

Comments and Communications

Sulfur in Ether Extracts of Lake Sediments

DURING a study of the carotenoids of mud from Linsley Pond, Conn., a relatively large amount of a crystalline substance was encountered in an ether extract. In order to get a sufficient amount of the material for analysis, 245 g of mud was dried at 75° C for 24 hr and then exhaustively extracted with diethyl ether. The crystals separated when the ether was cooled and concentrated over a stream of nitrogen. The yield of once-recrystallized material was 2.70 g, mp 119°–120° C. The sample was twice recrystallized from ether, with a final yield of 1.54 g of monoclinic crystals, melting point unchanged. A fraction was sent to Carl Tiedeke for analysis. The results were as follows: C: 0.00%, 0.00%; H: 0.00%, 0.00%; mol wt: 35, 28; 33, 32. Subsequent separation of the rhombic form, together with the above data, was sufficient to characterize the material as sulfur. Sulfur formed 1.1% of the dry weight of the mud. Total ether-extractable substances formed 2.1% of the dry weight of the mud, hence more than half the ether extract consisted of elementary sulfur.

The occurrence of sulfur in lake sediments is of interest, since some limnologists have interpreted ether and benzene extracts in terms of lipids only. The behavior of sulfur resembles lipids in that it leaves no ash on ignition, is insoluble in water, and is soluble in such solvents as ether, chloroform, and benzene. Unless supplemented by analysis for sulfur or organic carbon, such extracts will have at least a dual meaning and must be cautiously interpreted. This work forms part of a program supported by National Science Foundation Grant G-14 given to G. Evelyn Hutchinson.

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Use of Propositions in Examinations for the Doctor's Degree

DURING the past seventeen years the final examination for the doctor's degree for students majoring in chemistry at the California Institute of Technology has consisted in part of the oral defense, by the candidate, of a set of propositions prepared by him and submitted to the examiners two weeks before the day of the examination. It is the opinion of members of the staff of the Division of Chemistry and Chemical Engineering, after these years of experience, that the use of propositions contributes significantly to the effectiveness of the examination, as well as to the interest of the examiners.

In 1935 the members of our staff, after participation in several scores of doctor's examinations during the preceding fifteen years, had become bored by them. The thought occurred to me that the system of propositions (*stellingen*) that has been used in examinations

for the doctor's degree in the universities of Holland for hundreds of years might be introduced. One of my students, David Harker, agreed to prepare a set of propositions in order that a trial of the proposal might be made. His oral examination for the degree of Doctor of Philosophy in chemistry, with a minor in mathematics, which was carried out with the use of propositions on May 31, 1935, was much more interesting to the examiners, and apparently to the men being examined, than most of the earlier examinations had been. The members of the committee were also of the opinion that it provided a better test of the candidate than was provided by examinations of the sort previously given, in which the candidate was asked questions arbitrarily formulated by members of the examining committee. The decision was accordingly made that all candidates for the doctor's degree in chemistry should thereafter prepare propositions.

Dr. Harker introduced the system at the Johns Hopkins University when he was appointed a member of the staff there, and it is now in use in several other universities, including Princeton, the University of California, the University of Southern California, and Columbia. In some institutions (University of California and Division of the Geological Sciences at the California Institute of Technology) propositions are used in connection with the examination for admission to candidacy for the doctor's degree, rather than in the final examination.

The nature of the system may be indicated by the regulation in the Division of Chemistry and Chemical Engineering of the California Institute of Technology, which reads as follows:

5. The final examination will consist in part of the candidate's oral presentation of a brief résumé of his research and its defense against attack, and in part of the defense of a set of propositions prepared by the candidate. The candidate may also expect questions related to his minor subject.

The propositions should be about ten in number, of which about four should relate to the minor subject and to general branches of chemistry, and about six to the branch of chemistry of major interest to the candidate, including his research.

For students in chemical engineering about three propositions should relate to the minor subject, two to chemistry if this is not the minor subject or to mechanical engineering if chemistry is the minor subject, and about five to chemical engineering. The candidate may also include propositions not relating to his major and minor fields.

The propositions, prepared by the candidate himself, should display his originality, breadth of interest, and soundness of training; the candidate will be judged on his selection and formulation of the propositions as well as on his defense of them. It is recommended that the candidate begin the formulation of his set of propositions early in his course of graduate study.

Two copies of the set of propositions in final form must be submitted to the Division of Chemistry and Chemical

Engineering at least two weeks before the date set for the examination. A copy of the set of propositions must be submitted to the Dean of Graduate Studies as a part of each of the two copies of the thesis.

Some idea of the nature of the propositions themselves may be given by the presentation of representative examples. The set of propositions prepared by David Harker in 1935, on short notice, follows:

At the time of his oral examination for the degree of Doctor of Philosophy, David Harker will defend the following Propositions:—

1. Cadmium iodide can crystallize in either the structure proposed by Bozorth (*J.A.C.S.* 44, 2232 [1922]) or that proposed by Hassel (*Zeit. Krist.* 22, 333 [1933]).

2. The radial parts of the solutions of Schrödinger's equation for the isotropic three-dimensional harmonic oscillator, separated in spherical coordinates, are given by

$$R_{n,l}(x) = N e^{-\frac{x}{2}} Z^{\frac{l}{2}} \frac{d^{l+1}}{dx^{l+1}} [H_{n+l+z}(Z^{1/2})]$$

where $z = \frac{4\pi^2\mu_0 m}{h^2} r^2$, $n+l$ is always even, and N is a normalizing factor.

3. The series $\sum \frac{1}{h^2} \cos 2\pi \mathbf{r} \cdot \mathbf{h}$ is convergent if $\mathbf{r} \cdot \mathbf{h}$ is not an integer.

4. The number of spots on a Laue photograph within a given distance of the central image is independent of the orientation of the crystal and proportional to the volume of the primitive unit cell, under a given set of experimental conditions.

5. The use of the "spring-reservoir" in the definition of entropy is to be preferred to use of the Carnot cycle.

6. The anomalous crystal structures of the metals zinc, cadmium, and mercury can be explained on the basis of a tendency toward covalent bond formation.

7. The structure of the tri-iodide ion given by R. C. L. Mooney (*Zeit. Krist.* 90, 143 [1935]) must be incorrect. This error is probably due to the neglect of the ammonium ions in evaluating the iodine parameters for the crystal NH_4I_3 .

8. The behavior of the vapor pressure of hydrofluoric acid from its solutions in benzene can be explained on the basis of association of gaseous hydrofluoric acid to H_nF_n without the use of the very special assumptions used by J. H. Simons (*Chem. Rev.* 8, 213 [1931]).

9. A device for indexing oscillation and rotation X-ray photographs of crystals, consisting of a projection of the propagation sphere on a plane, has points of superiority over the method of the Bernal diagram.

10. The proof, given by Bochner (*Vorlesungen über Fouriersche Integral*) that every fraction that has an absolutely integrable derivative in an interval has limited fluctuations in that interval, is very elegant.

Examples of other propositions that have been given by candidates recently are the following:

I predict that a determination of the temperature coefficient of solubility of benzene in 0.2 *N* aqueous silver nitrate solution would reveal that there is a reversal in the sign of the coefficient somewhere between 10° and 70° C.

The pure L isomer of *sec*-butyl alcohol might be prepared by reduction with Raney aluminum-nickel alloy of L-erythro-3-chloro-2-butanol, which is obtainable from the available compound D-2,3-butanediol.

The measurement of Soret coefficients is notable for the lack of agreement among various observers. It is

likely that the disagreement arises from failure to suppress convection currents completely. I propose that thermal diffusion cells be constructed using a porous diaphragm between two thermostated reservoirs. The pores of the diaphragm can be small enough that convection is negligible. The solutions should be circulated within each reservoir.

It is proposed that electrophoretic mobilities calculated by the method of Longworth and MacInnes are in error, because no correction is applied by these authors for the volume change on the closed side of the cell resulting from the net transference of water due to the difference in hydration of the anions and cations which are transferred.

The Hammick reaction has hitherto been applied to aldehydes and ketones only. I propose attempts to apply it to esters and nitriles, as a new alcohol and ketone synthesis, respectively.

The heterogeneity of sensitized red blood cells toward hemolysis by antisera may be explained on the basis of rapid irreversible random combination of hemolysin with a homogeneous red cell population.

Ethers have been used almost exclusively for the extraction of complex metal acids (for example, $\text{HF} \cdot \text{FeCl}_4$) from aqueous solution. It is suggested that benzotrifluoride ($\text{CF}_3\text{C}_6\text{H}_5$), trifluoromethyl-cyclohexane ($\text{CF}_3\text{C}_6\text{H}_{11}$) or other fluorinated compounds be substituted for ethers.

A method for the determination of microquantities of water might be developed by using a modified Karl Fischer reagent and electrolytically generated iodine.

In his book *The Optical Principles of the Diffraction of X-Rays*, R. W. James states that the formula for the total intensity of the X-rays scattered by a molecular liquid, first derived by Menke, can be applied without regard to the partial ordering of adjacent molecules. This does not seem to be correct.

The apparently normal heat of hydrogenation of hydrogenene need not be regarded as contradictory to the thesis of Sidgwick and Springall that in this compound the benzene system is considerably perturbed by the Mills-Nixon effect.

The difficult task of indexing the lines on X-ray powder photographs would be considerably easier if the degeneracy of the lines were known. It should be possible to determine the degeneracy in many cases from the density of grains in the powder lines on a photograph taken of a closely ground sample.

The calculation by Penney and Sutherland of the valence angle of ozone is incorrect, and the conclusions which they drew therefrom as to the correct assignment of the fundamental vibration frequencies are not valid.

An interesting program of investigation would be the experimental study of low-temperature transitions in solids, using an automatically regulated adiabatic calorimeter. A design for the regulator is proposed.

The methods used for developing critical habits of thought in undergraduates at the California Institute of Technology can be improved.

The nature of scientific research is now such that a graduate student ordinarily has little opportunity to show his originality. Many fields of research require the use of large and expensive pieces of apparatus, which could not be designed and constructed by a single student. Most research problems require so much effort—extending over two or three years—that a student can tackle only one problem in his work for the doctor's degree, and very often the problem on

which he works has in fact been suggested by the faculty member under whose direction he is carrying on the work. The formulation of a set of propositions provides him with an opportunity for expressing his originality; a proposition may give the result of a small original investigation that the student has carried out, or may be a proposal that an investigation be carried out. The system of propositions in doctor's examinations may have its greatest value in encouraging originality in young scientists and in serving as a test of their originality.

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Isolation of *Salmonella schwarzengrund* from Turkey Poults

IN MARCH 1952, nine-day-old turkey poults from a farm in southern Indiana were submitted to the Diagnostic Laboratory. The poults showed a severe diarrhea and protruding vents. Internally there were

no observable lesions except a mild enteritis. The mortality in the group of 13,000 turkeys by weeks was as follows: 217, 327, 117, 93, 28, 14, 14, 14, 12, 14 up to and including the tenth week. These poults had been purchased from a hatchery in Michigan, which had obtained the turkey hatching eggs from breeders in California and Oregon.

A gram-negative organism isolated from the livers of the affected turkeys was identified by R. P. Edwards, of the Enteric Bacteriological Laboratories, of Chamblee, Ga., as *Salmonella schwarzengrund* I, IV, XII: d: 1, 7. Unlike the original of this organism identified by Kauffmann (1), the organism isolated in this case did not have XXVII antigenic factor in the O formula. This is believed to be the first isolation on this continent and the second recorded isolation of *Salmonella schwarzengrund*.

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Reference

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Book Reviews

Chemical Physiology of Endoparasitic Animals.

Theodor von Brand. New York: Academic Press, 1952. 339 pp. \$7.50.

The publication of this book will come as a welcome addition to the libraries of parasitologists and others who are interested in the more dynamic aspects of the biology of endoparasites. Professor von Brand has undertaken the problems of synthesis and integration of the accumulated information concerning parasite physiology with the authority of one who has seen the growth of this information, from the beginning of the modern period of accurate observation, and has contributed importantly to this growth. Those familiar with his work will recognize the excellent organization and the readable style of writing that have characterized his earlier efforts.

The book is divided into three main sections. The first of these is devoted to discussions of the chemical composition of endoparasites, wherein the author tells of the various organic and inorganic molecules, the vitamins, enzymes, and other structural and functional entities that are to be found within the protoplasmic make-up of many different parasites. The second section is an impressive presentation of the information that has accumulated in the subjects of intermediary metabolism, respiration, and nutrition of many diverse forms of parasitic life. In this section especially, the author has assumed that the reader will have a genuine interest in the context and will not be content to accept without question a superficial

account of parasite metabolism. He wisely presents the material in such a way that the student can make a critical analysis of the situation existing in regard to any one of the many aspects of parasite metabolism that have been investigated. Frequent reference is made to the original literature. The final section is devoted to a most interesting account of the physiological aspects of host-parasite relationships in which nutritional, metabolic, and hormonal factors are explored and the subject of chemotherapy is discussed. This section is well done and is noteworthy in that it creates within the reader a true insight into the intricate manner by which parasites and their hosts are physiologically interrelated. Included in this section are the results of some of the recent investigations involving the endocrine glands.

The author has recognized that controversy exists in many areas and has presented his material in such a manner that the reader is encouraged to consult the original literature. To this end he has compiled and included the most complete bibliography that has appeared in the field of experimental parasitology. This extensive citation of literature will be of particular value to the parasitologist who is not too well acquainted with the rapidly expanding work in parasite physiology and also to the student who is endeavoring to build up a bibliography in this field. The author has made frequent use of tables and charts. These are very clear and concise and where possible include the source of the material given. A feature of the book that may be especially helpful to those