

The National Academy of Sciences

Abstracts of Papers Presented at the 1949 Autumn Meeting, Rochester, New York

Reflection and Transmission Type Interference Filters

A. F. Turner, *Bausch & Lomb Optical Company*
(Introduced by F. E. Wright)

Thin films may be combined to produce narrow band pass filters, which owe their effectiveness to interference. By means of high vacuum techniques, such film combinations have been satisfactorily produced up to a diameter of 8 in., and larger sizes are feasible. A filter for transmission is made by depositing successively a film of silver, a spacer film of a dielectric, and a second silver film. The thickness of the spacer film controls the wavelength position of the pass band. The optical properties of the silver limit the use of this filter to a wavelength range of about 350–750 m μ . The best optical performance is obtained in the middle of this range, where a filter with 40% transmittance will have a half-width of 10 m μ . The wavelength range may be greatly extended with a reflection type filter in which the film sequence is opaque aluminum, followed by several transparent aluminum films separated by dielectric films. Such filters are operative from the ultraviolet into the infrared, but have relatively wide pass bands. In the visible a typical filter has a peak reflectance of 90%, with a half-width of 60 m μ . Both types of filter will be demonstrated.

Diffraction Gratings of Improved Efficiency

David Richardson, *Bausch & Lomb Optical Company*
(Introduced by F. E. Wright)

The efficiency of a grating is determined principally by the contours of the grooves and the reflectivity of its surface. The shape, orientation, and loading of the ruling diamond must be carefully controlled if the desired groove shape is to be achieved. The microinterferometer has proved to be invaluable for observing the groove shape of preliminary test rulings and thus assuring the correct adjustment of the diamond. Energy distribution measurements of completed gratings indicate the value of the method.

Invariants and Symmetry and Their Use in Geometric Optical Problems

Max Herzberger, *Eastman Kodak Company*
(Introduced by W. Albert Noyes, Jr.)

An optical system is in general symmetric around an axis. A special type of optical system is one with central symmetry, consisting of a series of spheres with the same center. The author has developed, together with his friend, H. Boegehold, a theory which gives complete information about their image formation. This leads to a new image error theory, in which symmetry or the lack of it is used as a method for analyzing an optical image.

In a system with point symmetry, there exists an invariant vector for every ray trace. In a system with areal symmetry, there exists an invariant scalar. The author has transformed the formula for tracing a ray or a bundle of rays through an optical system into a form in which the invariant scalar or vector forms one of the given data. This permits ray tracing to be reduced by one dimension—an important reduction, since the graphical methods connected with this step are a guide in the difficult problem of correcting an optical instrument.

Developments in the Field of Ultraviolet Microscopy

John V. Butterfield, *Bausch & Lomb Optical Company*
(Introduced by F. E. Wright)

The original conception of the ultraviolet microscope was evolved from a desire to extend the resolution limit of the microscope beyond the limit imposed by visual wavelengths. Of equal, and at present perhaps even greater importance, are its applications in biochemistry for direct photographic recording of biological tissue or for microphotometric determinations of biochemicals. With the advent of achromatic objectives applicable to the ultraviolet, the manipulation of the microscope in this region has been simplified, and the usefulness of the instrument extended considerably.

Fluctuations in the Photoconductivity of Films of Lead Sulfide

Brian O'Brien, Harry D. Polster, and
Walter P. Siegmund
Institute of Optics, University of Rochester
(Introduced by W. A. Noyes, Jr.)

The concept that photoconductivity in thin films of heavy metal sulfides is due to photosensitive barriers between regions of excess and defect conductivity has received considerable support from several recent investigations in which a film surface has been scanned with a small spot of light. To extend this, provision has been made for exploring such surfaces with much smaller light spots, limited in minimum size only by the diffraction pattern of a high numerical aperture objective. An interrupted tungsten filament source is projected on the film with an apochromatic system corrected for the near infrared, and yielding an image of effective width about 1.5 μ . The photoconductivity appears as an alternating voltage recorded by a curve-drawing instrument synchronized with the film scan.

Films of lead sulfide formed by distillation and by wet precipitation have been investigated. The photoconductivity shows large and rapid fluctuations with position of the illuminated spot, which are highly reproducible in successive traces. Photoconductivity may change by a fac-

tor of two or more in a distance of 10 μ . However, the most common pattern observed consists of sharp drops below, rather than sharp peaks above, a general level of photoconductivity, which is difficult to reconcile with a barrier theory.

Correlations between Photographic and Photoconductive Sensitivity in Silver Halides: The Effects of Silver Sulfide and of Divalent Positive Ions

W. West and B. H. Carroll, *Eastman Kodak Company*
(Introduced by W. Albert Noyes, Jr.)

The electrical conductivity of photographic films changes slightly on exposure to light, the effect being measurable in some cases at exposures corresponding to normal latent image formation. The usual effect is an increase in conductivity, corresponding to liberation of electrons by light. It has been found that chemical sensitization of emulsions by compounds forming silver sulfide decreases the photoconductivity. The decrease is about 50%, which is a reasonable value for the trapping of electrons by the sensitivity nuclei. The evidence indicates that emulsion grains contain many shallow traps for electrons, to which chemical sensitization adds a few deep traps.

Silver bromide containing small amounts of lead or cadmium bromide has increased electrolytic conductivity and darkens very slowly on exposure to light. It has been found that fused, unannealed films containing these divalent cations show normal photoconductivity, although corresponding films of pure silver bromide decrease in conductivity on exposure. This result may be explained best in terms of Mitchell's theories of sensitivity, based on the existence of Schottky defects.

The Theory of Micrometeorites

Fred L. Whipple, *Harvard College Observatory*
(Introduced by L. H. Adams)

The term *micrometeorite* is here defined as an extra-terrestrial body that is sufficiently small to enter the earth's atmosphere without being damaged by encounter with the atmosphere. The limiting circumstance arises when the micrometeorite radiates energy rapidly enough that its temperature remains below its melting point as its motion is retarded by atmospheric resistance. The theory of the maximum dimension for such a particle with prescribed geocentric velocity and physical characteristics is developed in this paper. The solution depends upon the height-density relation adopted for the atmosphere. Two types of such relations permit explicit solutions for the limiting ratio of meteoric mass to radiating area, or, if the particle is spherical, for the limiting radius. These atmospheric relations are a) constant temperature, and b) constant temperature gradient, both for constant molecular weight with respect to height. The second case appears to give a sufficiently accurate results for present needs.

The limiting radius for a spherical micrometeorite varies approximately as the fourth power of the melting temperature, the inverse cube of the velocity, the inverse

logarithmic density gradient at the point of maximum temperature, and the secant of zenith distance. Heights of maximum temperature increase with velocity but lie in the neighborhood of the E-layer. For an iron meteorite at a velocity of 23 km/sec, the limiting spherical radius is 3–5 μ . Long cylindrical particles may have a minor diam of 4–7 μ —in good agreement with the minor dimensions of the "wedge-shaped opaque" magnetic particles that H. E. Landsberg associated with the great Giacobinid meteor shower in October 1946 (velocity 23 km/sec). His larger "round" particles (20–40 μ diam) may have been partially vaporized. This general agreement provides secondary confirmation of the assumed atmospheric relations at the 100-km level.

The writer heartily encourages the collection and study of micrometeorites, as they may provide the only laboratory samples of cometary material; ordinary meteorites probably arise from a different source. Deep oceanic sediments, as suggested by the *Challenger Expedition*, polar snows, or even geological strata may also contain evidence of astronomical phenomena.

Chemical Constitution and Photographic and Allergic Activities of Color-forming Developing Agents

A. Weissberger, *Eastman Kodak Company*
(Introduced by W. A. Noyes, Jr., Chairman,
Local Committee on Arrangements)

The only developing agents useful for processes involving formation of dyes in the photographic layer are *p*-aminodialkylanilines. These compounds are, as a class, rather weak developing agents. Moreover, they cause a sensitization dermatitis like poison ivy.

A considerable number of compounds were synthesized and their polarographic half-wave potentials and developing and color-forming activities were measured. The results lead to an understanding of the electrochemical and sterical factors which regulate the activity of these developing agents. Groups which increase the affinity of the compounds to gelatin (keratin) and decrease their lipid solubility reduce their allergic properties. A number of photographically highly active, low allergenic, dye-forming developing agents have been synthesized.

On the Possible Existence of Antinucleons

J. Ashkin, T. Auerbach, and R. Marshak
University of Rochester

(Introduced by W. A. Noyes, Jr.)

Recent evidence for the gamma instability of neutral mesons and the possibility of detecting relativistic charged mesons in the new electron-sensitive plates renews interest in the possible existence of antinucleons, in particular negative protons. Rigorous expressions have been obtained for the annihilation cross sections of proton pairs using weak coupling theory and spin zero mesons. The annihilation cross section vanishes in the limit of zero velocity for the emission of two neutral mesons but reaches a maximum for the emission of two charged mesons. The charged meson annihilation therefore dominates over the proton annihilation. The total

probability for annihilation of the negative proton in flight has been computed, taking account of its ionization loss and the effect of nuclear collisions. The prospects of detecting negative protons annihilating in flight or at rest in photographic plates exposed at 100,000 ft appear hopeful.

Proton-Proton Scattering

C. L. Oxley, Physics Department, University of Rochester
(Introduced by W. A. Noyes, Jr.)

This paper is to review the proton-proton scattering program at Rochester, to present future plans of the program, and to connect the program with the problems of the field and with work in other laboratories.

General features of the Rochester program are photographic plate experiments with the small cyclotron at energies of 7 Mev and less, counter experiments with the undeflected beam of the new synchrocyclotron at energies from 250 Mev to 50 or 100 Mev, and a search for inelastic proton-proton scattering as might occur with the excitation of isobaric proton states.

The program was initiated by and has progressed with the guidance of S. W. Barnes. Support is derived from grants of the Research Corporation and the joint program of the Office of Naval Research and the Atomic Energy Commission.

Prediction of Compressibility of Real Gases and Gaseous Mixtures from Critical Pressure and Temperature

Gouq-Jen Su, Ramesh G. Soparkar and Robert J. Lockhart
Department of Chemical Engineering,
The University of Rochester
(Introduced by W. A. Noyes, Jr.)

Based on a modified "law" of corresponding states, a system of generalized isometrics is presented, covering experimental data on seventeen gases over wide ranges of pressure and temperature and seeming to be applicable to all gases. A ternary gaseous mixture consisting of methane, *n*-butane and decane at five different compositions has been studied. Calculated and experimental values of compressibility factors agree well. Calculated changes of enthalpy with pressure, making use of a generalized form of the Beattie-Bridgeman equation of state, for the methane-ethane system agree well with experimental values reported in literature. The same method may be used to calculate isothermal changes of other thermodynamic functions.

The proposed method of correlating pressure-volume-temperature data by the generalized relationship has the advantage of not requiring knowledge of the critical volume.

The Heavy Nuclei of the Primary Cosmic Radiation

H. L. Bradt and B. Peters, University of Rochester
(Introduced by W. A. Noyes, Jr.)

The abundance of atomic nuclei of the light elements in the primary cosmic radiation has been determined at geomagnetic latitudes $\lambda = 30^\circ$, 51° , and 55° with the aid

of photographic emulsions exposed in balloon flights at 100,000-ft altitude.

The abundance ratios may be compared with the abundance of the atoms of the light elements in stellar atmospheres and interstellar space.

The most abundant nuclei in the primary cosmic radiation are H nuclei (relative intensity = 10,000). Next come He nuclei (1000), nuclei of C, N, O, and possibly F or Ne (60), nuclei of Mg, Si and neighboring elements (10) and nuclei of charge $Z > 15$ up to the neighborhood of Fe (10).

The abundance of nuclei in the primary cosmic radiation may be determined by several factors, among them: (a) the abundance of atoms (or ions) in the region where acceleration took place; (b) the dependence on charge and mass of the efficiency of the acceleration process; and (c) the breakup of heavier nuclei into lighter ones by collision with interstellar H atoms. This latter factor will be important if cosmic rays are of galactic origin.

The relative importance of factors (a) and (c) may be obtained from a determination of the abundance of primary nuclei whose cosmic abundance is known to be extremely low (Li, Be, and B).

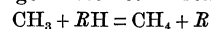
The Pre-exponential Factor for Some Reactions of Methyl Radicals

Leon M. Dorfman and Robert Gomer
Department of Chemistry, The University of Rochester
(Introduced by W. A. Noyes, Jr.)

Recent kinetic data on the role of methyl radical reactions in the photochemistry of various compounds permit the evaluation of relationships between the pre-exponential factor for the association reaction



and that for hydrogen abstraction reactions of the type



Evaluation of the relative steric factors is possible upon the assumption of arbitrary collision cross sections for these reactions. For the reaction of methyl radicals with acetone, dimethyl mercury, ethylene oxide, butane, and ditertiary butyl peroxide, the data indicate that the steric factors for the methane-forming reactions are lower than has normally been assumed. On the basis of these data an upper limit of $p \approx 5 \times 10^{-4}$ must be assigned.

γ -Aminobutyric Acid: A Constituent of the Potato Tuber?

F. C. Steward, J. F. Thompson,¹ and C. E. Dent²
University of Rochester
(Introduced by W. Albert Noyes, Jr.)

The first examination by Dent, Stepka, and Steward of the free amino acids of the potato tuber by partition chromatography on paper revealed 27 different substances which react with ninhydrin. Of these substances 21 were either amino acids or amides or their derivatives which, though they may not have been previously demonstrated

¹ Postdoctoral Fellow, National Institutes of Health.

² Present address: University College Hospital, London, England.

in a single plant extract, were nevertheless known to occur in plants. Three unidentified substances reacted like amino acids to ninhydrin. Of these, two occurred only in small amount, one was tentatively recognized as β -alanine, but the third was present in relatively large amount. It is this substance, which—after glutamine and asparagine—is the most abundant soluble nitrogen compound in the potato tuber, that is now recognized as γ -aminobutyric acid.

γ -Aminobutyric acid occurs in the phenol: collidine-lutidine chromatograms in a position almost immediately below that of value. The naturally occurring product may be isolated by the methods of paper chromatography and freed from all other known ninhydrin-reacting compounds. It is stable to hydrolysis and to hydrogen peroxide and is chromatographically identical with synthetic γ -aminobutyric acid (prepared from the lactin). Since, however, this acid has not hitherto been recognized as a normal constituent of plants, some confirmation by an alternative method is desirable.

As isolated by paper chromatography from cold alcoholic extracts of potato tuber, the γ -aminobutyric acid is difficult to crystallize—more so than the synthetic product when present in comparable amount. This appears to be due to a substance which does not react with ninhydrin but which causes the formation of a noncrystalline glass. This has made it difficult to obtain satisfactory x-ray diffraction patterns to compare with those of crystalline synthetic γ -aminobutyric acid.

One of us (C. E. Dent) has, however, shown that γ -aminobutyric acid forms a compound on boiling with urea in presence of copper salts. This compound can be adsorbed on acid alumina. The ureide takes up a characteristic position on the standard phenol: collidine-lutidine chromatograms near to that of methionine sulfone, where it may be detected by a yellow color formed with acid *p*-dimethyl-aminobenzaldehyde. In this behavior the natural product from potato tuber exactly matches the synthetic substance. However, pure γ -aminobutyric acid or its ureide have not yet been isolated in sufficient quantity for ultimate analysis. The identity of this substance as a normal constituent of the potato tuber seems, however, to be certain.

The analysis, by quantitative paper chromatography, of the alcohol-soluble nitrogen compounds of the potato tuber (variety Katahdin) shows that the amount of γ -aminobutyric acid present is greater than that of any amino nitrogen compound other than glutamine and asparagine. The content of the major constituents is here recorded in the approximate sequence in which they occur on the chromatograms, and in the units $\mu\text{g/g}$ fresh weight, as follows: aspartic acid, 161; glutamic acid, 121; serine, 108; asparagine, 2300; threonine, 52; alanine, 189; glutamine, 2493; γ -aminobutyric acid, 540; valine, 358; leucine, 478. Thus γ -aminobutyric acid accounted for about 5% of the alcohol-soluble and for 3.7% of the total nitrogen in these tubers.

Glutamic acid decarboxylase activity in the tubers was demonstrated manometrically but the activity was small; so that it is even open to question whether the γ -aminobutyric acid does arise by decarboxylation of glutamic

acid (α -aminobutyric acid, the other possible decarboxylation product, occurs in potato only in minute amounts). In view of the importance of glutamic acid and glutamine in nitrogen metabolism, the role of γ -aminobutyric acid and its relation with these substances is of great interest.

γ -Aminobutyric acid does not occur among the hydrolytic products of potato proteins; it is, however, utilized as a nitrogen source if the potato cells are brought under conditions conducive to protein synthesis.

From the evidence of chromatography, free γ -aminobutyric acid seems to be somewhat widespread in plants.

Electric Moments of Polar Polymers in Relation to Their Structure

Peter Debye and F. Bueche, *Cornell University*

From the observed angular dissymmetry of the light scattered by polymer solutions it has been possible to draw conclusions on the average size of the polymer coil. In general, the actual coil diameter found in this way is much larger than that calculated from a model with free rotation. (For polystyrene in benzene the factor is about 3.5). This increase in size can satisfactorily be attributed to hindering of rotation around the chemical bonds. In order to obtain information about structural details of this hindered rotation, however, the size determination will have to be combined with evidence derived from other sources than light scattering. As such, the dipole moment, as derived from measurements of the dielectric constant of polymer solutions, obviously is a good choice. If N polar monomers are influenced independently by the electric field, their contribution to the polarization will be N times the contribution of a single monomer. If they are connected to each other in the chain, the contribution of the whole chain may be larger or smaller, depending on whether positions of parallelism or antiparallelism of the elementary electric moments are preponderant, taking the average over all the possible forms the coiling molecule can assume. A theory of this effect has been worked out and experiments have been carried out on solutions of several polar polymers. One of the examples is *p*-chloropolystyrene, for which the average contribution to the polarization of one chain element is substantially smaller in the polymer than that of the corresponding monomer.

Adsorption Isotherms and Liquid Solutions

George Scatchard, *Massachusetts Institute of Technology*

It has long been known that Langmuir's equation for monolayer adsorption is identical in form to the equilibrium expression for chemical reaction between quasi-perfect gases or quasi-ideal solutes. The Brunauer-Emmett-Teller equation for multilayer adsorption may be shown by factoring to have the same form as the equilibrium expression for a chemical reaction between the solvent and solute in a quasi-ideal solution in which each mole of solute, on the average, can react with one mole of solvent.

Factoring offers a simple and reasonable, but not very useful, method of adding a third parameter to the BET equation. Its chief use for surfaces is to enable a large scale picture even at high activities.

For liquid solutions the method gives a measure of the deviations from ideal solution laws, analogous to the activity coefficient or osmotic coefficient, which is especially adapted to the study of combination in quasi-ideal solutions without association. Association and electrostatic interaction are relatively unimportant in concentrated solutions.

For salt solutions in water, the hydration is much greater than mole per mole. The most important extensions are for different intrinsic constants for hydration of anion and of cation and for constants changing with the number of groups added, and next come the variations in activity coefficients with changing composition.

The Saturation Equation in Chemical Kinetics

W. H. Rodebush, *University of Illinois*

One can easily demonstrate that the typical adsorption isotherm, expressed mathematically in various forms, is only a special case of a much more general type of phenomenon which appears wherever molecular interactions occur. Olsen has applied the idea to the activity of strong electrolytes. The same idea turns up repeatedly in homogeneous catalyzed chemical reactions where a catalyst or inhibitor at first shows effects proportional to concentration and then gives diminishing returns. In the absence of a better term, the phenomenon may be described as saturation and so represented by a typical curve. Since "pure" uncatalyzed reactions are of academic interest chiefly, it is felt that this idea may be of considerable practical significance.

Factors Determining Solubility among Nonelectrolytes

Joel H. Hildebrand, *University of California*

The variety of factors that must be considered in interpreting solubility relations among nonelectrolytes will be illustrated by the solubilities and colors of iodine in solvents of various types. New, unpublished data obtained for this purpose will be considered, along with the extensive body of information available from previous work. The theory of regular solutions, with its formulations of the energy and entropy of mixing, will be applied to the violet, "regular" solutions, which represent over a thousandfold range in solubility, and the deviations therefrom which may result from dipole moments, hydrogen bonding, molecular shapes and sizes, or acid-base interaction will be discussed.

Cyanic Acid and the Allophanates

John R. Johnson and Louis L. Ferstandig
Cornell University

Studies have been made of the mechanism of the reaction of cyanic acid with alcohols to form esters of allophanic acid, $R-O-CONHCONH_2$. The evidence indicates that neither "dicyanic acid" nor the alkyl carbamate is an intermediate under the usual conditions for transforming alcohols into allophanates.

The mechanism of hydrolysis of allophanates in neutral, acidic, and basic media has been investigated. Allophanates of tertiary and allylic alcohols undergo hydrolysis

rapidly in neutral aqueous medium at 100° by a process involving cleavage of the alkyl-oxygen bond. Under alkaline hydrolytic conditions the alkyl-oxygen bond remains intact.

The allophanates are crystalline compounds particularly suited for characterization of tertiary alcohols.

Studies in Diagnostic Cinefluorography: Familiar Radiographic Views as Seen in Slow Motion

G. H. S. Ramsey, J. S. Watson, Jr., J. J. Thompson,
F. Dreisinger, R. T. Weinberg, and S. Weinberg
University of Rochester
(Introduced by Wallace O. Fenn)

Equipment designed and built in the Department of Radiology, University of Rochester, has been used to produce a cinematographic record of the shadows produced by x-rays on the fluorescent screen. A number of scenes have been incorporated in a film that will be shown. This film will serve to demonstrate the range of usefulness of this method of study in teaching, diagnosis, and research.

Production and Utilization of Plasma Proteins Studied with Radioactive Lysine

Leon L. Miller, *University of Rochester*
(Introduced by George H. Whipple)

DL-Lysine labeled with C^{14} in the epsilon position has been fed to normal dogs and the relative apparent rates of incorporation of the labeled amino acid in the various plasma protein fractions have been studied. The data indicate that the plasma globulin fraction is synthesized more rapidly than the plasma albumin. This conclusion is substantiated by experiments in which plasma proteins labeled with C^{14} were transfused into a normal recipient dog. Here the labeled globulin fraction disappears from the circulation faster than the labeled albumin fraction. These experiments permit estimates of the half-life of the plasma albumin and globulin fractions.

In vitro studies of surviving rat livers perfused with whole blood containing added DL-lysine- ϵ - C^{14} have yielded direct evidence of the hitherto presumed role of the liver in the production of plasma proteins.

Hemoglobin Synthesis and Turnover in Dogs Measured with Radioactive Lysine

Charles L. Yuile, *University of Rochester*
(Introduced by George H. Whipple)

Following the feeding of racemic lysine labeled with C^{14} to an essentially normal dog, about 70% of the total incorporation that occurred in hemoglobin in a 12-day period took place in the first three days. In an anemic and hypoproteinemic dog 80% of the maximum incorporation occurring over a period of 22 days took place in the first five days. These data suggest that the period of bone marrow maturation of the red cell during which its related hemoglobin is synthesized does not exceed three to five days. Evidence based on the rate of decrease of the C^{14} content of circulating blood cells over a prolonged period indicates an average life span of 115 days for the erythrocytic protein, which corresponds closely to estimates of the life span of dog erythrocytes by other methods. Fol-

lowing breakdown of blood erythrocytes, the protein comprising them is not used preferentially for the formation of new erythrocytes.

Solubilization and Separation of Components of the Heart Muscle Oxidase System

Elmer Stotz, *University of Rochester*
(Introduced by Wallace O. Fenn)

Cytochrome oxidase, cytochromes A, B, and C, and succinic dehydrogenase have long been recognized as having prime importance in the oxidative capacity of animal, bacterial, and probably of many plant cells. Heart muscle, because of its high content of these substances, has been a favorite tissue for study. Ground heart muscle can be extensively washed with water without removing these substances, although a weakly alkaline extraction with grinding yields a preparation of finely suspended insoluble particles containing all of the above components. Only cytochrome C, because of its exceptional stability toward acid, has been shaken loose from its combination with these particles and satisfactorily characterized. The other components remain attached, have been unsusceptible to the usual methods of protein purification, and are consequently ill-defined as chemical entities.

Following leads provided by studies of natural digestive processes, the heart muscle particle suspension has been dispersed by the addition of sodium cholate and subjected to the digestive action of several types of enzymes. After the action of some of these enzymes, the particles are so reduced in size that the cytochrome oxidase activity nearly all remains in solution upon centrifugation at 20,000 *G*. Furthermore, the digested preparation is then susceptible to a fairly sharp fractionation with ammonium sulfate. The oxidase has thus been purified several fold and is free of cytochrome C, but still contains cytochromes A and B and some succinic dehydrogenase.

Suitable modification of the above procedure has led to cytochrome A preparations with very low cytochrome oxidase activity. With the same starting material a soluble succinic dehydrogenase, highly concentrated and purified about 40 $\times$, has been obtained. With the various compounds brought into soluble form, the application of classical protein fractionation procedures may lead to further purification and separation of the components, whose interrelationships in oxidative metabolism may then be revealed.

The Phenomenon of Gel Formation by Isolated Cell Nuclei

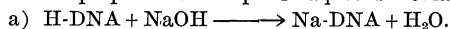
Alexander L. Dounce, *University of Rochester*
(Introduced by Wallace O. Fenn)

The formation of gels as the result of adding dilute ammonia or strong saline solutions to different types of isolated cell nuclei has been described previously. In this paper further observations are reported on gel formation by isolated nuclei, particularly those obtained by a modification of the technique of Behrens. It is shown that nuclei isolated from rat liver or rat tumor (Walker carcinoma 256) at pH 4.0, or lower, form a gel upon adding dilute ammonia or sodium hydroxide, whereas nuclei

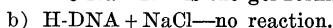
obtained from chicken erythrocytes at pH 6.8, as well as nuclei isolated from rat liver or tumor by the modified Behrens technique, yield a gel upon adding strong saline as well as dilute alkali.

It is assumed that the desoxyribonucleic acid of the nuclei is responsible for gel formation. The fundamental reactions involved are thought to be as follows:

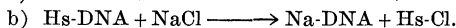
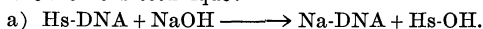
1. Nuclei prepared at low pH in aqueous media:



The Na-DNA is the gel-forming substance.



2. Nuclei prepared at pH 6.0 to 7.0 in aqueous media or by the Behrens technique:



Again the Na-DNA is the gel-forming substance.

In these equations, H-DNA stands for free desoxyribonucleic acid; Hs stands for histone, and Hs-DNA for the nucleohistone.

Nuclei prepared at pH 6.0 from normal rat liver by the use of very dilute citric acid do not form a gel, although they yield a highly polymerized, easily extractable sodium salt of desoxyribonucleic acid. The sodium salt of the desoxyribonucleic acid of nuclei capable of forming gels is, on the other hand, difficult or impossible to extract and it is thought that the latter type of nucleic acid represents a hitherto unrecognized "native" nucleic acid present in the intact cell, whereas desoxyribonucleic acid extracted even by mildest methods thus far available represents the product of some kind of intracellular autolysis or degradation.

A New Analytical Method for Adrenal Cortical Hormones

Robert B. Burton, Alejandro Zaffaroni, and
E. Henry Keutmann, *University of Rochester*
(Introduced by George H. Whipple)

An adaptation of the technique of paper partition chromatography, utilizing nonaqueous solvent systems, is the basis of a new method for analysis of adrenal cortical hormones. The procedure permits separation and identification of microgram quantities of the individual cortical hormones in mixtures of known compounds, and in urinary and adrenal extracts.

Evidence will be presented which indicates the presence of Kendall's Compound E and 17-hydroxycorticosterone in extracts of urine from normal individuals.

Estimation of Physical Fitness

Robert A. Bruce, Frank W. Lovejoy, Jr., Paul N. G. Yu,
Raymond Pearson, and Marion McDowell
University of Rochester
(Introduced by George H. Whipple)

A preliminary appraisal of the estimation of physical fitness from cardiorespiratory measurements during a standardized stress of exercise has been made in healthy normal subjects, as well as in patients with a variety of diseases, especially of the heart and lungs. The method involves a battery of simultaneous and continuous observations of ventilatory, respiratory, and circulatory per-

formance, including electrocardiographic changes, before, during, and after walking on a motor-driven treadmill at a moderate rate for a fixed period of time, or to the limits of tolerance. The duration of the walking effort times the average respiratory efficiency during exercise divided by the total pulse for the first three minutes of recovery equals the fitness index. This index shows a satisfactory correlation with clinical performance and symptomatic distress in ambulatory patients with disease. The spectrum of results ranges from complete and total disability in abnormals to better than average performance in normals. The limiting factors to physical fitness are chiefly circulatory; accessory studies in various patients provide further insight into these mechanisms.

The Work of Breathing

Wallace O. Fenn, Arthur B. Otis, and Hermann Rahn
University of Rochester

During breathing, the respiratory muscles do work in overcoming the elastic forces of the lungs and chest, viscous resistance of the air and tissues, turbulence of the moving air, and inertia. Measurements have been made to determine how the total work of breathing is subdivided among these various fractions. From such data, the respiratory apparatus can be described as a mechanical system. For any given minute volume of ventilation of the lungs this system has a frequency that is optimal (in the sense of minimal work), because if the frequency is too slow the elastic work becomes very great and if the frequency is too rapid much work is wasted in ventilating the dead space (air passages to the lung). Calculated optimal frequencies agree reasonably well with the frequencies observed in normal breathing. The theoretical maximal work that can be done by the respiratory muscles has been estimated on the basis of direct measurement of pressures that can be developed by the chest at various volumes and by calculation from anatomical data assuming that the respiratory muscles have properties similar to those of other skeletal muscles. Good agreement was obtained between the results of the two methods.

Hemolytic Anemia in Newborn Dogs Due to Absorption of Isoantibody from Breast Milk During the First Day of Life

Richard M. Christian, Donald M. Ervin, Scott N. Swisher, William A. O'Brien, and Lawrence E. Young
University of Rochester
(Introduced by George H. Whipple)

Four different antigenic factors have thus far been identified serologically in dog erythrocytes. One of these which may conveniently be called the "Do factor" appears to be somewhat analogous to the Rh factor of human red blood cells. Dogs lacking this factor in their red corpuscles are accordingly labeled "Do-negative" and those whose cells contain this factor are called "Do-positive."

Do-negative bitches that have been immunized by transfusions of Do-positive blood develop Do-antibodies that appear in high concentration in the colostrum after pregnancy and persist for several weeks in the breast milk. Experience with nine litters has shown that Do-positive

puppies regularly develop hemolytic anemia if they suckle such an immunized dam during the first day or two of life. The lack of antibody absorption from milk after the second day has not yet been explained. There is evidence that natural immunization of the dam by fetal red cell factors may occur during pregnancy, thus producing hemolytic disease in dogs similar to that recently discovered as a naturally occurring phenomenon in horses.

The Electronic Spectra of Sulfur Hexafluoride

A. B. F. Duncan, *Department of Chemistry,*
University of Rochester
(Introduced by W. A. Noyes, Jr.)

The electronic transitions of lowest energy in SF_6 were found to lie far in the vacuum ultraviolet region. The transition of lowest energy is at 1054 Å, and a few additional transitions were observed below a strong continuous absorption, which begins at about 815 Å.

A theory of the electronic energy levels has been developed, based on the method of molecular orbitals. The orbitals employed were linear combinations of fluorine and sulfur atomic orbitals, chosen with regard to the established octahedral symmetry of SF_6 . The relative energies of the orbitals are computed in terms of integrals over atomic orbitals of the Slater form. Use was made of the experimental S-F distance and relative electronegativities of the atoms, but no other experimental data were available. Probable transitions of lowest energy are predicted, with estimates of the corresponding intensities.

Vapor-Liquid Equilibria in Synthetic Rubber Latex-Monomer Systems

O. E. Dwyer, L. C. Liberatore,³ and W. A. Gleich⁴
Department of Chemical Engineering,
The University of Rochester
(Introduced by W. A. Noyes, Jr.)

Two systems were studied—styrene/latex and α -methyl styrene/latex. The styrene/latex system could be more completely described as the styrene-polymer-water system, since the latex was essentially an emulsion of soap-stabilized butadiene-styrene copolymer in an aqueous medium which was more than 99.9% water. Similarly, the AMS/latex system could be described as the AMS-polymer-water system, where the polymer is actually a copolymer of butadiene and α -methyl-styrene.

The chemical and colloidal natures of the systems were such that a static, rather than a dynamic, method of equilibrium measurement had to be used. Data were obtained over temperature ranges of 40–95°C for both systems, styrene-polymer ratios up to 0.17, and AMS-polymer ratios up to 0.30. The experimental data agree quite well with vapor-liquid equilibria calculated on the basis of theoretical considerations. During and since the war, considerable advances have been made in understanding the thermodynamic behavior of polymer-solvent systems. Experimental measurements, particularly swelling meas-

³ Present address: Taylor Instrument Co., Rochester, New York.

⁴ Present address: Shell Chemical Corporation, Houston, Texas.

urements, combined with statistical mechanical treatment, have led to expressions for entropy and enthalpy changes in solvent-polymer interaction.

Curariform Activity and Chemical Structures⁵

V. Boekelheide, *University of Rochester*

(Introduced by W. A. Noyes, Jr.)

The use of drugs having curariform activity in the treatment of certain spastic and hyperkinetic disorders has demonstrated the need for a satisfactory drug of this type. An investigation of certain synthetic and natural drugs has been undertaken in the hope of relating curariform activity to chemical structure.

The compounds, prepared for study as possible peripheral curariform agents, have included derivatives of piperidine, the tetrahydro- β and γ -carboline, quinolizidine, benzyltetrahydroisoquinoline, and indolylmethyltetrahydroisoquinoline. Of these the indolylmethyltetrahydroisoquinoline derivatives showed the highest activity, which is of interest in view of their possible relationship to the calabash curare alkaloids.

In regard to compounds causing muscular relaxation through a central effect, several interesting results were obtained. It was found that β -erythroidine, a peripheral agent, is converted by acid to a derivative, apo- β -erythroidine, which has a central action of long duration. It was also discovered that a group of compounds of rather simple structure, derivatives of 4-hydroxymethyl-1, 3-dioxolane, have high activity as central agents in effecting muscular relaxation.

The Formation and Structure of Some Vinyl-derived Polymers with Heterocyclic Rings

L. M. Minsk, *Eastman Kodak Company*

(Introduced by W. Albert Noyes, Jr.)

Two polymers containing heterocyclic rings derived by reaction upon preformed linear polymers will be discussed. Though purely synthetic in nature, these have certain physical properties found in naturally occurring materials. The method of preparation will be given and some proof of structure presented. The first of these polymers belongs to the family of ester-lactones and is derived from poly- α -chloroacrylic acid by reaction with an alcohol. It has certain of the physical properties of cellulose and cellulose esters, as well as a structure which in one particular respect is related to cellulose. The other is a highly imidized polyacrylamide, whose aqueous solutions will, under suitable conditions, yield thermally reversible gels. The general phenomenon of gelation, viewed from the behavior of this polymer, will be discussed.

Problems in the Experimental Study of Flash Burns

Herman E. Pearce, *University of Rochester*

(Introduced by Wallace O. Fenn)

The brief exposure to a high intensity of thermal energy causes a lesion called a "flash burn." This was first seen

at Pearl Harbor, but its importance was not fully appreciated until the study of the atomic bomb casualties at Nagasaki and Hiroshima; there were approximately 68,000 cases of burns at Hiroshima alone. This tremendous clinical problem needs further experimental study.

We have succeeded in creating the lesion both by igniting an inflammable substance and by using a large carbon arc with a shutter mechanism.

This discussion deals with the problems of devising suitable sources, of measuring the energy and spectrum they create, of calibrating the energy delivered, of analyzing the threshold of the energy and its spectral components in burn production, of determining the time-temperature relationships of these, and finally of comparing the flash burn with the ordinary low temperature burn from the standpoints of pathology, bacteriology, the systemic effects on protein and fluid changes, and mortality.

The Role of Glomerular Filtration Rate in the Pathogenesis of Edema

Robert F. Pitts, *Syracuse University*

(Introduced by Eugene F. DuBois)

About 20% of the weight of the body is extracellular fluid, i.e., a balanced salt solution which either circulates rapidly through the vascular system as the liquid blood plasma (about one-quarter of the total) or slowly through the tissue spaces between the cells as interstitial fluid (about three-quarters of the total). The fact that the weight of a normal individual remains constant from day to day despite wide fluctuations in the quantity of salt and water ingested is due to the fact that his kidneys excrete each day just enough of these components of the extracellular fluid to maintain balance. The capacity of the normal kidneys to compensate for fluctuations in intake is remarkable. In heart disease, in kidney disease, in liver disease, and, in truth, in all diseases characterized by weight gain due to fluid logging (storage of excess extracellular fluid as edema) the kidneys exhibit a reduced capacity to compensate for fluctuations in intake, especially of salt. Salt and water are retained and are stored in the highly elastic interstitial fluid compartment.

It is assumed that two disabilities of kidney function account for water and salt retention in edematous states: a deficient formation of a filtrate of the blood plasma in the glomerular tufts (the initial stage of urine formation) and excessive absorption of water and salt from that filtrate as it passes through the kidney tubules. Diuretics used clinically to promote the excretion of edema fluid act by partially blocking this latter tubular absorptive process. Although a few years ago the factor of reduced glomerular filtration was emphasized as a cause of edema, the tendency today is to emphasize tubular overabsorption and even to deny the significance of glomerular filtration.

In animals it is possible to vary glomerular filtration at will by constricting the blood supply to the kidneys and thus reducing the pressure head upon which filtration depends. When filtration is so reduced there is an immediate reduction in the excretion of salt and water. This disability is immediately reversible on removing the constricting clamp. The degree of reduction in filtration

⁵ Aided by a grant from the National Foundation for Infantile Paralysis.

rate necessary to produce this disturbance in salt and water excretion is no greater than that which is observed clinically in diseases characterized by edema. It has been observed clinically that in patients who have very low filtration rates, diuretics are relatively ineffective in promoting the excretion of salt and water. In animals, constriction of the renal blood supply reduces the effectiveness of diuretics very greatly. It is concluded that insofar as filtration rate is reduced in disease it will adversely affect the capacity of the kidneys to compensate for fluctuations in salt and water intake and will favor retention as edema. A reduction in filtration rate will also reduce the effectiveness of diuretic agents. It is admitted that reduced filtration rate is only one of several significant factors in fluid retention and resistance to diuretics.

Conference on the Ultracentrifuge

Duncan A. MacInnes

Rockefeller Institute for Medical Research

A group of 21 workers interested in the ultracentrifuge met under the auspices of the National Academy of Sciences for a three-day conference June 14-16, 1949, at the Ram's Head Inn, Shelter Island, Long Island. The program of discussion was arranged around the formula for interpreting ultracentrifuge results:

$$M = \frac{RTs}{D(1-PV)}$$

in which M is the molecular weight of, for instance, a protein, s is the sedimentation velocity, D the diffusion coefficient, V the partial specific volume, P the density of the solution, and R and T the gas constant and absolute temperature respectively.

The determination of s involves problems of centrifuge design. The use of magnetically supported and driven rotors was forecast, and, also, interference methods for following boundary movements.

Great progress was reported in the precision determination of diffusion coefficients, D , by widely differing methods.

The precision of the values of M is largely dependent upon the accuracy of the product, PV , which depends upon density measurements of solutions. A magnetic float method for this determination was reported, as was also a procedure for obtaining the temperature, T , of the rotor while turning at high speeds.

An outstanding result of the conference was the agreement that the trend of research will be away from high speeds, and toward a greater use of equilibrium, as against the sedimentation velocity, method. An important suggestion concerning the utilization of states approaching equilibrium in obtaining molecular weights was advanced.

Some Recent Approaches to the Experimental Study of Human Fatigue

Leonard Carmichael, John L. Kennedy,
and Leonard C. Mead, *Tufts College*

The paper briefly reviews some current definitions of fatigue from the standpoint of physiology and psychology. Experimental studies are then reported on the measurement of performance (primarily visual or motor) under

various conditions of stress and prolonged work. Among the conditions studied were the following: (1) eye movement and reading accomplishment during six hours of continuous reading; (2) performance of tasks requiring stereoscopic vision, eye-hand tracking, and "lookout" performance, all during three-day period of work with only brief and irregular rest periods; (3) eye movements, various visual tasks, reaction time, steadiness, and certain psychological processes in subjects who worked for fifty hours without sleep; (4) the effect of a three-day sleep deficit on performance in a complex task requiring continuous and simultaneous coordination of several sensorimotor operations.

A generalization which pertains to all the experimental results in the experiments outlined above is that the subjective indices of fatigue are dependent upon the motivation of the individual being studied. This motivation or eagerness or willingness to continue to exert oneself is not a continuous function of the duration of work. Rather, the experiments indicate the presence of high motivation at any stage during the long continued performance of a task will allow the behavior under observation to appear in an essentially unchanged form from that recorded when the subject is "unfatigued."

An electronic apparatus has been developed in an attempt to measure a physiological variable (muscle spike output from the supraorbital musculature) which shows promise as an indicator of the general alertness of subjects while performing tasks during long periods of time. It is tentatively suggested that the early stages of certain states of fatigue in monotonous work may be identified in terms of alterations in the integrated electrical output of muscle spikes from localized muscle areas. There is some evidence that the fluctuations or periodicity noted in this electrical output have a psychological correlate in the temporary blocks in "mental" or physical work which have been observed in our own experiments and in recent experiments by other investigators.

A Hypothesis Regarding the Origin of the Movements of the Earth's Crust

Harold C. Urey

Institute for Nuclear Studies, University of Chicago

If it is assumed that the radioactive content of the core and mantle of the earth are respectively equal to the radioactive content of the iron and stone meteorites, it is found that the earth must be getting warmer. It is assumed therefore that this is the case, that the earth was formed in a cold condition, and that to a first approximation it was a uniform mixture of iron and stony phases throughout, with a possible modification at the center to be mentioned later. Rough calculations show that the gravitational energy stored which would be dissipated in the formation of the present core of the earth is greater than the radioactive heat that has been generated in 2 billion years from all radioactive materials. Kuhn and Rittman have shown that iron droplets cannot sink in the present mantle of the earth because of its high viscosity, but it is maintained here that the iron flows to the center of the earth through channels due to the wetting of some constituent of the stony phase by the iron phase. The

falling of the iron through the mantle generates a large amount of heat, and if there is a sharp layer some distance below the crust of the earth, perhaps at the Rapetti discontinuity, high temperature silicate phase is generated at depth. This leads to convection in the outer mantle of the earth and the formation of mountains, as has been postulated by Griggs. The forces are adequate to account for the formation of mountains and roughly the time of convection estimated is approximately that required by geological evidence, being somewhat too rapid, using a viscosity of 10^{23} poise for the outer earth.

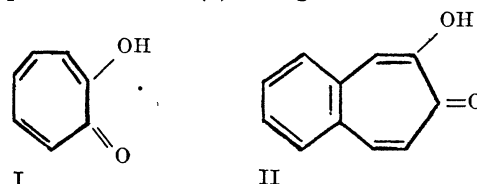
The chemical differentiation in the crust can be explained as separation of olivene from other constituents by sinking in a molten magma at a temperature in the neighborhood of $1500-1600^{\circ}\text{A}$. This temperature also is appropriate for explaining the constituents of the atmospheres of Mars, Venus, and the earth on the basis of chemical reactions taking place at this temperature and below. The difference in density of the moon and the earth may be explained if low density material condensed first and higher density material (iron) later. This hypothesis leads to an initial structure of the earth with a core of moon-like material surrounded by a layer of silicate and iron phase. If this central core remained at the center of the earth for some time, then on rising to the surface it should have produced the Pacific Basin, with its floor of basaltic rock. It is interesting to speculate upon what time in the earth's geological history this may have occurred.

Studies on the Structure of Colchicine⁶

D. S. Tarbell, *Department of Chemistry,
University of Rochester*

(Introduced by W. A. Noyes, Jr.)

The alkaloid colchicine is of biological interest because of its antimitotic action, but its chemical structure is not completely elucidated. Evidence will be presented to support the suggestion of Dewar that colchicine contains the "tropolone" structure (I) in ring C. This evidence



is based on periodic acid oxidation of hexahydrocolchicine, and on the study of infrared absorption spectra of colchicine derivatives and other compounds known to contain the tropolone ring. The synthesis of simpler compounds containing the tropolone ring has been studied, and a compound believed to be benzotropolone (II) has been obtained by condensation of hydroxyacetone with phthalaldehyde; a by-product in this condensation has been proved to be phthiocol (2-hydroxy-3-methyl-1,4-naphthoquinone). The chemical behavior of II will be discussed in relation to that of the colchicine series.

⁶ Aided by a grant from the National Institutes of Health.

TECHNICAL PAPERS

General Method for Paper Chromatographic Analysis of Reducing and Nonreducing Carbohydrates and Derivatives

E. Pacsu, T. P. Mora, and P. W. Kent

*Frick Chemical Laboratory, Princeton University,
Princeton, New Jersey*

The paper chromatographic procedure for the investigation of reducing sugars (3, 4) or their methylated derivatives (1, 2) depends for its success on the ease with which the substances under test will reduce certain inorganic ions at elevated temperatures. It has been found that not all ketosugars or disaccharides will bring about reduction. Efforts have been made to find a more general method of developing chromatograms in order to detect these nonreducing substances. It was proposed by Partridge (4) that acidic naphthoresorcinol could be used to detect such carbohydrates. In the course of investigation in this laboratory of complex mixtures of these substances, we have found the use of acidic reagents and of excessive drying undesirable. Experiment showed

that excellent results can be obtained by developing the chromatograms with aqueous potassium permanganate (1%) containing sodium carbonate (2%). The chromatograms were removed from the chamber and dried at room temperature, or rapidly at 100°C . By spraying with the permanganate reagent, the bands appeared, with varying rapidity, as striking yellow zones on purple background, even at room temperature. In a short time, as the chromatograms dried, the spots took up their final color as gray regions on a brown background. In view of this change of color, it was expedient to mark the position of each band as soon as it was developed.

Using the partitioning solvents as specified by Partridge (3, 4)—viz., butanol (40%), ethanol (10%), water (50%)—it was possible to separate sugar alcohols, glycosides, and reducing and nonreducing sugars. Attempts to separate acetylated or partly methylated sugars using this modified procedure were not successful, since these substances did not readily reduce permanganate.

In an attempt to obtain a better separation of trisaccharides and the higher sugars, the usual solvent mixture was reversed, i.e., the aqueous layer was used as the eluting solvent in place of the usual butanol layer. Some separation was indeed obtained, but this was ac-