

A solution of the purple substance exhibits a simple infrared spectrum with a broad band from 8.5 to 11.0 μ possessing two poorly resolved peaks at 9.4 and 9.95 μ , respectively. One other weak band centered at 13.05 μ is observed.

Dodecaboron undecachloride, $B_{12}Cl_{11}$, is a deep red crystalline solid which sublimes *in vacuo* at 100° and melts with little apparent decomposition at 115 \pm 1°. The formula was established by elemental analysis: *Anal.* Found with a 99.1% material balance: B, 24.7; Cl, 74.4; Cl/B, 0.918; calculated for $B_{12}Cl_{11}$: B, 24.9; Cl, 75.1; Cl/B, 0.916, and by molecular weight determinations using the isopiestic method. Found: 523 \pm 12; calculated for $B_{12}Cl_{11}$: 520.1.

In cyclopentane the red subchloride exhibits a single broad paramagnetic resonance at a g value of 2.011 with a breadth of 25 gauss between points of extreme slope. Unlike the purple subchloride, no hyperfine splittings could be observed in this case although various attempts were made using the spectrometer at high resolution with the probe at low temperatures.

The infrared spectrum of a similar solution exhibited a band from 8.75 to 10.7 μ with a peak at 9.85 μ . A sharp peak at 11.02 μ also was observed. The latter is a characteristic absorption of the B_2Cl_4 group in B_2Cl_4 .²

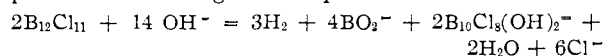
The red subchloride, $B_{12}Cl_{11}$, absorbs in the visible and ultraviolet regions of the spectrum with a broad strong band centered at 420 $m\mu$ and a weak band at 310 $m\mu$.

The strong infrared band in the region of 9.3 to 10.0 μ common to both of the new radical species appears to be characteristic of boron cage structures since similar absorptions have been reported for $B_{10}H_{10}^-$, $B_{12}H_{12}^-$,³ $B_{10}Cl_{10}^-$ and $B_{12}Cl_{12}^-$.⁴

(2) M. J. Linevsky, E. R. Shull, D. E. Mann and T. Wartik, *J. Am. Chem. Soc.*, **75**, 3287 (1953).

We also have observed a similar band in the case of the simpler boron cage in B_4Cl_4 .

Acidic hydrolysis of $B_{12}Cl_{11}$ occurs slowly even at 80° with the reaction virtually ceasing when 9.5 moles of hydrogen have been evolved per mole of initial $B_{12}Cl_{11}$. In basic solution hydrolysis proceeds according to the equation



Ions similar to $B_{10}Cl_8(OH)_2^-$ already have been reported.⁵

Potassium and tetramethylammonium salts can be precipitated from the alkaline hydrolysis solution. The infrared spectra of these indicate retention of the cage structures.

Treatment of $B_{12}Cl_{11}$ in cyclopentane with an excess of trimethylamine results in a complete discharge of the red color with the formation of the 2:1 complex, $[B_{12}Cl_{11} \cdot 2N(CH_3)_3]_n$. In this case also an infrared spectrum characteristic of cage compounds is obtained.

The new radical species are unusual in that the boron cage resonance forms probably contribute to their stability.

Further characterization of the purple species is being undertaken. Similarly, an investigation of the clear yellow crystalline solid is underway since in many of its reactions free radicals of limited stability can be observed.

(3) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **82**, 3228 (1960).

(4) E. L. Muettterties, R. E. Merrifield, H. C. Müller, W. H. Knoth and J. R. Downing, private communication.

(5) W. H. Knoth, H. C. Müller, D. C. England, G. W. Parshall and E. L. Muettterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

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RECEIVED MAY 2, 1962

BOOK REVIEWS

Polyelectrolyte Solutions. A Theoretical Introduction. By STUART A. RICE, University of Chicago, and MITSURU NAGASAWA, Nagoya University. With a contribution by HERBERT MORAWETZ, Polytechnic Institute of Brooklyn. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1961. xv + 568 pp. 16 \times 23.5 cm. Price, \$16.50.

Polyelectrolytes have, during the last decade or so, become one of the most active and fruitful fields of research in physical chemistry, as a consequence of advances in two superficially unrelated fields, synthetic polymers and biochemistry. Pioneer work by Kern, A. Katchalsky and Fuoss on synthetic polymers which were designed to be simultaneously polymers and electrolytes gradually built up a store of descriptive information about these hybrid substances, from which a qualitatively useful molecular model was deduced. The polyelectrolytic nature of many biochemical substances was then recognized, and naturally occurring compounds such as nucleic acids and proteins began to be investigated as polyelectrolytes. Furthermore,

E. Kachalski, Doty and others commenced the deliberate synthesis of polyelectrolytes which were designed to be chemical as well as electrochemical models of natural substances. Meantime, attempts were made to construct a theory which would correlate the observed macroscopic properties of polyelectrolytes with molecular parameters. The difficulty the theoretician faced was in the working model to use as his starting point: if it were made simple enough to be amenable to mathematical treatment, it departed too far from reality; if it were made elaborate enough to realistically describe all the details of behavior which one would like to account for, it became too complicated for mathematical analysis.

Rice and Nagasawa have summarized in this first book to appear on polyelectrolytes the various theoretical approaches to the problem, together with sufficient experimental examples to show how far the theory in its present state of development can go in accounting for observations. The development is presented in logical sequence, so that a graduate student with a firm background of thermody-

namics, statistical mechanics and advanced calculus can follow the arguments, and use the book as an introduction to research in polyelectrolytes, which was the authors' stated purpose for the book. Considering the intended reader, the book begins with a review of the statistical mechanical treatment of general solutions and of the equilibrium properties of simple electrolytes before proceeding to polyelectrolytes. Then rigid polyelectrolytes (exemplified by many inorganic colloids) are treated. In Chapter 5 (by Morawetz), the goal is finally reached: the flexible charged polymer is brought on stage, and becomes the center of interest from there on. Chapters 6 and 7 present the current theory of polyelectrolytes, much of the material based on work of one of the authors. The last four chapters then apply the theoretical treatment to reversible and dissipative processes in solutions of polyelectrolytes; these are the chapters which will be especially useful both to the graduate student and also to the experienced researcher in biochemistry who realizes the necessity of considering most of the substances with which he works as both natural products of biochemical importance and as members of a special category of compounds for which the theoretical chemist and the physical chemist have established a general pattern of properties and behavior. Finally, the book is recommended to the research worker in polyelectrolytes as a convenient and well organized reference source for much of the material which previously was only available in a multitude of articles scattered through many journals in the library, or many reprints in his files.

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Die Elektronenspektren in der Theoretischen Chemie.
By CAMILLE SANDORFY. Übersetzt und Bearbeitet von H. v. HIRSCHHAUSEN. Verlag Chemie, G.m.b.H., Pappelallee 3, Weinheim/Bergstr., Germany. 1961. x + 207 pp. 14.5 × 21.5 cm. Price, DM. 28.--.

This book is a translation into German of a book in French by the same author, entitled "Les Spectres Électroniques en Chimie Théorique" (Paris, Éditions de la Revue d'optique théorique et instrumentale, 1959). Added in this edition have been a number of examples, a few new references, and a useful listing of quantum-theoretical calculations by molecule and method.

The main topic discussed is the quantum theory of the visible and ultraviolet spectra of organic molecules. The author wanted not so much to cover the literature in this field as to introduce his readers to it by working through illustrations of the various methods. He well presents in this way the valence bond method, the simple molecular orbital method, the method of antisymmetrized products of molecular orbitals (erroneously called the method of antisymmetric molecular orbitals), and the method of free electrons, as these methods were practiced in about 1950. According to the reviewer's count, the more than 300 references cited fall as follows, year by year, beginning with 1930: 4, 6, 4, 13, 9, 9, 9, 8, 14, 6, 5, 11, 6, 4, 5, 8, 19, 18, 30, 22, 17, 14, 12, 4, 13, 6, 1, 4, 4, 4, 1. The recent book by Daudel, Lefebvre and Moser, "Quantum Chemistry" (Interscience Publishers Inc., New York, N. Y., 1959) provides a better introduction to the current literature in, and the current understanding of, this branch of theoretical chemistry.

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Protein Structure. By HAROLD A. SCHERAGA, Department of Chemistry, Cornell University, Ithaca, New York. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. xiv + 305 pp. 16 × 23.5 cm. Price, \$8.00.

This book is based on a series of lectures given by Professor Scheraga in Melbourne, Australia, in December, 1959. The author has extended the notes of his original lectures in such a way as to make the treatment of most of the subjects that are included quite complete and informative. Dr. Scheraga states in his preface that he planned the presentation so that

the material could be managed by students not previously exposed to formal physical chemistry beyond the elementary level. There is some question in this reviewer's mind whether this aim has indeed been achieved. A number of his theoretical treatments, particularly those dealing with denaturation, and with the hydrodynamic and elastic properties of proteins and protein fibers do require, if not formal background in physical biochemistry, at least some of the sophistication that only a particular variety of protein chemist is likely to have. On the other hand, bright students with a natural talent for physical chemistry and mathematics should find the subject matter straight forward and provocative.

The title of the volume, "Protein Structure," is, in my opinion, slightly misleading since what is presented is a discussion of proteins as visualized and studied by the author and his colleagues. Scheraga has been intimately involved, experimentally and theoretically, with all of the subjects he discusses in his book. His competency in the physical aspects of protein chemistry makes it possible for him to write with authority. The theoretical approach taken, however, occasionally involves assumptions that would not be universally accepted by all experts in the field. For example, although it is clear from the work of Kendrew and his colleagues that a variety of non-covalent interactions can and do exist in a globular protein (myoglobin), it is perhaps premature to develop sets of thermodynamic equations governing some of these interactions before their presence in the proteins under consideration has been demonstrated in an unequivocal fashion. However, even these sections of the book serve as a useful didactic treatment for students who hope to achieve facility in the construction and analysis of physicochemical models for the behavior and properties of proteins in solution.

The volume is supplied with an excellent collection of references. It can be quite sincerely recommended to students of protein chemistry who wish to become thoroughly familiar with one of the active approaches to the subject.

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Gas Chromatography. By D. AMBROSE, Ph.D., F.R.I.C., and BARBARA A. AMBROSE, B.Sc. George Newnes Limited, Tower House, Southampton Street, London, W.C. 2, England. 1961. vii + 220 pp. 14 × 22 cm. Price, 40s.

Several years ago, anyone could learn all there was to know about gas chromatography by reading a handful of papers. Now, with over one thousand papers appearing annually, it is impossible even to read the titles of them all. It is clear that a chemist wishing to use this technique intelligently needs a compact source of information on the theory, practice and present state of the art. Ambrose fills the need for a wide survey which will enable the technologist to construct an apparatus and use it wisely. The book provides a basic introduction but does not attempt to carry through to the fine points of theory which are in the current literature. To this extent the authors have succeeded in producing the best introduction now available.

The apparatus is described in detail with emphasis on home-made equipment. There is a comprehensive treatment of retention parameters and their value to the analyst. The theoretical plate concept is treated adequately, but very little on the rate theory of van Deemter and others is given. Qualitative and quantitative analysis are clearly described. Numerous key references to the literature are given, some as late as 1961. For the most part, however, the book represents the state of the art as it existed in 1959, and much of the material is from the 1956 London Symposium.

This reviewer would have suggested more emphasis on recent developments at the expense of detailed instructions on how to build and understand a thermal conductivity detector (20 pp.). For example, the rate theory approach is discussed in only six pages; only the abbreviated version of the van Deemter equation is given, and no discussion of recent modifications leading to optimizing speed. Capillary columns are discussed in two pages and programmed heating in one page, which is far less than these two important topics occupied in two similar books appearing in 1959. In other