction of X with 96% H₂SO₄

Set up a 250-ml quickfit flask with a double surface reflux condenser and equipped for magnetic stirring and oil bath heating. Add to the flask 1.5 g of X and 5 ml of 96% $\rm H_2SO_4$: connect the top of the condenser to the end of the vacuum system by means of pressure tubing and evacuate the system. When the system is leak free, place liquid $\rm N_2$ round the two traps. Heat the reaction flask (a time of $\simeq 30$ min, at an oil-bath temperature of $\rm 150^{\circ}C$ is suggested) and collect hovolatile products. Pump away any non-condensible gases which form: When the reaction is complete allow the reaction flask to cool, and continue pumping as it does so. The subsequent identification of the volatile products is made as in part (a).

Spectral Interpretation for X

The students are given the empirical formula $C_2H_2N_2S_3$: with this and the infrared, mass spectral, and $^{13}\mathrm{C}$ and $^{15}\mathrm{N}$ NMR data the structural formula can be established.

The infrared spectrum indicates the presence of NH₂, C=N, and C=S, but not CH or SH bonds (10). The ¹³C NMR spectrum contains only two quaternary resonances, confirming the absence of CH bonds; the low field ¹³C resonance at +208.6 p.p.m. is characteristic of C=S. The ¹⁵N NMR spectrum which contains one resonance with a positive nuclear Overhauser effect (n.O.e.) and one with a negative n.O.e. indicates that only one of the nitringen atoms is bonded to hydrogen.

The mass spectrum (11) contains no ions having m/z > 150, confirming $C_2H_2N_2S_3$ as the molecular formula: the iuns at m/z values of 86, $(M_-S_2)^+$, and at 64, $(S_2)^+$ indicate two sulfur atoms bonded together, those at 74, $(M_-CS_2)^+$, and 76, $(CS_2)^+$, indicate a carbon bonded to two sulfur atoms, so that the molecule probably contains a fragment SCSS. In addition, the ions at m/z 60 and 59 suggest the

fragment H2NCS. Three major fragmentations (II) accommodate all the observed ions.

All the spectral data together are consistent with the molecular structure (I) for the product X.

This has been confirmed by an X-ray analysis (4): the same structure persists in solutions (5) and in the gas phase (11).

Identity of Volatile Reaction Products

From part (a), the volatile reaction products are primarily OCS and CO2, with lesser quantities of SO2 and HCN. If the CO2 is removed effectively, the remaining product is almost pure OCS which has a mean apparent molecular weight usually in the range 60-62. Variation of the concentration of the sulfuric acid within the range 60%-96% causes little significant change in the volatile products except that at the lowest concentration employed (60%) no sulfur dioxide is detected. The solid residue contains elemental sulfur and mixed ionic sulfates, but no xanthan hydride.

In part (c) the principal volatile products when 96% sulfuric acid reacts with xanthan hydride are CO_2 and SO_2 with only small quantities of OCS and a trace of HCN. As the concentration of the acid is decreased, the proportions of both OCS and SO2 decrease. The solid residue contaius elemental sulfur, ammonium sulfate, and thiourea (5).

Discussion

Xanthan hydride does not react at room temperature with water or with aqueous sulfuric acid of concentrations up to 965. Chattaway and Stevens reported (2) that superheated water hydrolyzes the compound to CO2, H2S, elemental sulfur, and ammonium thiocyanate, but they suggested that the primary hydrolysis products were OCS, thiourea, and sulfur. Further hydrolysis converts OCS to H2S and CO2 while the high temperature of the reaction (≈200°C) converted the thiourea to ammonium thiocyanate. These products are entirely intelligible in terms of the structure (4) of xanthan hydride as we now know it, but at the time (1897) of Chattaway and Stevens' investigation not only was the structure of the

compound unknown but also the molecular formula then accepted was incorrect; xanthan hydride was believed (2) to be a low polymer of C₂H₂N₂S₃. The reaction of xanthan hydride with concentrated sulfuric acid, on the other hand, yields CO2, SO₂ and OCS. The SO₂ probably arises from the oxidizing action of the hot concentrated sulfuric acid. As the molar ratio H₂SO₄:H₂O decreases, the proportion of SO₂ in the product decreases, as the more dilute acid is a poorer oxidizing agent. The proportion of OCS decreases also as the more aqueous medium can effect its hydrolysis.

Since ionic thiocyanate reacts rapidly with concentrated sulfuric acid at room temperature to give CO_2 and OCS with very little SO2, and xanthan hydride reacts rather slowly with hot concentrated sulfuric acid, yielding much SO₂, it is concluded that xanthan hydride is not a significant intermediate in the formation of carbonyl sulfide from MINCS/H2SO4 mixtures. This raises interesting questions concerning the mechanisms of the various reactions of thiocyanate ions with

The pK_n of HNCS is -1.85 (12), so that only in very acidic media is the thiocyanate ion extensively protonated. The mechanism (5, 13) for the formation of xanthan hydride (I) in aqueous acid solution of overall stoichiometry.

$$3NCS^{-} + 3H^{+} \rightarrow (1) + HCN$$

is shown in the scheme. The intermediate (VI) is a doubly protonated form of the N-cyanocarbonimidodithioate anion, which may be formed either from xanthan hydride and alkali (14), when the by-product is elemental sulfur, or from the cyanamide anion with carbon disulfide (15); all steps up to the formation of (VII) are reversible, and the conversion of (VII) into (I) via a tautomer of (I) depends on the huge difference between the pK_a values of HNCS (-1.84) and of HCN (9.21). In the medium employed, HCN is entirely un-ionized and so is a good leaving group for the protonation of (VII), whereas HNCS is partly ionized, and, in fact, formation of (VII) requires free NCS" anions to react with (VI). If the medium is insufficiently acidic, protonation of (VII) will not be effected, and no (I) will form. If the medium is too acidic there will be insufficient free thiocyanate ion present to form (VII), so again no (I) will form: it is under just these conditions that OCS is formed. There appears to be a critical range of acidity for the formation of xanthan hydride from thiocyanate ions in aqueous solution. Beyond the upper limit of this range, thiocyanate ions are merely hydrolyzed and/or oxidized yielding OCS and other gases; beyond the lower limit of this range, essentially no detectable reaction occurs.

Literature Cited

- (1) Vanino, L., "Handbuch der Präparativen Chemie," Ferdinand Enke, Stuttgart, 1921,
- Chattaway, F. D., and Stevens, H. P., J. Chem. Soc., LXXI, 607 (1897), Wöhler, F., Ann. Phys., 69, 273 (1821).
- Hordvik, A., Acta Chem. Scand., 17, 2575 (1963).
 Butler, A. R., and Glidewell, C., J. Chem. Research, (S) 65, (M) 0801 (1982)
- (6) Marr, G., and Rockett, B. W., "Practical Inorganic Chemistry," Van Nostrand Reinhold, London, 1972, p. 338.
 Glidewell, C., J. CHEM. EDUC., 57, 286 (1980).
 Glidewell, C., and Pogorzelec, P. J., J. CHEM. EDUC., 57, 740 (1980).

- (9) For descriptions of standard varuum line manipulations, see Jully, W. L., "The Synthesis and Characterization of Inorvanic Compounds," Prentice-Hall, Englewood Cliffs, N.J., 1970. (10) Emeléus, H. J., Haas, A., and Sheppard, N., J. Chem. Soc., 3165 (1963).
- (11) Bews, J. R., and Glidewell, C., J. Mol. Structure, 86, 377 (1982). (12) Morgan, T. D. H., Stedman, G., and Whincup, P. A. E., J. Chem. Soc., 4813 (1965).
- (13) Hall, W. H., and Wilson, I. R., Aust. J. Chem., 22, 513 (1969).
 (14) Cotton, F. A., and McCleverty, J. A., Inorg. Chem. 6, 229 (1967).
 (15) Fackler, dr., J. P., and Coucouvanis, D., J. Amer. Chem. Soc., 88, 3913 (1966).

 $^{^{1}}$ In the preparation of (I) described in the Experimental part, a 2 Msolution of KNCS is used: if the added sulfuric acid is of concentration less than 90%, no (i) is formed: 96% acid is recommended.

edited by DAVID L. BYRUM Globe High School 501 Ash Globe, AZ 85301

Potentiometric Titrations Using Pencil and Graphite Sensors

Walter S. Selig

Lawrence Livermore National Laboratory University of California Livermore, CA 94550

The cost of various commercial indicating electrodes ranges from about \$40 for pH electrodes to as much as \$355 for a potassium ion-selective electrode. This cost can be reduced to less than \$1.50, and in some cases to mere pennies by making sensors from graphite rods and pencils for use in potentiometric titrations. The same sensor can be used for many types of these titrations (acid/base, compleximetric, precipitation, and redox).

Background

Hoke and Collins (1) recently used a membrane of polyvinyl(chloride) (PVC) plasticized with dioctylphthalate (DOP) as a sensor in the potentiometric titration of alkyl aromatic sulfonate with a cationic surfactant. We have found (2, 3) that a spectroscopic graphito rod and various pencils can serve as inexpensive support materials for this membrane. This sensor can be considered a variant of the "coated-wire" electrodes introduced by Cattrall and Freiser (4) in 1971.

Preparation of Coated-Graphite Electrodes

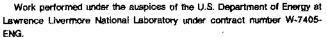
The graphite rods (Spectroscopic graphite, UF-4S, Ultra Carbon Corp., Bay City, Michigan) were 152.4 mm (6 in.) long and 6.35 mm (¼ in.) in diameter. They cost \$1.29 each and were purchased in 12 in. lengths. Other grades of graphite such as Ultra carbon U-7 and Poco graphite AXF will serve equally well, and the diameter is not critical.

The coating solution is prepared by dissolving 1 g of low-molecular weight PVC and 1 g of DOP in 30 ml of tetrahy-drofuran in an Erlenmeyer flask, applying heat, and occasionally shaking to promote solution. The graphite rod is dipped for a few seconds to a depth of about 13 mm (½ in.) into the cooled coating solution and air-dried. This coating process is repeated 3–5 times. The cost of the coating solution is less than \$0.01 per electrode; one batch of the PVC/DOP solution will coat many electrodes and will keep indefinitely in a stoppered glass vessel.

When the coating deteriorates, as indicated by decreasing and/or less steep endpoint breaks, it can be entirely removed with hot tetrahydrofuran. The graphite rod can then be recoated and reused.

Measurements

Any convenient reference electrode can be used in conjunction with the PVC/DOP-coated sensor. We have used a plastic, single-junction, silver/silver-chloride reference electrode containing a salt-bridge of 0.1 N sodium nitrate. The electrodes are connected to the measuring instrument, which can be any convenient pH/millivolt meter. The coated



¹ These prices were valid in spring 1983.

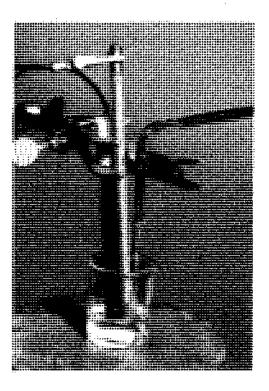


Table 1. Some Feasible Potentiometric Titrations Using a Graphite Sensor Coated with PVC-DOP

ion measured	Titrant	Titration type	Endpoint break, mV
Perchlorate	Cetyipyridinium	Precipitation	120
Hexafluorophosphate	Cetylpyrldinlum	Precipitation	220
Peroxydisulfate	Cetylpyridinium	Precipilation	120
Nitroform	Cetylpyridinlum	Precipitation	190
Picrete	Cetylpyridinium	Precipitation	170
Tetraphenyl- borate	Cetylpyridinium	Precipitation	45 0
Dodecylsulfate	Cetylpyrldinium	Precipitation	310
Thalious	Tetraphenyl- borate	Precipitation	310
Bromide + lodide	Silver (t)	Precipitation	
Fluoride	Lanthenum (III)	Precipitation	30
Tungstate	Lead (II)	Precipitation	25
Acid phthalate	Sodium hydroxide	Acid-base	70
Ferrous	Chromate	Oxidation-reduction	250
Ethylenediamine tetraacetate	Lead (II)	Compleximetric	

graphite sensor is connected to the meter by means of an alligator clip. A typical titration cell is shown in the figure.

What Type of Titrations can be Monitored?

A list of titrations we have monitored with the coated graphite sensor is given in Table 1. Full details on these titrations are presented in reference (2) which gives representative titration curves, magnitudes of endpoint breaks, and standard deviations. No doubt many more are possible, and

Table 2. Comparison of Sensors in the Potentiometric Titration of an Aqueous Nitroform Solution versus 0.05 N Cetylpyridinium Chloride.

Sensor	Source of supporting material	Mean endpoint break (mV)	Standard deviation	Number of replicates
Fluoroborate	Orion Research	165	0.10	5
PVC/DOP-coated graphite	Ultra Carbon UF-4S	190	0.04	4
PVC/DOP-coated mechanical pencil	Turquoise Eagle Drawing lead	110	80,0	4
PVC/DOP-coated No. 2 pencil	Astro 155 Bondexed lead	30	0.03	4

Titration cell with a coated no. 2 pencil sensor end a single-junction reference electrode.

the writer wishes to learn of titrations which cannot be performed. A limitation of the sensor is its applicability in aqueous media only (acids and bases are alright), because organic solvents will attack the membrane.

Pencil Electrodes

The next obvious reduction in cost is to use less expensive graphite-containing materials such as pencils. For one titration, nitroform, C(NO2)3H, versus cetylpyridinium chloride, we have used the following sensors:

- (1) A mechanical pencil "lead" (Turquoise Eagle drawing lead) sealed into a glass capillary for mechanical strength. The cost of each "lead" is \$0.07. It needs to be crimped into a support because it breaks easily.
- (2) A No. 2 Astro Bondexed "lead" pencil from which the eraser was removed and the resulting cavity filled with solder to make electrical contact with the graphite core. The cost of the pencil is \$0.04.

Both variants were coated with PVC/DOP as described above. A comparison of mean endpoint breaks and standard deviations for this particular titration is presented in Table 2. Included are previously obtained data using a fluoroborate commercial sensor (5). The largest breaks were obtained with the PVC/DOP-coated graphite sensor, followed by the commercial fluoroborate sensor. The smallest break was obtained with the coated No. 2 pencil. It seems that the surface area in contact with the solution, as well as the presence of impurities (the wood of the No. 2 pencil was in contact with the solution) have a significant effect. All PVC/DOP-coated sensors yielded lower standard deviations than the commercial sensor.

Although we have, as a tour de force, tested the No. 2 pencil electrodes in only one type of titration, we have no doubt that many other titrations can be monitored in this manner. In fact, this idea may lend itself to a research project for students.

Simpler Yet-No Coating at Ail

It is well known that some titrations yield better endpoint breaks in partially nonaqueous media because of reduced solubilities of the precipitated species. This is particularly true for the titration of fluoride versus lanthanum(III) or thorium(IV), and of sulfate versus lead or barium nitrate. All of the variants described above, minus the PVC/DOP coatings, can be used for the following titrations

- 1) fluoride versus Lá $^{3+}$ in 60% methanol (6),
- 2) fluoride versus Th4+ in 60% methanol (6),
- 3) sulfate versus Pb2+ in 80% methanol (7),
- 4) sulfate versus Ba2+ in 80% methanol (7).

The magnitude of the endpoint break can be improved by dipping the bare sensors for several minutes into a neutral 0.2 M potassium permanganate solution. The increased activity resulting from this treatment was explained by Bercik et al. (8) as resulting from either the formation of a quinone-hydroquinone redox system on the electrode surface during the activation process, or from the establishment of a mixed potential between separated manganese dioxide on the electrode surface and the solution.

While any graphite rod can be used, including the pencils, we have obtained the largest endpoint breaks with Poco graphite, grade AXF-9QBG1 (Poco Graphite Inc., 1601 S.

State Street, Decatur, Texas 76204). However, this material is somewhat more costly, \$6.31 for a 6-in, rod of 1/4-in, diameter (but still inexpensive compared to the \$295 fluoride ion-selective electrode).

In summary, pencils can be used not only to write with or chew on, but also to monitor various potentiometric titrations.

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Literature Cited

- (1) Hoke, S. H., and Collins, A. G., Report 1979, BETC/RI-79/10; cf. Chem. Abstr., 93:
- 19641q (1990). (2) Selig, W., Analyt. Letters, 15[A3], 309 (1982). (3) Selig, W.S., Energy & Technology Review, Lawrence Livermore National Laboratory, August 1982, p. ii.
- (4) Cattrall, R. W., and Freiser, H., Anal. Chem., 48, 1905 (1971).
- (5) Selig, W., Mikrochim. Acta, H., 437 (1979)
 (6) Selig, W. S., Microchem. J. (in press).
- Selig, W. S., work in progre
- (8) Bercik, J., Hladky, Z., and Cakrt, M., Z. anal. Chem., 261, 113 (1972).

Rubber Bulb Modification for Pipetting

Joe B. Davis

Winthrop College Rock Hill, SC 29733

Learning to use a rubber bulb with a pipet properly is frequently frustrating for all concerned. Placement of the neck of the bulb firmly and squarely against the end of the pipet is difficult for many students to master. Their usual tendency is to force the end of the pipet into the neck of the bulb, resulting in improper filling and contamination of the solution by contact with the bulb. Worse yet, they sometimes become so frustrated with the pipet bulb that they resort to the dangerous practice of pipetting by mouth. A simple modification

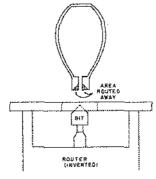


Diagram showing proper procedure for bulb modification.

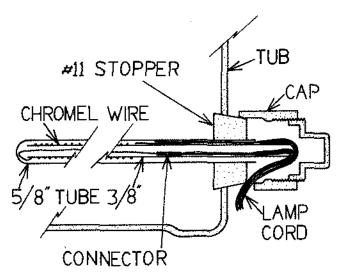
of rubber bulbs used in my quantitative analysis laboratory has alleviated these problems. The straight opening in the neck was routed to a conical shape with a 45° bit (total included angle-90°). The simplest method is to press the bulb neck against the rotating bit of an inverted router until the desired depth is reached (see figure). Only light pressure, applied intermittently to prevent overheating and melting of the rubber, is required. CAUTION: Router speeds are about 25,000 rpm. Preferably, the router should be mounted on a router table. Alternately, it may be firmly held or clamped on a bench top with a vibration-damping surface (a folded

towel was sufficient to prevent "walking"). The router bit should be in the retracted position and the wrist should be supported on the router base or table. Use of a portable drill is NOT recommended. Suction can be applied to the pipet in the usual manner by lightly pressing the self-centering neck of the bulb against the end of the pipet. Pipet aids employing a polyethylene fitting with a conical opening are available from Dynalab Corp., Interex Corp., Cole-Parmer and others. Bulbs modified as described have proved satisfactory for a number of years.

A Convenient Glassware Cleaning Bath

Over the last few years a method has evolved in our laboratory which provides truly clean glassware with minimal effort and apparatus. Although originally designed for a biochemical research laboratory where traces of metallic ions could not be tolerated, the method has become favored in student laboratories as well.

The procedure involves mechanically removing any bulk dirt from the glassware, completely immersing the glassware in 0.25% PEX cleaner, heating for several hours, rinsing several times in tap water and then in deionized water, and drying in an oven. A major drawback of this procedure has been the lack of a convenient, reliable heating bath. A vertically mounted electrical immersion heater requires a stirrer, often melts plasticware which floats into the heater, and sometimes even damages the heating tub. A steam immersion heater constructed of heat-resistant nonmetallic tubing avoids these problems but is very expensive and lasts only a few months. An external heater, such as a hotplate, cannot be used with a plastic tub. Construction of a heating bath which avoids the shortcomings of previous designs is described here.



Scale drawing of the horizontal immersion heater for the glassware cleaning bath.

The bath consists of a 30-gal. polyethylene tub, a homemade 1000-W immersion heater, and a 24-hr timer.

Six inches of insulation are removed from a 5-ft section of 18/2 heater ("lamp") cord (with plug). An uninsulated, solderless connector is used to attach one end of an 11-ft piece of 22-gauge Chromel wire (total resistance = 10.7 ohms) to one of the heater cord wires. The connected wires are slipped into a $12 \times \%$ in. O.D. Vycor tube and the majority of the Chromel wire wound around the outside of the tube to form a 6-in.-long heater coil. The other end of the Chromel wire is then attached to the other heater cord wire and the solderless connector pounded flat. The entire heater assembly is then slipped inside an $11 \times \%$ -in. O.D. Vycor tube which has been sealed at one end. This assembly, in turn, is inserted into a hole (#10 borer) in a #11 Neoprene stopper as shown in the figure. Note that the Vycor tubes are arranged so that the uninsulated portions of the heater cord wires cannot touch. The heater is pushed firmly into a 2-in.-diameter hole which is drilled just above the bottom of the tube. A cap of PVC pipe fittings is notched to accommodate the heater cord and pushed onto the Neoprene stopper to protect the bare wires. To protect the Vycor tubes from heavy glassware, a rigid plastic grill (a refrigerator pop can dispenser manufactured by Rubbermaid) is epoxied to the buttom of the tub. Setting the time to heat for 2.5 hr provides a maximum temperature of about 75°C (except for a region within $\frac{1}{2}$ in. of the tub bottom) and yields truly clean glassware.

Tom Lyons Fisher Phyllis M. McGinnis Junista College Huntingdon, PA 16652

Electrode Potential Diagrams and their Use in the Hill-Bendall or Z-Scheme for Photosynthesis

Peter Borrell and Denis T. Dixon

University of Keele, Staffordshire, England

Electrode potential diagrams provide a common way of representing biochemical electron-transfer processes in photosynthesis (1-3) and respiration (4). However, we have found that when students approach these diagrams from the viewpoint of physical chemistry or photochemistry they become confused by their apparent similarity to molecular energy-level diagrams such as the Jablonski diagram.

Also, the diagrams are difficult to understand in themselves, and confusions arise for several reasons: the use of a reverse scale; the use of the term "oxidation/reduction potential" to describe the ordinate; the depiction of single substances on the diagram rather than reactions; misunderstanding of the meaning of various arrows; and misunderstanding of the nature of the "energy" which can be calculated from the height.

The aim of this article is to help clear away some of the confusions by providing a description of electrode potential diagrams in terms of a simple and probably familiar example, that for zinc and copper sulfate. Various cautions are offered and then a brief description of the Hill-Bendali or Z-scheme for photosynthesis is given to emphasize the main points.

While we have used an up-to-date diagram for photosynthesis, it is not the aim here to provide a current view of the topic; our object is simply to present a correct physical-chemical description of the diagram.

An Electrode Potential Diagram for the Zn/Cu2+ System

The example chosen to illustrate the principles is the Zn/CuSO₄ system. It will be recalled that zinc reacts with aqueous copper(II) sulfate to give metallic copper and zinc sulfate:

$$Z_{n}(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Z_{n}^{2+}(aq)$$
 (1)

In the laboratory the reaction goes to completion for all ordinary concentrations of Cu^{2+} . The standard change in the Gibbs function for the reaction, ΔG^{\ominus} , is -212.8 kJ mol⁻¹.

If the system is set up as an electrochemical cell (the Daniell Cell)

$$Zn(s) \mid Zn^{2+}(aq) \mid Cu^{2+}(aq) \mid Cu(s)$$

then the EMF for the standard activities is +1.103 V, the copper electrode being positive. In this case, with unit activities of reactants and products, the EMF would be E^{\odot} , the standard EMF of the reaction, which in turn is related to the standard change in free energy by

$$E^{\phi} = -\Delta G^{\phi}/nF$$

where F is the Faraday constant and n is the number of electrons exchanged in the reaction. Using such a cell, work could be obtained from the reaction.

Now the work, w, in a process is related to the change in Gibbs function, at constant temperature and pressure, by the inequality

$$w > \Delta G$$

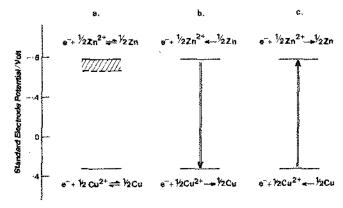


Figure 1. (a) An electrode potential diagram for the Zn/Cu system, showing the levels, half reactions and the effect of a hundredfold change in concentration. (b) The diagram showing the spontaneous reaction with electron transfer from Zn to Cu (note the directions of the arrows). The height gives the maximum work available from the reaction. (c) The nonspontaneous reaction: work is required to drive the reaction and the height gives the minimum quality needed. Again note the direction of the arrows.

so that extra work must always be done on the system to achieve a given increase in the Gibbs function.

For a spontaneous reaction ΔG is negative so that if any work is obtained from the process, it will be less than that given by the value of ΔG ; i.e., for reaction (1) with standard activities, the work obtained (=-w) will be less than 212.8 kJ mol⁻¹.

Reaction (1) can be driven backwards in an electrochemical cell

$$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$$
 (2)

by applying a higher opposing voltage, in other words by doing work on the cell. Now the calculated work required,

$$w_{\min} = \min_{i=1}^{n} w_{\min} = w_{\min} = \Delta G$$

is a minimum quantity and in practice, more work would be needed to drive the reaction back.

Figure 1a shows an electrode potential diagram for the Zn/Cu^{2+} system. The reactions are shown as half-cell reactions; values of E^{\odot} , the standard electrode potentials, are taken from tables of standard values (7).

Each potential refers to the EMF of a cell in which the left-hand electrode is a hydrogen electrode, e.g.,

$$H_2(g; 1 \text{ atm})Pt \mid H^+(aq) \mid Zn^{2+}(aq) \mid Zn(s)$$

for which the overall reaction is

$$H_2(g) + Zn^{2+}(g) \rightarrow 2H^+(aq) + Zn(s)$$

The half-cell reaction is an abbreviated form of this equa-

The actual value of E^{\odot} given refers only to this reaction and so, when using the diagram, only differences in the values of the EMF are important. Absolute values have no special significance other than for the reaction with hydrogen.

 $^{^{1}}$ The Gibbs Function is now the recommended name (5, θ) for the more commonly used "free energy."

Figure 1b shows a representation of the spontaneous reaction (1). The vertical arrow shows the direction of electron transfer, from zinc to copper. With reversible reactions at the top and bottom of the vertical arrow there is an ambiguity in the direction of the overall reaction. This is eliminated if it is noticed that the reaction at the arrow head is proceeding in the normal direction (left to right) depicted here by a single arrow, while that at the tail is in the reverse direction.

So, when electron transfer occurs, the electrons are produced in the (tail) reaction $(Zn \rightarrow Zn^{2+} + 2e^-)$ and consumed in the (head) reaction $(Cu^{2+} + 2e^- \rightarrow Cu)$. If reaction takes place in an electrochemical cell, electrons flow from the negative electrode to the positive electrode.

The downward direction of the vertical arrow shows that the reaction is spontaneous. The convention in physical chemistry is to use a downward arrow in an energy diagram to represent energy evolved and thus, usually, a spontaneous reaction.

The EMF of the cell, for reactants and products at standard activity, is $E^{\odot}(\text{head}) - E^{\odot}(\text{tail})$; i.e.,

$$EMF = E^{\Theta}(head) - E^{\Theta}(tail) = 0.3402 - (-0.7628) = +1.103 \text{ V}$$

which is the standard electrode potential for the overall reaction.

For a spontaneous reaction (downward arrow), the work is then

$$w = \Delta G^{\Theta} = -nFE^{\Theta}$$

or for two-electron transfer in reaction (1),

$$w = -212.8 \text{ kJ mol}^{-1}$$

The negative sign indicates that work is available and the equality between w and ΔG^o shows that the maximum work available has been calculated.

The reverse process is shown in Figure 1c by an upward arrow. Again electron transfer is shown by the arrow direction with the reaction at the head proceeding normally, i.e., left to right, consuming electrons, and that at the tail proceeding right to left, producing electrons. The EMF however is now negative $(E^{\odot}(\text{head}) - E^{\odot}(\text{tail}) = -1.103 \text{ V})$ and so w is a positive quantity $(+212.8 \text{ kJ mol}^{-1})$. Thus work must be done on the system to drive the reaction in the direction indicated by the arrow and the value of w, calculated from the change in Gibbs function, is the minimum work required.

The Electrode Potential Diagram in Teaching Electrochemistry

Diagrams such as those shown in Figure 1 could be of much help in teaching electrochemistry where sign conventions often seem to be a stumbling block to understanding. The conventions are, of course, implied in the diagram and in the reaction directions assumed for head and tail of the electron-transfer arrow, but the correct sign is yielded easily and the treatment seems to operate in a more natural way.

The principal disadvantage is the scale, which is reversed, with the positive end at the bottom. The diagram is constructed in the same sense as we use for energy diagrams, with the notion of "energy in," represented by an upward arrow. The electrode potential diagram is thus essentially a free energy diagram with the upward arrow representing minimum work required as well as electron transfer. Since ΔG^{\odot} and E^{\odot} have opposite signs the standard electrode potential scale must be a reverse scale.

Free energy diagrams are met with elsewhere in physical chemistry, for example in the Ellingham diagram representing the reduction of metal oxides to metals (8).

Cautions in Using the Diagram

One difficulty that has been mentioned already is that when the height is used to calculate the work for a given reaction then minimum (upward) or maximum (downward) quantities are given. The processes by which the work is obtained, be they direct such as drawing electric current, or indirect such as the coupling between this reaction and another via an enzymic mechanism, are subject to the limitations of the second law of thermodynamics. All real processes involve loss of work as heat and so to drive a reaction more work than that indicated by the height of the arrow will be needed, whereas for a spontaneous reaction less work would be obtained.

Another problem arises in how the work which is available from a spontaneous reaction is used to drive another reaction. An example of this will appear with the synthesis of ATP in the photosynthetic scheme. Imagine we have one reaction

$$\mathbf{A} \hookrightarrow \mathbf{B}$$

which is spontaneous, with a large decrease in the Gihbs function, and another

$$C \rightarrow D$$

which has a small increase in the Gibbs function.

If both are independent of one another so that energy can only be transferred from one to another in the form of heat, then, even if the reactions are occurring together in the same pot, the second cannot proceed since no work has been provided.

If, however, there is a mechanism, such as

$$A + C \rightarrow [AC] \rightarrow B + D$$

in which both steps are spontaneous, then both B and D will be formed.

In particular, if the reactions are coupled enzymically through a membrane so there is some sort of common intermediate, then both the reactions will proceed. It is in this sense that biochemical reactions are coupled so that reactions which are not spontaneous can be driven by those that are.

Also there is the effect of concentration. The values in Figure 1 obtained from the tables are those for the hypothetical standard state with standard molality and fugacity. In using such values in qualitative discussion, the effect of non-ideality may be small so that activity can be replaced by concentration, but the effect of concentration can be appreciable. Thus for the reaction

4/2H2 + oxidized form → reduced form + H+

then if H+ and H2 are in their standard states,

$$E = E^{\phi} - \frac{RT}{nF} \ln \frac{[\text{reduced}]}{[\text{oxidized}]}$$

The shaded portion in Figure 1 a shows the effect of decreasing the Zn^{2+} concentration by a factor of 100.

Provided the half-cell reactions have large differences in standard electrode potentials, valid qualitative conclusions as to the feasibility of a particular reaction can be drawn from the diagram. If, however, the two half-cell reactions have similar potentials, then changes in concentration can render a spontaneous reaction impossible.

Photosynthesis

The overall process in photosynthesis in green plants is the absorption of CO_2 and H_2O in the presence of light to give carbohydratas and oxygen

$$CO_2(g) + H_2O(l) + Light \rightarrow (CH_2O) + O_2(g)$$
 (4)

(CH₂O) represents a "proto-carbohydrate." Photosynthesis can be divided in three steps (1).

- Light collection via chlorophyll and other pigments and conveying the energy to a reaction center.
- The oxidation of H₂O to O₂ and the reduction of NADP+ to NADPH (nicotinamide adenine dinucleotide phosphate), The overall equation is

$$2NADP^{+} + 2H_{2}O + light \rightarrow 2NADPH + 2H^{+} + O_{2}$$
 (5)

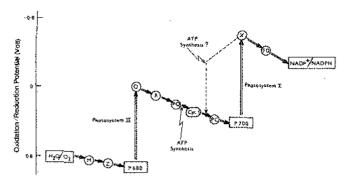


Figure 2. A hiti-Bendail or Z-diagram for electron transport in a chloroplast. The details are discussed in the text together with some suggestions for improving the clarity. See also the addendum concerning the phoophytin intermediate.

ATP (adenosine triphosphate) is also formed from the diphosphate, ADP, in this step.

 The absorption of CO₂, oxidation of NADPH and formation of (CH₂O):

$$2NADPH + 2H^{+} + CO_{2} \rightarrow (CH_{2}O) + 2NADP^{+} + H_{2}O$$
 (6)

The process requires three molecules of ATP.

Process (3) is the Calvin-Bassham cycle, which involves a large number of carbohydrates and their various mono- and diphosphates. Process (1), the light-collection step, is the subject of much current work since the nature of the energy transfer steps and the mechanism by which the photoreceptors act is still not well-understood.

It is process (2) to form NADPH which we are concerned with here. The mechanistic scheme was first suggested by Hill and Bendall (9), and it is often known as the Hill-Bendall scheme or as the Z-scheme because of its general shape.

The Hill-Bendall or Z-scheme

A simplified but recent version of the diagram is shown in Figure 2. It can be seen that Figure 2, like Figure 1, is an electrode potential diagram.

Immediately, several points can be made.

1) The majority of the substances are depicted as single entities. In the electrode potential diagram, Figure 1, each level represents not a single species but a half reaction between at least two species.

In Figure 2, most of the materials are not completely characterized chemically, and so presumably, from the viewpoint of those familiar with field, for the electron acceptor in photosystem II, the term Q represents both the reduced and oxidized forms. However, from a novice's viewpoint, single substances with an arrow between them represent a chemical transformation, but this is not the case at all here. The vertical arrows represent electron transfer in the sense of Figure 1.

Ideally each level should show the reaction with hydrogen but, practically it would seem preferable to depict Q as

$$Q_{os} + e^- \rightleftarrows Q_{red}$$

or perhaps as $Q_{\rm ox}/Q_{\rm rod}$ when the position of the charges is still not clear and as Q^+/Q or Q/Q^- when the position of the charges is known. It should not be shown as simply Q.

Further, in some representations, the reductions are written in the wrong sense, i.e.,

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

This is to convey the particular direction of the reaction during electron transfer but it can lead to difficulties in calculation if the E^{\odot} value is taken, mistakenly, to refer to this direction.

2) The axis is labelled "oxidation/reduction potential,"

presumably because the reactions are reversible. In fact, a scale of standard electrode potentials is used.

- 3) For those reactions which are well-characterized (e.g., O_2/H_2O) the values given in the diagram are E^{\ominus} values rather than E^{\ominus} values. Because it is usual in biochemical systems (4, 10) to determine quantities at the physiologically convenient pH of 7, E^{\ominus} and ΔG^{\ominus} values refer to standard quantities at this pH.
- 4) For the remaining reactions (e.g., $Q_{\rm ox}/Q_{\rm red}$, etc.) the values are known approximately from practical measurements and are therefore simply electrode potentials, E values, for the unknown concentrations in the cell.

In a complicated system, under active study, the mixing of precise and imprecise information is unavoidable in order to gain the overall understanding which the diagram gives.

5) The vertical arrows represent two things: (a) the direction of electron transport between the reduced form of one substance and that of another; (b) the quantity of work required to effect the transfer in the upward direction or the work available from a transfer in the downward, spontaneous, direction as indicated in Figure 1. In particular, the upward arrows do not represent the difference in energy between molecular energy levels in the chlorophyll molecule such as would be found in a Jablonski diagram (11). The energy absorbed by the chlorophyll certainly provides the work to effect the transformations in photosystems I and II but the energy used must be greater than the work required.

An Outline Mechanism

The Z-scheme is a suggested mechanism for the overall reaction. It is simplest to follow an electron through the sequence but it must be understood that in the dark all the various reactants and products are at concentrations determined by the equilibrium constants for the reactions (in the absence of side processes). Illumination shifts the equilibria to steady state values which will depend on the light intensity. The process can be looked at sequentially as follows.

1) Light is entrapped by photosystem II (PSII) in which it is thought a complex of the photo-receptor, P680, with a quinone electron acceptor, Q, is excited and undergoes charge transfer

$$(P680_{red} \cdot Q_{ox}) + h\nu \rightarrow P680_{ox} + Q_{red}$$

The oxidized form, $P680_{ox}$ undergoes, via intermediate reactions, a reaction with water

$$P680_{ox} + \frac{1}{2}H_2O \rightarrow P680_{red} + H^+ + \frac{1}{4}O_2$$

So the net effect is the transfer of an electron as water is oxidized

$$\frac{1}{2}H_2O \rightarrow H^+ + \frac{1}{4}O_2 + e^-$$

and Qox reduced

$$Q_{os} + e^- \rightarrow Q_{red}$$

As the diagram shows, this requires work to be done on the system, the minimum work being

$$w_{\min} = \Delta G = -nF[E(Q_{ox}/Q_{red}) - E^{\Theta'}(O_2/H_2O)]$$

 $\simeq .77 \text{ kJ mol}^{-1}$

It is the photon which provides the energy for the work to he done.

2) The reduced quinone ($Q^-_{\rm red}$) reacts with a plastocyanin via a series of reactions involving a quinone, a plastoquinone and a cytochrome; again an electron is transferred

$$Q_{red} \rightarrow Q_{ox} + e^{-}$$

The transfer is a downhill process so it is a spontaneous step and work is available

$$w_{\text{max}} = \Delta G$$
$$= -38.6 \text{ kJ mol}^{-1}.$$

Some of the available work is thought to be used for the conversion of adenosine diphosphate (ADP) to the triphosphate

$$ADP + P \rightarrow ATP$$

for which the standard change in Gibbs function is

$$\Delta G^{\oplus'} = 30.5 \text{ kJ mol}^{-1}$$

It is known that half a mole of ATP is formed per mole of electrons transferred and so it appears that less than half of the available work is used in this conversion.

The synthesis of ATP presents a further problem in using the electrode potential diagram: it is not a redox reaction and so cannot be represented by electron transfer or by a standard electrode potential and so cannot be shown by a level on the diagram.

3) In photosystem I, the photoreceptor P700 reacts in an electron-transfer reaction with the substance, X,

$$(P700_{red} \cdot X_{ox}) + h\nu \rightarrow P700_{ox} + X_{red}$$

and the oxidized, P700_{ox} reacts with the reduced plastocyanin

$$P700_{ox} + PC_{red} \rightarrow P700_{red} + PC_{ox}$$

so that the overall process is electron transfer from PQred to

The minimum work required is

$$w = \Delta G = -nF[E(X_{ox}/X_{red}) - E(PQ_{ox}/PQ_{red})]$$

\(\sim + 96.5 \text{ kJ mol}^{-1}\)

which is provided by the photon.

4) The final steps involve the reduction of NADP+ and oxidation of X_{red} again through a sequence involving a ferridoxin

$$X_{red} \rightarrow X_{ox} + e^-$$

 $\frac{1}{2}NADP^+ + \frac{1}{2}H^+ + e^- \rightarrow \frac{1}{2}NADPH$

The work here is

$$w = \Delta G = -nF[E^{\odot}(NADP^{+}/NADPH) - E(X_{ox}/X_{red})]$$

= -26.6 kJ mol⁻¹.

The process is spontaneous but the work available is not apparently used.

The mechanism has been described sequentially in a chemist's way, but, in fact, all the reactants and products together with the enzymes which catalyse the reactions are part of a membrane in the chloroplast which absorbs light thus providing the energy for proton transfer through the membrane. The protons are used to synthesize ATP. The NADPH produced is used in CO₂ fixation.

Quantum Requirement and Energy Yield

The diagram can be used to calculate the minimum quantum requirement and the maximum energy yield.

To produce 1 mole of O2 and 2 moles of NADPH at an intermediate stage and absorb I mole of CO2, 4 moles of electrons are required, and these must pass through the sequence of reactions outlined. At the wavelength corresponding to the threshold for photosynthetic activity (~700 nm) the energy absorbed (171 kJ mol⁻¹) for each photon is more than sufficient to raise I electron in either photosystem. Much of the energy is lost in the initial steps by vibrational relaxation and by second law effects, but, if we assume that 1 photon per electron is required, then there is a minimum quantum requirement of 8 for the passage of 4 electrons through the two photosystems.

Three moles of ATP are also required to fix 1 mole CO2 in the Calvin cycle. The passage of 4 electrons will produce 2 molecules of ATP in step (2) above, so a further molecule is required. Ideas on where this is formed have varied; one suggestion is that it is formed in an alternative pathway to the production of NADPH in a cycle which includes photosystem I. The second possibility would require extra photons so the requirement would then be more than 8. The actual value is difficult to measure but is thought (12) to lie between 8 and

The value of 8 can be used to calculate the maximum energy yield for the Z-scheme. The 8 photons at 700 nm provide an equivalent energy of 1368 kJ mol-. The minimum work required to reduce H₂O and form NADP is given by

$$2H_2O + 2NADP^+ + 2NADPH + 2H^+ + O_2$$

 $w = \Delta G^{\odot} = -nF[E^{\odot}(NADP^+/NADPH) - E^{\odot}(O_2/H_2O)]$
 $= +440 \text{ kJ mol}^{-1}$

for 4 electrons and so the maximum yield is 32%.

Some of the energy is used in the formation of ATP. The remainder appears as heat, with losses occurring at every stage: in the rapid vibrational relaxation in the excited singlet state of chlorophyll, in the energy transfer to the reaction center, and in all the various reactions which, because they occur in an actual system, are subject to second law losses. There will also be substantial further losses in the Calvin Cycle.

Conclusion

This article has outlined the use of electrode potential diagrams in a simple system, and in the Hill-Bendall scheme for photosynthesis, for which the diagram provides a basis for understanding the mechanism.

Emphasis has been placed (1) on the use of arrows to depict electron transfer, with a rule to give the correct direction of the coupled reactions: (2) on the fact that the diagram is a free-energy diagram and not an energy diagram, and (3) on the fact that the energy quantities corresponding to heights represent the maximum work available or the minimum work required for particular processes.

It has been suggested that to help people less familiar with these diagrams, the scales should be lahelled as electrode potentials and that each level should be shown as a redox reaction rather than as a single substance.

While the mechanism has been described in outline, the purpose has not been to give the experimental evidence or the fine details which are well described elsewhere (1-3).

The various conclusions could also be applied to the description of the cytochrome electron-transport scheme in respiration (4).

Addendum

The referee has kindly pointed out a recent suggestion that a pheophytiu (Ph) acts as a further intermediate between P680 and Q in photosystem II. Two measurements have indicated that electrode potential for the reduction of the pheophytin $(e^- + Ph^- \rightarrow Ph)$ is ~610 mV. The implication of these findings is that the presently accepted mechanism, outlined in Figure 2, may need substantial revision. However, the conclusions of the present article are still valid since it is concerned with the interpretation of electrode potential diagrams rather than with the detailed mechanism.

Literature Cited

- Govindjee and Jursinic, P. A., Photochem. Photobiol. Rev. 4, 125 (1979).
 Arnon, D. I., Proc. Natl. Acad. Sci. (U.S.A.), 68, 2883 (1971).
 Levine, R. P., Sci. Amer., 58 (Dec. 1969).

- (a) Levine, R. P., Sci. Amer., 88 (Dec. 1989).
 (b) Levininger, A. L., "Short Course in Biochemistry," Worth, New York, 1975.
 (c) McGlashan, M. L., "Chemical Thermodynamics," Academic Press, London 1979.
 (d) Atkins, P. W., "Physical Chemistry," Oxford Press 1979.
 (7) Weast, R. C., "Handbook of Chemistry and Physics," Chem. Rubbar Publ. Co.,
- Cleveland, 1975.
- Clevensy, 1975.
 (8) Dannat, C. W., and Ellingham, H. J. T., Discuss. Faraday Soc., 4, 126 (1948).
 (9) Hill, R., and Bendall, F., Nature, 186, 136 (1960).

- Sober, H., "Handbook of Biochemistry," Chem. Rubber Publ. Co., Cleveland, 1978.
 Sober, H., "Handbook of Biochemistry," Chem. Rubber Publ. Co., Cleveland, 1978.
 Calvert, J. G., and Pitts, A. N., "Photochemistry," John Wiley, New York, 1966.
 Pong, F. K., J. Amer. Chem. Soc., 98, 7840 (1976).
 Rutherford, A. W., Mullet, J. E., and Crofts, A. R., F.E.B.S. Letters, 123, 235 (1981).
 Klimov, V. V., Allakverdiev, S. I., Demeter, S., and Krasnovskii, A. A., Dokl. Akad.
- Nauk. SSSR (Biophys.), 249, 227 (1979).

The Prototype Compound for the Oral Anticoagulants

3,3'-Methylene bis(4-hydroxycoumarin)

Rodney C. Hayward

School of Pharmacy, C.I.T., Private Bag, Trentham P.O., New Zealand

The coumarin anticoagulants provide illustrative, carbanion-mediated, bond-forming reactions and interesting target heterocycles for the undergraduate laboratory. The story of the introduction of the title bishydroxycoumarin (Dicumarol, USP) (Ia, Fig. 1) into the rapeutics is a particularly interesting one (1). Dicumarol was established (2) as the cause of the hemorrhagic sweet clover disease in cattle fed spoiled hay made from the sweet clovers, *Melilotus alba* or *M. officinalis*. This compound provided the leading structure for the family of oral anticoagulants shown in Figure 1. A series of similarly acidic 1,3-indandiones has been found to constitute an additional class of anticoagulants.

Dicumarol was usefully introduced into medicine (4) to lower blood coagulability in, for example, the treatment and prophylaxis of thromboembolic disorders in veins and, to a lesser extent, arteries. However, a slow onset of action and an idiosyncratic variation in adsorption and metabolism made dicumarol a less-than-ideal drug. Of the many analogues (e.g., structures Ic-e) ultimately synthesized, the most useful has been racemic warfarin² (Ic) as its sodium salt (6). The high activity of warfarin as an anticoagulant caused it to be originally proposed for rodent control. It became the world's most useful rodenticide.

Pivotal to an open-ended synthetic laboratory schedule on the coumarin anticoagulants³ was a facile synthesis of 4-hydroxycoumarin (Ib). The published strategies in this area fall roughly into two categories: (1) condensation of a phenol with a derivative of malonic acid (7), and (2) a carbanion-mediated condensation effected in a phenolic ester or ketone (8). From the latter group, we have found that condensation of v-hydroxyacetophenone with diethyl carbonate in the presence of sodium hydride as a base (8d) to be an easily manipulated and high-yield reaction. The reaction could conceivably proceed by either a β -keto ester or alternatively via the O-acyl derivative: cyclization will afford the same product.

Dicumarol was simply prepared by condensation of the 4-hydroxycoumarin with aqueous formaldehyde solution (Fig. 2) (2). 4-Hydroxycoumarin and its derivatives have many of the chemical properties of β -keto esters. The reactions develop in a straightforward way from ethyl acetoacetate.

⁴ Purified for procedure see ref. (9).

Figure 1. Structural families of the oral anticoagulants.

NaH/(E4G)₂CO toluene,
$$\Delta$$

OH

HCHO (uq)

(fa

Figure 2. Reaction pathway producing Dicumarol.

Experimental Procedure

4-Hydroxycoumarin (lb)

A solution of o-hydroxyacetophenone (0.022 mole) and diethyl carbonate (0.055 mole)⁴ (**Fumehood**) in dry toluene (30 ml) is added dropwise over 20 min to a stirred suspension of sodium hydride (0.033 mole)⁵ in dry toluene (30 ml) held in an oil bath maintained at 110°C. The ethanol formed during the reaction is removed by distillation. When all the ethanol has been removed, the thick mixture is allowed to cool and is extracted with water. The aqueous layer and washings are combined, treated with a little charcoal, filtered, and the chilled filtrate acidified by the dropwise addition of hydrochloric acid to precipitate the product. The product is filtered off, washed with cold water and sucked as dry as possible. It is recrystallized from 50% aqueous ethanol to give the product in 90–91% yield (two crops) as needles, m.p. 213–214°C (ref. 10); m.p. 213–214°C).

3,3'-Methylene bis(4-hydroxycoumarin) (la)

4-Hydroxycoumarin (1.0 g) is dissolved in boiling water (300 ml). The solution is allowed to cool to 70°C and 40% aqueous formaldehyde solution (10 ml) (Fumehood) quickly added with stirring. The mixture is then chilled, the crude product filtered off and washed well with water, dried and recrystallized from cyclohexanone/toluene as prisms, 0.89 g (85.8%), m.p. 292–295°C (ref. 11): m.p. 287–293°C).

¹ The administration of vitamin K can reverse the dicumarol-induced hypoprothrombinemia. Anticoagulants such as the coumarin derivatives are indirect in action, depressing the hepatic vitamin-K-dependent biosynthesis of prothrombin and other clotting factors. See, for example, ref. (3).

² Warfarin is an acronym for the patent holder Wisconsin Alumni Research Foundation, plus the suffix derived from coumarin (5).

³ For example, warfarin can be synthesized by a Michael addition of the 4-hydroxycoumarin enotate anion to (E)-4-phenyl-3-buten-2-one (benzalacetone).

⁵ The sodium hydride was used as a 50% dispersion in oil and as such is an easy-to-use, powerful base. **Safety in using sodium hydride must be emphasized.** Provided that normal care is taken and all apparetus is dry, use of an inert atmosphere for weighing the dispersion or for the subsequent reaction is not necessary. Any dispersion adhering to spatulas, etc., can be safely destroyed by submerging them in absolute ethanol.

Literature Cited

- Link, K. P., Circulation, 19, 97 (1959); Harvey Lect. Ser., 39, 162 (1943-44).
 Stahmann, M. A., Huebner, C. F., and Link, K. P., J. Biol. Chem., 138, 513 (1941).

- Silverman, R. B., J. Amer. Chem. Soc., 163, 3910 (1981).
 Butt, H. R., Alten, E. V., and Bollman, J. L., Mayo Clinic Proc., 16, 388 (1941).
 Ikawa, M., Stahmann, M. A., and Link, K. P., J. Amer. Chem. Soc., 66, 902 (1944).
 O'Reilly, R. A., in "The Pharmacological Basis of Therapeutica." 6th ed., Gilman, A. G., Goodman, L. S., and Gilman, A. (Editors), Macmillan, New York, 1980.
- (7) Ziegler, E., and Junek, H., Monatsh. Chem., 86, 29 (1955); Mentzer, C., Vercier, P., Beaudet, C., and Ville, A., Bull. Soc. Chim. Fr., 480 (1957); Shah, V. R., Bose, J. L.,

and Shah, R. C., J. Org. Chem., 28 677 (1960); Gorden, J. F., Hayes, N. F., and Thomson, R. H., J. Chem. Soc., 3315 (1956).
(8) (a) Pauly, H., and Lockemann, K., Chem. Ber., 48, 26 (1915); (b) Boyd, J., Robertson, A., and Whalley, W. B., J. Chem. Soc., 174 (1948); (c) Dickenson, H., U.S. Patent 2,449,162 (1948); Chem. Abstr., 43, 694. (d) Abbott Laboratories British Patent 705,316 (1954); Chem. Abstr., 50, 1088d.

(9) Vogel, A. I., "A Textbook of Practical Organic Chemistry," 4th ed., Longman, Inc., New York, 1978, p. 372.

(10) "CRC Handbook of Chemistry and Physics," 58th Ed., CRC Press 1977-78.
(11) "The Merck Index," 9th ed., Merck & Co., Rahway, NJ, 1976.



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.

Topic: "The Importance of Hands-On Science Activities in K-12 Education".

For further information, contact: Joseph Kamsar, 822 Derry Drive, Toms River, NJ 06753, (201) 341-9200, X510.

March 5-9, 1984

PITTSBURGH CONFERENCE ON ANALYTICAL CHEMISTRY AND APPLIED SPECTROSCOPY AND EXPOSITION 1984 to be held in Atlantic City, NJ.

Conference theme will highlight New Horizons in Nuclear Magnetic Resonance Spectroscopy.

For further information, contact: The Pittsburgh Conference, 437 Donald Road, Dept. J-224, Pittsburgh, PA 15235.

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, contact: James Miller, Chemistry Dept., Drew University, P.O. Box HS-7, Madison, NJ 07940, (201) 377-3000, X389.

March 26-28, 1984

NEW YORK ACADEMY OF SCIENCES CONFERENCE ON MACRO-MOLECULES AS DRUGS AND AS CARRIERS FOR BIOLOGICALLY ACTIVE MATERIALS to be held at the Roosevett Hotel, New York, NY.

To be presented by David A Tirrell, Carnegie-Mellon University and L. Guy Doneruma, Polytechnic Institute of New York.

For further information, contact: Ellen A. Marks, New York Academy of Sciences, 2 East 63rd Street, New York, NY 10021.

Southeast

edited by NANCY LEMASTER D. W. Daniel High School Central, SC 29630

ADVANCED PLACEMENT SEMINARS

February 9, 1984

Birmingham Southern College, Hitl Recital Heli, Birmingham, AL 35204.

For further information, contact: Robert D. Dortch, (205) 328-5250.

February 15, 1984

Augusta College, Continuing Education Bidg., Augusta, GA 30910. For further information, contact: Oreg Witcher, (404) 828-3621.

February 28, 1984

Southern Mississippi University, University Union, Hattlesburg, MS 39401.

For further information, contact: Frances A. Karnes, (601) 266-7011.

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

Calawba College, College Community Centre, Saliabury, NC 28 144.

For further information, contact: James A. Nesbitt, (704) 637-4402.

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.

University of Kentucky, Student Center Annex, Lexington, KY 40508

For further information, contact: Timothy R. Burcham, (606) 257-1608.

April 10, 1984

Tennessee Technological University, University Center, Cookesville, TN 38501.

For further information, contact: James C. Perry, (615) 528-3888.

For the state of Florida, the list of AP seminars may be obtained from the College Board, Suite 200, 17 Executive Park Drive, N.E., Atlanta, QA 30329, or by contacting Neila Connors, Bureau of Curriculum Services, Florida Department of Education, Tallahassee, Fl. 30231, (904) 487-1020.

Northcentral

edited by ROBERT SUITS D. H. Hickman High School Columbia, MO 65201

April 6-7, 1984

THE 83RD 2YC, CONFERENCE at the St. Louis Community College at Florissani Valley, 3400 Parshall Road, St. Louis, MO 63135, in contemption with the 187th ACS National Meeting April 8-13, 1984.

Theme: "Chemistry Instruction: Content, Strategies and Materials" For further information, contact: Raigh Burns, St. Louis Community College, Meramed, 11333 Big Bend Blvd., St. Louis, MO 63122, (\$14) 966-7718.

April 8-13, 1984

187TH ACS NATIONAL MEETING, St. Louis, MO.

Topics include:

- State-of-the-Art for Chemical Educators IX: Chemical Education for the 80's, George Bodner, Invited Papers Only;
- Industrial Applications of Genetic Engineering, J. Fayerman, Eli Lilly & Co.
- Research in Chemical Education, Rick Steiner, Dept. of Chemistry, University of Utah.
- Cosmochemistry, Michael Lipschutz, Dept. of Chemistry, Purdue University.
- Workshop on the Use of the Microscope in the Chemistry Laboratory.
 W. McCrone, McCrone Research Institute.
- Breakthrough Lecture. "Research in Chemical Education." Alex Johnstone, Dept. of Chemistry, University of Glasgow, Scotland.

For further information on the ACS National Meeting contact: George Bodner, Meeting Chair, Dept. of Chemistry, Purdue University, West Latayette, IN 47907, (317) 494-5313.

April 9, 1984

"HIGH SCHOOL DAY" AT THE ACS NATIONAL MEETING, St. Louis, MO.

Theme: "Curriculum Developments----Dreyfus institutes 1982 and 1983".

For further information, contact: Kathleen J. Dombrink, McCluer North High School, 705 Waterford Drive, Florissant, MO 63033, (314) 595-2300.

Southcentral

edited by Jan Harris Cypress-Fairbanks High School Houston, TX 77064

March 2-3, 1984

82ND TWO-YEAR COLLEGE CONFERENCE, Tarrant County Junior College, Northeast Campus, Hurst, TX 76053.

For further information, see the December 1983 issue of this Journal.

Southwest

edited by
ERIC STREITBERGER
University of California-Fullerton
Fullerton, CA 96231

February 18-19, 1984

MID-WINTER MEETING OF THE NATIONAL ASSOCIATION OF CHEMISTRY TEACHERS, California Polytechnical Institute San Luis Obispo, CA.

Program includes water pollution, chemical safety in the academic claseroom and cooperative education programs between chemistry and industry.

For further information, contact: Rod Oksen, Northern Section of the California Association of Chemistry Teachers (CACT), Dept. of Chemistry, San Jose City College, 2100 Moore Park Avenue, San Jose, CA 95218.

LETTERS

Clearing-up Misconceptions about Millikan's Oil Drop Experiment

To the Editor:

I wish to correct some misconceptions incorporated in the article entitled, "Some Misunderstandings about Millikan's Oil Drop Experiment," Castellion, M. E. and Bailar, Jr., J. C., J. CHEM. EDUC., **59**, 970 (1982).

It is stated that the parallel plates in Millikan's experiment were charged 3000-8000 V but usually close to 8000 V. Examination of the article, Millikan, R. A., *Physical Review*, **32**, 349 (1911) shows that Millikan stated "an electrical field strength between 3000 V and 8000 V per cm is created between the plates by means of battery, B." This shows that it was

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.

February 4, 1984

A.M. Crystallography

P.M. Problem Solving and Sharing

Speakert R. D. Witters, Colorado School of Mines, Golden, CO

March 3, 1984

Metallurgy—to be held at Hifl Haff, Colorado School of Mines.

Speaker: Dr. Copeand and Staff, Colorado Scheol of Mines, Golden, CO

April 7, 1984

Descriptive Chemistry of Metals

May 5, 1984

Descriptive Chemistry of Nonmetals

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:

March 7, 1984

Very Large Scale Integrated Circuits—Technical & Oesign

Speaker: R. E. Bryant, Asst. Professor of Computer Dosign, California institute of Technology.

April 4, 1984

The Crack: the Most Expensive "Nothing"

Speaker: W. T. Knauss, Professor of Aeronautics & 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 Lee F. Browne, or Phyllis Brewster, California institute of Technology, Pasadena, CA 91125, (213) 356-6624.

SUMMER 1984

EDUCATIONAL BRIDGES TO OPTIONS IN HIGH TECHNOLOGY EM-PLOYMENT at San Diego State University, San Diego, CA

For further information see the December 1983 issue of THIS JOURNAL.

March 24, 1984

CALIFORNIA STATE TEACHERS ASSOCIATION SPRING CONFERENCE, Redding, CA

For further information, contact this editor.

electric field intensity or strength and not battery voltage which was being described. In the experimental portion of this paper, Millikan describes the distance between the parallel plates as 1.600 cm. A simple calculation shows that the battery voltage was much greater than 8000 V. (SI units are used.)

$$\frac{8000 \text{ V}}{1.000 \times 10^{-2} \text{ m}} \times 1.600 \times 10^{-2} \text{ m} = 12,800 \text{ V}$$

If 12,800 V potential difference is placed aeross 1.600×10^{-2} m, we obtain the maximum electric field strength, 8000 V/cm or 8×10^5 V/m. Millikan used a voltage divider-to bring his lowest electric field intensity to 3000 V/cm or 3×10^5 V/m. A similar calculation shows that at the lowest electric field intensity, the voltage divider had reduced the output voltage to 4,800 V (Harris, S. P., J. CHEM. EDUC., 59, 988 (1982)).

A further quotation from the same sentence used previously follows: "if the droplet had received a frictional charge of the proper sign and strength as it was blown out from the atomizer, it is pulled up by this field against gravity, toward the upper plate." Evidently, the charge was frictional in origin.

A charge cannot be produced from the electric field.

There is a uniform electric field between the parallel plates except at the edges. The electric force, F_e , is directly proportional to the electric field intensity, ϵ , and to the charge, q, on the oil drop.

$$F_e = q\epsilon$$
 (1)

Everywhere between the charged and parallel plates, the electric field intensity is the same, a maximum of 8×10^5 V/m or 8×10^5 nt/coulomb. Within this uniform field, the charged body moves with uniformly accelerated motion toward the plate having an opposite sign. The net force accelerating the charged oil drop is the difference between $F_{\rm e}$, the electric force and the gravitational force, on the oil drop, $F_{\rm g}$.

Millikan states that the frictionally charged oil drops were blown out of the atomizer and fall into the viewing chamber. At the same time he states that the parallel plates are shortcircuited by means of a switch, S. The oil drop is timed in its fall. Following this procedure, the electric field is switched on and the rate at which the droplet moves upward under the influence of the electric field is timed for the same distance between two cross hairs. If the droplet meets an ion, the speed of travel between the two cross hairs is increased. Millikan was able to calculate from this kind of experiment "the sign and exact value of the charge carried by the captured ion." Sometimes, Millikan produced ions in the viewing chamber "by any of the usual ionizing agents like radium or x-rays." Millikan observed some drops for periods as long as an hour by utilizing a switch to reverse the polarity of the parallel plates.

Millikan realized that his results were "limited in accuracy only by that attainable in the measurement of the coefficient of viscosity of air." The error in air viscosity was eventually shown to be the cause of the 2.50% error in Millikan's measurements.

Sidney P. Harris

Queens College Flushing, NY 11367

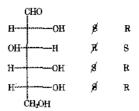
Specification of R/S in a Multichiral Molecule To the Editor:

The recent note¹ describing the specification of R or S to a chiral molecule by an even number of group exchanges becomes extremely difficult for a multichiral molecule. Since an odd number of interchanges is equivalent to inversion,² the following method might be useful regardless of the number of involved chiral centers.

 If the Fischer projection formula has the lowest priority group, generally hydrogen, to the top or bottom, then R or S is specified in the usual manner. For example,

If the Fischer projection formula has the hydrogen to the left or to the right, then the R or S is determined and then inverted. For example,

For a multichiral molecule, each chiral center can be quickly and correctly assigned without the possible confusion associated with the switching of groups. For example,



Before incorporating the above adjunct method into a discussion of stereochemistry, it is best to present the traditional three dimensional representations for chiral molecules. The required restrictions for using the planar Fischer projection formula also should be stressed.

Justin W. Diehi

St. Bonaventure University St. Bonaventure, NY 14778

To the Editor:

In the July 1982 issue of the JOURNAL, John P. Idoux wrote an article, "A Simple Method for Specifying the R/S Configuration about a Chiral Center," in which he outlines a procedure for identifying the R/S configuration of a chiral center via Fisher projection. He also suggests that this method has not been presented in undergraduate organic texts or chemical education journals.

However, Carl R. Johnson has written and published a book, "Organic Nomenclature: A Programmed Study Guide," Worth Publishers, Inc., 1976, devoting almost an entire chapter to finding the R/S configuration of a chiral center using Fisher projections. I have been using his manual in undergraduate organic chemistry for several years.

Louis Milakofsky

Pennsylvania State University-Berks Campus Reading, PA 19608

To the Editor:

Two communications have appeared [J. CHEM, EDUC., 56, 451 (1979), 57, 528 (1980); Biochem. Educ., 8, 105 (1980)] in which simple ways to relate R, S stereochemical designations to Fischer projections were presented. Any system, simple or complex, cannot be used successfully to relate the R, S designations to Fischer projections if an incorrect two-dimensional projection is made of the three-dimensional model of the structure [Appendix 2, IUPAC Tentative Rules for the Nomenclature of Organic Chemistry, Section E. Fundamental Stereochemistry, J. Org. Chem., 35, 2849 (1970)]. These Rules (Section E-7.1) point out that one cannot rotate a Fischer projection 90° in the plane without changing the projection of the vertical bonds to in front of the plane. In many biochemistry texthooks the standard projection rules are not being applied to the amino acids, but are being used as if the rotated vertical bonds project forward. The amino acid in Dietzel's note [J. CHEM. EDUC., 56, 451 (1979)] is indeed (R), but is frequently assumed to be L(S)—see below. This assumption is only acceptable when it is clearly stated that it is being used [Biochem. Educ., 2, 76 (1974)].

$$CO_2H$$
 90°
 H_2N-C-H
 OCH_3
 OC

John N. Aronson

State University of New York at Albany Albany, NY 12222

¹ Idoux, J. P., J. CHEM. EDUC., 59, 553 (1982).

² Natta, G., Farina, M., "Stereochemistry," Harper and Row, New York, 1972, pp. 241-242.

BOOK REVIEWS

General, Organic and Biological Chemistry: Foundations of Life

Dorothy M. Felgl and John W. Hill, Burgess Publishing Company, Minneapolis, MN, 1983, xiv \pm 383. Figs. and tables. 19.5 \times 24,5 cm. \$21.95.

"General, Organic, Biological Chemistry—Foundations of Life" by Dorothy Fiegl and John Hill is a text designed to introduce the student to elementary chemistry and to relate the chemistry to living, life, and the real world.

The text starts with a chapter on matter and measurements. The next seven chapters cover the general chemistry block of material: atomic structure, chemical bonding, nuclear processes, gases, chemical reactions, solutions, and acid-base chemistry. Chapters nine through thirteen discuss the structure, the nomenclature, the physical properties, and the chemistry of the different classes of organic compounds. The final five chapters cover the topics of carbohydrates, lipids, amino acids, proteins, nucleic acids, vitamins, minerals, and hormones.

The elementary level of the text is the result of the size of the text, three hundred fifty-three pages, compared to the large number and variety of topics covered. The material is covered in a complete but descriptive manner with an emphasis on its application to practical and real problems. This interface between the hasic chemistry and the real world is enhanced by the use of numerous well-chosen pictures, excellent figures and diagrams, and tables of relevant data. A series of clever cartouns is used throughout the text to help the student visualize and clarify chemical concepts.

The following selected topics represent the manner in which the authors integrate the real world and the basic principles of chemistry; nuclear medicine, respiration and partial pressure, oxidation and antiseptics, blood and pH, polymers, physiological properties of alcohols and amines, digestion and carbohydrates, and digestion and proteins.

The authors fulfill very well their stated goals of presenting the principles of chemistry and relating them to life. This reader found the text clearly written with good content at the elementary level. The text is highly recommended for consideration for those desiring an elementary text designed for one semester that presents the principles of general, organic, and biological chemistry with applications to life.

J. L. Kirsch Butler University Indianapolis, IN 46208

The Elements of Style in Chemistry, A Computer-assisted Instruction Supported Text

James W. Beatty, and James J. Beatty, University Press of America, Lanham, MD, 1982, v + 104 pp. Figs. and tables. 13.5 X 20.5 cm. \$7.25 PB.

According to the preface, "The book is the text for a two-hnur course entitled "Prerequisites for Chemistry." The course is intended for students who, because of prior experience or lack of experience in problem solving, have difficulty in solving problems which are important to survival and satisfactory performance in an introductory course."

Given the purpose of the book and the audience to which it is directed, quality of content is important; yet lack of quality is one of the major failings of this book. This lack of quality is exhibited by statements that are either unclear, confusing, or just plaiu incorrect. Because of limitations of space, it is not possible to go into full detail to support this assertion and so attention is called to the following examples which are chosen at random. On page 26 one reads that "Physical

measurements yield numbers with dimensions. The dimension is given with the number. Examples: 6 feet, In addition and subtraction all numbers must have the same dimensions and the result will have this dimension. Example: You cannot add 16 grams to 2 ounces without converting one quantity to the other." The authors are confusing dimensions and units. Measurement is an operation of comparison; thus, 6 feet is the result of a measurement of length in which the unit of comparison is the foot; 16 grams and 2 ounces are quantities having the same dimension and therefore the masses may be expressed in the same unit.

On page 40, paragraph 2, it is stated that "Atoms of the elements combine with each other and themselves in definite combinations called compounds. . . . Chlorine combines with itself forming molecules of chlorine, Cl2." When two atoms of the same element unite to form molecules the product is not a compound! In paragraphs 4 and 5, respectively, on page 40 one reads "the atomic mass of an element is the mass of the element relative to the other elements . . . the atomic mass is the mass of one atom of the element." "In laboratory units, the atomic weight is the weight in grams of the same number of atoms as there are in 12.000 grams of the isotope of carbon mass 12." These statements are not good enough; the atomic weight of an element, or better, the relative atomic mass of an element is a dimensionless quantity. The actual mass of an individual atom, however, is expressed in terms of the atomic mass unit, u, and by definition of the latter, the average mass of the atoms of an element in atomic mass units is numerically equal to the relative mass of those atoms; i.e., their atomic weight. At the top of page 21 is the statement, "one mole of a compound is defined as one molecular weight of a compound." This will come as a surprise to IUPAC. There is no reason why beginning students of chemistry should not be taught that mole is the amount

(Continued on page A28)

Reviewed in this Issue-

Dorothy M. Feigl and John W. Hill, General, Organic and Biological Chemistry: Foundation of Life

James W. Beatty and James J. Beatty, The Elements of Style in Chemistry: A Computer-Assisted Instruction Supported Text

Arthur M. Lesk, Introduction to Physical Chemistry

Robin K. Harris, Nuclear Magnetic Resonance Spectroscopy

Titles of interest

Reviewer

J. L. Kirsch

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Victor A. Crawford

Dewey K. Carpenter

Nancy S. True

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BOOK REVIEWS

of substance (Stoffmenge, in German) of a system that contains as many elementary entities as there are carbon atoms in 0.012 kg of carbon. We do not do students a service if we teach them fundamental ideas that later must be unlearned or relearned. On page 65 one learns that "the NaOH has only one OH" ion per mole." What is meant, of course, is that there is one mole of OH~ ions per mole of NaOH. Stoichiometry is an essential component of any beginning chemistry course and a clear understanding of the concepts atomic weight or relative mass of an atom, molecular weight or relative mass of a molecule, atomic mass, molecular mass, and mole is crucial for further study and for success in solving problems.

The examples given are serious short-comings in a book whose preface claims that "experience shows that the student who masters the material in this little book goes into college chemistry without serious deficiencies." Given the purpose of the book, basic concepts must be stated clearly and in an impeccably correct manner, and this the authors have failed to do. I do not see any useful purpose that could be served by this text and I cannot recommend it.

Victor A. Crawford Rockford College Rockford, IL 61101

Introduction to Physical Chemistry

Arthur M. Lesk, Prentice-Hall Inc., Englewood Cliffs, NJ, 1982. vii + 746 pp. Figs. and tables, 18 × 24 cm. \$38.95 HB.

Here is a fine treatment of all the main topics of physical chemistry. The writing is clear, the illustrations are appropriate, and the problems are excellent. It would be a sensible choice as a text for use with well-prepared and motivated students. It suffers from some organizational peculiarities, occasional haziness regarding definitions, and a level of exposition which demands a level of physical insight which is unfurtunately not common in undergraduates.

To elaborate on these remarks, consider first the really good things. Lesk shows a concern both for overall perspective and for attention to details. Throughout the book there is no mathematical pedantry, and there are many fine examples of clear explanation which do not allow the distance between theory and experiment to become very great. Among these are the chapters on applications of thermodynamics, statistical mechanics. solids, X-ray crystallography, the fluid state, and electrochemistry. Topics are treated thoroughly and amply illustrated by numerical examples, figures, and tables. The use of actual literature data in the latter as well as in many prublems is to be commended. There are several places in the book where important compilations of data and bibliographies are presented; e.g., in chapters 1, 6, 14, and 17. No other physical chemistry text does as good a job in relating itself to the chemical literature. The book rewards close attention with numerous new ways of thinking about familiar topics.

This leads to some critical observations. Although the mathematical level is low, the conceptual level is not. Lesk argues his case convincingly and non-trivially, and I fear that frequently only mature students will be able to follow him. A case in point is the way in which such a large number of topics (e.g., solids, liquids, gases, phase transitions, thermodynamics, quantum mechanics, and statistical mechanics) are introduced in an overview of physical chemistry in chapters 2 and 3. As a book for gradnate students reviewing the subject these chapters will be very helpful; as a first exposure to neophytes they will probably bewilder.

There are other problems with the organization. (1) If the statistical mechanics of ideal gases is treated before quantum mechanics, there are too many formulas for eigenvalues which must be pulled out of the hat. (2) A more serious matter concerns the division of thermodynamics into two blocks of material. After a conventional introduction to thermodynamics and some of its applications, there is an intrusion of eight chapters before thermodynamics is applied in chapters 15, 16, and 17 to real gases, binary solutions, and Galvanic cells, respectively. This will present a problem to those of us who prefer to treat thermodynamics and its applications before moving on to molecular phenomena because chapters 15, 16, and 17 utilize material from the intervening chapters and chapter 17 also contains non-thermodynamic topics; e.g., conductance.

Although the exposition is generally very clear, Lesk occasionally faiters in defining hasic quantities; e.g., although the First Law is clearly stated and expertly applied, I find the definitions of work, heat, and temperature to be somewhat vague.

At the beginning of each chapter "learning goals" are stated and a study guide is provided which gives a good summary of the chapter.

On balauce, there is more good than bad here. I would expect the book to be most successful in situations where the majority of the students are highly motivated. If there were such a thing as a second-level course in physical chemistry, this would be a good text to use.

> Dewey K. Carpenter Louisiana State University Baton Rouge, LA 70803

Nuclear Magnetic Resonance Spectroscopy

Robin K. Harris, Pitmen Publishing Inc., Marshfield, MA, 1983. xx + 250. Figs. and lables. 19 \times 24. \$34.95.

Robin K. Harris has written a physically oriented introductory NMR text directed toward the advanced undergraduate and beginning graduate student which should also prove useful for chemists who use NMR as a structural tool. The organization of this excellent book reflects the increased experimental emphasis un time domain NMR spectroscopy which has occurred over the last decade while retaining the principal features of an earlier text by the same author ("Nuclear Magnetic Resonance Spectroscopy" by R. Lynden-Bell and R. K. Harris, Thomas Nelson and Sons, Ltd., 1969).

Material is presented in eight largely selfcontaining chapters preceded by a complete symbol and abbreviation list which facilitates easy reference. Emphasis is on theoretical aspects with many practical applications discussed with the aid of figures and presented in accompanying problems. Each chapter contains excellent illustrations, useful tables, up-to-date specific and general references and problems of varying difficulty. The chapter sequence is somewhat arbitrary; for example, chemical shifts and coupling constants are discussed in the final chapter although this material logically follows topics covered in the introductory chapters.

Basic principles, spectral analysis of isotropic systems, chemical shifts and coupling constants are thoroughly covered at a level appropriate for the advanced undergraduate student who has some prior exposure to basic principles of quantum mechanics. The mathematical level is elementary and density matrix formalism is not utilized. For example, the chapter on analysis of complex spectra begins with a discussion of operator algebra and proceeds through the formulation and solution of spin matrices for complex coupled systems. Time-dependent perturbation theory and selection rules appear in an appendix.

Relaxation measurements and mechanisms, multiple-pulse experiments, double resonance, spin decoupling, the nuclear Overhauser effect, and Fourier transform techniques are discussed in detail in early chapters in the book. Time domain spectroscopy is emphasized not only for its signal enhancement capability but also fur the structural and dynamical information multiple pulse sequence experiments can provide. The latter is an especially unique and important feature of the text. Spin echoes and selective pulse sequences are discussed with emphasis on INEPT experiments and heteronuclear and homonuclear 2D J-resolved spectroscopy.

A chapter combining material on chemical exchange and quadrupolar effects is also included and its coverage is greatly expanded from the earlier book. Topics include lineshapes for uncoupled equally populated site exchange, exchange rates from spin-lattice relaxation and saturation transfer, as well as exchange involving paramagnetic species. Effects of coupling of spin ½ nuclei to quadrupolar nuclei are discussed.

The author has included a thorough and timely discussion of NMR of solids including magic angle rotation, a discussion of second moment effects, motional effects on relaxation time, cross polarization, shielding anisotropy, ubtaining high resolution NMR spectra in the solid state including CP/MAR techniques. In contrast, applications of NMR spectroscopy to gases is completely omitted. Other areas not covered include biological applications, CIDNP, spin imaging and related topics.

Although this text would be most suitable fur an undergraduate special topics course in NMR spectroscopy most chemistry departments in the U.S. do not provide such a course and a special strength of this book is its amenability to self-directed study. The author's style is concise and clear. The book's contents allow interested individuals to master the basic principles of NMR spectroscopy and gain an appreciation of the present capabilities of this powerful technique, and extensive references and a bibliography provide direction for further study in specific areas.

Nancy S. True University of California Davis, CA 95616

Titles of Interest

Monographs

Advances in Physical Chemistry: Current Developments in **Electrochemistry and Corrosion**

Ya. M. Kolotyrkin (Editor), Mir Publishers, Moscow, Russia, 1982, 0 + 191 pp. Figs. and tables. 14 × 21.5 cm. \$6.45.

Adrenoceptors & Catecholamine Action, Part B

George Kunos (Editor), John Wiley & Sons, Somerset, NJ, 1983. vii + 327 pp. Figs. and tables. 16.5 × 24 cm. \$75.00.

List of contents and contributors: Structhre-Activity Relationships of Alpha-Adrenoceptor Agonists, R. R. Ruffolo, Jr.; Phosphatidylinositol Metabolism and a-adrenoceptor Mechanisms, J. W. Putney, Jr.; Release-Modulating Adrenoceptors, E. S. Vizi; Adrenergic-Cholinergic Interactions, W. R. Roeske and H. I. Yamamura; Adrenoceptors in Skeletal Muscle, I. W. Rodger and W. C. Bowman; Adrenergic Influence on Peripheral Hormone Secretion, J. B. Young and L. Landsberg; Adrenoceptors and Central Cardiovascular Regulation, H. Schmitt and M. Lanbie; Adrenoceptors and the Regulation of Salivary Gland Physiology, B. J. Baum, H. Ito, and G. S. Roth; Microscopic Localization of Adrenoceptors, J. M. Palacios and J. K. Wamsley.

Biosynthesis of Indole Alkaloids

Atta-ur-Rahman and Anwer Basha, Oxford University Press, New York, NY, 1983. 0 + 270 pp. Figs. and tables. 16 X 24 cm.

Chemistry and Technology of Water-Soluble Polymers

C. A. Finch (Editor), Plenum Publishing Corporation, New York, NY, 1983. xvi + 358 pp. Figs. and tables. 17 imes 25.5 cm.

Chemistry of Pesticides

K. H. Buchel (Editor), John Wiley & Sons, Somerset, NJ, 1983, xii + 518 pp. Figs. and tables, 17 X 24 cm, \$90.00.

The interpretation of Analytical Chemical Data by the Use of Cluster **Analysis**

D. Luc Massart and Leonard Kaufman, John Wiley & Sons, Somerset, NJ, 1983. x + 237 pp. Figs. and tables. 15.5 × 23.5 cm, \$45.00.

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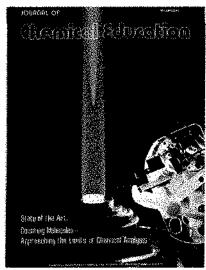
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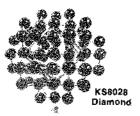
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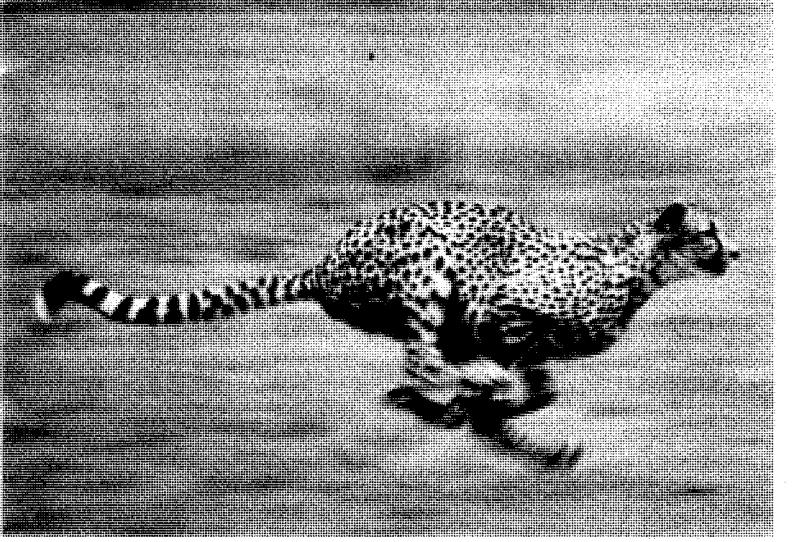
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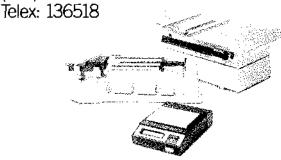
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