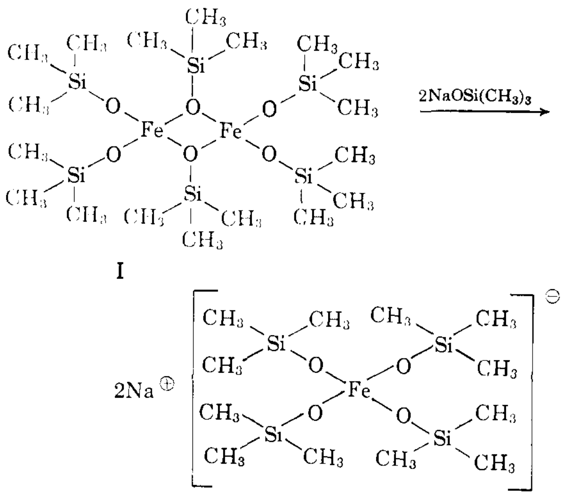
anion are precipitated. Calcd. for $Na[Fe(OSiMe_3)_4]$: Na, 5.28; Fe, 12.82. Found: Na, 5.47; Fe, 13.20. Calcd. for $K[Fe(OSiMe_3)_4]$: K, 8.66; Fe, 12.37. Found: K, 8.71; Fe, 12.51.

Not melting up to more than 200° and insoluble in organic solvents these "heterosiliconates" are typical salt-like substances. The infrared spectra of the sodium and potassium salt (in Nujol mull) show a new and characteristic [ν Si–O–Fe]- band at 11.05 and 10.92 μ, respectively. All the bands of the spectra are almost independent of the cation and exhibit the existence of a discrete $[Fe(OSiMe_3)_4^-]$ anion, as proposed in formula II.

The compounds I and the anion II again[1,4,5] are examples for a class of "complex silicones," which give evidence that the siloxy group, in spite of its strong $d\pi p\pi$ bond character between silicon and oxygen is able to act as a mono- and divalent ligand to form stable complex compounds. The preparation, properties, n.m.r. and infrared investigations of analogous alumino- and gallo-siliconate anions will be reported elsewhere.[5]



I

II

INSTITUT FÜR ANORGANISCHE CHEMIE
DER UNIVERSITÄT MARBURG
355 MARBURG/LAHN
GUTENBERGSTR. 18, GERMANY

HUBERT SCHMIDBAUR
MAX SCHMIDT

RECEIVED JUNE 25, 1962

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(4) H. Schmidbaur and M. Schmidt, *J. Am. Chem. Soc.*, **84**, 1069 (1962).

(5) H. Schmidbaur and M. Schmidt, *Angew. Chem.*, **74**, 589 (1962).

BOOK REVIEWS

Notes on Molecular Orbital Calculations. By JOHN D. ROBERTS, Professor of Organic Chemistry, California Institute of Technology. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1961. ix + 156 pp. 15 × 23 cm. Price, $4.95.

This small book very effectively shows how the organic chemist can use Hückel LCAO molecular orbital theory in its simplest form to obtain values of bond orders, atomic charges, free-valence indexes, and other quantities and conclusions of importance to him. Numerous exercises give opportunity for helpful practice in the application of methods and rules.

The chapters are entitled "Atomic Orbital Models" (22 pages), "Molecular Orbital Calculations. Electronic Energy Levels" (30 pages), "Bond Orders, Free-Valence Indexes, and Charge Distributions" (8 pages), "Application of Group Theory to Simplification of MO Determinants" (12 pages), "Aromaticity" (4 pages), "Molecules with Heteroatoms" (5 pages), "Nonplanar Systems" (9 pages), "Molecular Orbital Theory and Chemical Reactivity" (14 pages), "Approximate Methods" (10 pages) and "Higher-Order Calculations (3 pages). Following these are three Appendices, one on solutions of typical exercises, the second including reprints of two articles, the third a brief bibliography of reference books.

The appearance of the book is very attractive, and diagrams (prepared by the author personally) are numerous, clear and helpful. Only a few unimportant misprints were noted. In a few places terminology seems to be rather unorthodox or confusing. Thus on p. 28, a secular equation (that is, a secular determinant equated to zero) seems to be called a "secular determinant." On p. 59, "self-consistent field" is used in what seems to the reviewer a strange way. On p. 66, the author describes the operations of a symmetry group which he calls D_{2v}, although others call it D_2; however, the group which he actually needs for π-electron systems is C_{2v} (one rotation and two reflections instead of three rotations); but by ignoring the fact that two of the rotations turn π-orbitals upside-down, correct results are obtained. Similarly, on p. 70 the group C_2 (with one rotation) is described instead of C_s (with one reflection), but again correct results are obtained. But, if "a rose by any other name would smell as sweet," the above-mentioned deviations do not matter. They do not affect the value of the book as an extremely useful, practical primer for the application of Hückel theory to organic chemical problems. However (though again this does not affect the usefulness of the book), the reviewer does not see why on p. 56 the author uses "trimethylenemethane" with three double bonds from a central carbon atom, hence for the latter a valence of six, as a reference standard for the free valence index.

The author might have provided helpful orientation for those wishing to go deeper, if in the last chapter he had briefly pointed out certain characteristic quantitative faults of the simple Hückel theory, such as that it exaggerates the charges on atoms when charges are present, and exaggerates the bond orders of conjugated "single" bonds, like the central bond in butadiene.

PHYSICS AND CHEMISTRY DEPARTMENTS
THE UNIVERSITY OF CHICAGO
CHICAGO 37, ILLINOIS

ROBERT S. MULLIKEN

Progress in High Polymers. Volume 1. Editors, J. C. ROBB, PH.D., D.SC., and F. W. PEAKER, PH.D. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1961. vii + 340 pp. 16.5 × 25.5 cm. Price, $12.00.

This work, intended to be the first of a new series, is a collection of critical review articles in the field of polymer chemistry. The diversity of topics covered is such that at least portions of the book should be useful to anyone active in polymer research.

The first article, "The Theory of High Polymer Solutions" by T. B. Grimsley, rather than being primarily a review of the literature in the broad field defined by the title, presents a systematic, concise exposition of the theory. The author assumes a strong background of statistical mechanics on the part of the reader. Some references to introductory material in this field, particularly on the use of Markoff chains, would have made this article of greater value to those not specialists in this area. The next two articles, "Ebulliometry Applied to Polymer Solutions" by R. S. Lehrle, and "Fractionation of High Polymers" by G. M. Guzmán, are excellent detailed surveys of the literature. The emphasis in both articles is on the experimental techniques and results, but more than adequate summaries of and references to the literature on the relevant theory are given.

G. J. Howard, in an article entitled "The Molecular Weight Distribution of Condensation Polymers," reviews the experimental evidence and the theoretical treatments of this subject. Much of the experimental work has been the study of the nylons, although other polymers are considered as well. The discussion of the so-called "step-addition" polymers such as polyethylene oxide is very brief. A large part of this article is devoted to examining the rival theories of Flory and of a Russian school headed by Korshak; the author leans heavily toward the Flory theory.

The article by L. B. Morgan, "The Fibre-Forming Properties of Polymers," is entitled rather misleadingly, at least in terms of United States usage. Basically this is a review of the current (1959) status of the picture of the structure of crystalline polymers and of crystallization mechanisms and kinetics. This field is currently very active and many contributions have been made since the article was written; nevertheless it may be recommended as a useful introduction to the subject.

In the final chapter W. Cooper reviews the mushrooming field of "Stereospecific Polymerization." In view of the vast amount of literature, particularly patents, it would have been impossible to cover in one chapter of a volume such as this all that has been published. The author has written therefore a critical rather than an exhaustive article that should be of particular interest to those entering this field. An appendix brings the literature survey up to date as of August, 1960.

An inevitable, often belabored, shortcoming of review volumes is the time lag between writing and publication. For the most part, except for the appendix to Cooper's article, the most recent references are to 1959 publications. However, when one balances this against the mass of literature published prior to this time that has been surveyed by the contributors to this volume it becomes easier to accept this shortcoming, as well as the minor errors and omissions which the specialists in each of the fields covered will undoubtedly detect. If the general level of the articles is maintained at that of this volume, future issues in this series should be welcome to every polymer chemist.

RESEARCH LABORATORIES
CELANESE CORPORATION OF AMERICA KURT F. WISSBRUN
SUMMIT, N. J.

An Introduction to Theoretical Physical Chemistry. By SIDNEY GOLDEN, Department of Chemistry, Brandeis University. Addison-Wesley Publishing Company, Inc., Reading, Mass. 1961. xi + 307 pp. 16 × 23.5 cm. Price, $9.75.

This textbook for physical chemists presents some basic material in classical thermodynamics, statistical thermodynamics and quantum mechanics. The level of presentation is somewhat higher than in a good undergraduate first course in physical chemistry, but it is not generally as high as in a graduate course devoted entirely to any one of the three topics.

The first 87 pages are concerned with classical thermodynamics. This is a concise and reasonable treatment. Much of the material should be familiar to the student who has already had a course in physical chemistry. The point of view is formal and axiomatic. For example, the second law is developed according to Caratheodory.

The next hundred pages deal with statistical thermodynamics. The ideal gas is treated in great detail, using the Maxwell–Boltzmann method of the most probable distribution. Then Gibbs' version of statistical mechanics is presented. (The canonical ensemble is described incorrectly as a collection of replicas of a system, all in weak mechanical interaction.) This is followed by some standard applications, the theory of almost ideal gases, the Debye–Hückel theory of electrolytes, Debye's theory of specific heats of solids, and the Bragg–Williams approximation in order–disorder problems. In treating the non-ideal gas, Prof. Golden falls into a classic trap: he asserts, wrongly, that the second virial coefficient $B(T)$ must obey the inequality $N^2B(T)/V < 1$, where N is the number of atoms contained in a volume V.

The book ends with a hundred page survey of quantum mechanics, containing a curious selection of highbrow and elementary topics. For example, one can read about the wave functions of a harmonic oscillator in the momentum representation, or Mathieu's equation, or the characters of irreducible representations of Abelian groups, or Heisenberg's form of the quantum mechanical equation of motion. But the hydrogen atom is not treated at all. Electron spin is mentioned only in a few casual remarks. Chemical binding is discussed by means of a one-dimensional model of adjacent rectangular potential wells. However, the *formalism* of quantum mechanics is essentially all there; only the useful applications are lacking.

The style throughout is elaborate—"The negligible interaction which has been supposed is nevertheless nonzero.", for example. Mathematical details are handled with great care. The book contains no pictures or diagrams, no numerical examples or problems. About one-fourth of the problems read "Verify Eq. (–)". The lack of reference to the real world is often distressing. As an example, Debye's T^3 law of specific heats is derived, but no indication is given as to typical orders of magnitude for the Debye characteristic temperature.

This text can be recommended for use in an introductory course in theoretical chemistry only if the teacher is prepared to fill in many of the missing applications and illustrations. The serious student of theoretical chemistry is urged to learn his statistical thermodynamics and quantum mechanics from standard texts where the subjects are treated in greater depth.

DIVISION OF PHYSICAL CHEMISTRY
NATIONAL BUREAU OF STANDARDS ROBERT W. ZWANZIG
WASHINGTON 25, D. C.

Statistical Mechanics. By NORMAN DAVIDSON, Professor of Chemistry, California Institute of Technology. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1962. ix + 540 pp. 16 × 23.5 cm. Price, $14.50.

This is a textbook. It is devoted mainly to those parts of statistical mechanics that are interesting and useful to physical chemists. The book should be suitable for a one-year graduate course in a chemistry department; it was actually developed from such a course at Cal Tech.

The general tone is set in Davidson's dedication to the late William Moffitt: "In his own way, Bill Moffitt was a theorist with a passion for elegance and generality; but he insisted that the function of the theorist was to be useful. I hope that, were he still alive, he would think this book useful."

Because of this tone, it is not a book for the student who wants to work specifically in statistical mechanics, to develop new methods, and solve new problems, although he is advised to read it anyhow just to see what has been accomplished in this field. It is recommended for the student who wants to apply known results of statistical mechanics to problems in physical chemistry. For this purpose it is well organized and written.

The book covers all the standard topics that one has come to expect in an introductory course in chemical statistical mechanics, and many special topics also. As a random sample, we mention (1) the most comprehensive treatment we have seen in a textbook of black body radiation, including a discussion of radiative recombination; (2) a long chapter on fluctuations and noise, including the statistical part of the theory of light scattering from multicomponent solutions (but not the beautiful derivation by Einstein of the basic formula), and also a simple derivation of the Wiener–Khintchine formula; (3) the theory of the helix–coil transition; and (4) a discussion of electrical birefringence. This illustrates the remarkable variety of topics covered.

The style is clear and direct, with an occasional flash of humor. (I suspect that this will encourage the student to