Book Reviews

Exposition of a Useful Chemical Theory

The Molecular Orbital Theory of Conjugated Systems. LIONEL SALEM. Benjamin, New York, 1966. 592 pp., illus. $19.75.

The ideas and techniques of theoretical chemistry have been increasingly used, over the last decade, by physical and organic chemists, and, in particular, the application of molecular orbital methods to the understanding of experimental observations has advanced very rapidly. This is so, perhaps, because it is one of the most useful theories that has been introduced into chemistry, but the experimentalist often finds that dealing with its primary literature is difficult. There has been an outpouring of books in this period, but most have been either qualitative and introductory in nature or too advanced and rigorous. Salem has succeeded in producing a work that will be *used* by the practicing physical and organic chemist.

The Molecular Orbital Theory of Conjugated Systems is a well-written, comprehensive study of the structure and properties of molecules containing π-electrons. Under one cover Salem has discussed clearly a wide variety of topics, each in a reasonably uniform fashion. The chapters follow an admirable plan of beginning at an elementary level and progressing to advanced topics; he gives historical perspective when it is important to do so, and the theoretical development of each topic is usually elaborated concisely. The theoretical background given in the first two chapters, which deal broadly with Hückel and self-consistent field theories, along with the theoretical treatments given throughout the book, should be sufficient to enable the physical organic chemist to follow the later applications, with the exception of the chapters dealing with magnetic phenomena. The strength of the book lies in its timeliness, its up-to-date coverage, and the wealth of examples of applications of modern molecular orbital methods; one is grateful that the examples are worked out in detail. Most of the book is devoted to problems that are of current interest in chemistry, and most of the research cited is more recent than 1957, much of it from the last five years.

The chapters following the first two deal in turn with properties of the ground state, magnetic properties of closed-shell systems, radicals and open-shell systems, molecular orbital theory of the transition state, electronic spectra, and distortions of conjugated systems. In each of these chapters, I found points of theoretical interest of the kind that are often difficult to uncover in primary sources or elsewhere, and this facet has led to many underscorings in my copy for future reference. Perhaps the greatest value of the book to the experimentalist will be in the several "how to calculate . . ." sections. These sections are followed by clear discussions of recent theoretical developments that for the most part are found only in the original literature.

The chapter on the properties of the ground state contains a detailed description of the Longuet-Higgins and Salem theory of bond alternation and a good qualitative account of the bonding in conjugated rings containing *d*-electrons. The chapter on magnetic properties of closed-shell systems gives clear, modern accounts of the London theory of aromatic diamagnetism and magnetic anisotropy due to ring currents. This is followed by sections dealing with the calculation of chemical shifts in aromatic structures, carbon-13 chemical shifts, and spin-spin coupling. The chapter on radicals and open-shell systems deals only briefly with the theory of electron-spin-resonance spectra, and most of the chapter is devoted to the calculation of spin densities, including the Pople-Nesbet theory of "different orbitals for different spins."

Chemical reactivity is treated in a straightforward manner, but few new ideas are found in this chapter, primarily because little progress has yet been made in this area. The chapter dealing with the theory of electronic absorption spectra is the longest in the book and one of the most thorough. Configuration interaction methods are clearly developed and applied in detail to benzene. This chapter also has a good description of Simpson's theory of excitation delocalization, which unfortunately has often been neglected in other texts. The final chapter deals in a comprehensible way with molecular distortions and Jahn-Teller considerations, and the important recent work of Hobey and McLachlan, Liehr, Synder, and others is described in a very readable manner. Cyclobutadiene and related molecules are discussed in terms of pseudo Jahn-Teller effects. The chapter ends with a lengthy section on bond alternation in the even polyenes, which contains a treatment original with Salem, who regards this phenomenon as a further example of pseudo Jahn-Teller effects.

By now, the reader will recognize that the reviewer welcomes this book to his collection. It has taken up where Streitwieser's *Molecular Orbital Theory for Organic Chemists* (Wiley, 1961) left off, and the two, in fact, make fine companion volumes. I expect that this one will be used to advantage as a text in chemical physics and advanced physical organic courses, but it should be of most value to the modern researcher who is interested in going beyond Hückel theory in understanding his problems.

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Myrmecology

An Introduction to the Behavior of Ants. JOHN H. SUDD. St. Martin's Press, New York, 1967. 208 pp., illus. Cloth, $8.25; paper, $3.95.

As a myrmecologist I am often asked to identify the best single general account of ants, and I always give the same rueful reply: the quality of books on ants published during the past several decades is uniformly very poor. D. W. Morley's *The Ant World*, published as a paperback by Penguin Books in 1953 and possibly one of the most widely read works on entomology in the English language, is also one of the most inaccurate and misleading. Two other popular books, Wilhelm Goetsch's *The Ants*, translated from the German by Ralph Manheim for the University of Michigan Press in 1957, and S. H. Skaife's *The Study of Ants* (Longmans, London, 1961), are somewhat more reliable, but nevertheless so provincial in view-

point and negligent of the literature as to be all but useless. Even W. M. Wheeler's *Ants: Their Structure, Development, and Behavior* (Columbia University Press), the beautifully written classic of myrmecology, is 57 years out of date.

It is therefore with pleasure and relief that I have read Sudd's *An Introduction to the Behavior of Ants*. Here at last is a clear, adequate account of these insects. The book goes well beyond the scope of its modest title, touching on many engrossing topics in physiology and ecology relevant to the core subject of behavior. In order to cope with the great backlog of literature—over 35,000 titles—Sudd has chosen for citation about 500 articles that are most representative of the field, and he has synthesized with skill the material they contain. The book contains no important new ideas and does not try to probe very deeply into old ones. It is, instead, a sober, didactic account of available information. It faithfully reflects the author's view that the day of the sweeping "supra-organism" analogy is past. "The main efforts of students of ant behavior now are in describing how ants actually behave, and how the behavior of one ant reacts on another ant." His book makes this research goal attractive. It should draw new students to the subject and serve as a stimulus and useful reference work for biologists and psychologists of many persuasions.

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The Uses of a Concept

The Concept of Energy. D. W. THEOBALD. Spon, London; Barnes and Noble, New York, 1966. 208 pp., illus. $7.50.

Energy, a term first used by Thomas Young in 1805 in the Bakerian Lecture to the Royal Society, has become central to a number of scientific theories only distantly related to Newtonian mechanics. An analysis of the function and structure of the energy concept within each of its theoretical contexts and of the analogies that are used to justify the widespread use of this single term should therefore illuminate the general problem of the roles played by scientific concepts in the formulation of our knowledge and help to enhance our understanding of the concept itself. Such an analysis is attempted in *The Concept of Energy*.

Potential readers who are seeking a popularized or simplified discussion of the energy principle and its applications will find nothing of interest to them here. Nor will they find the kind of historically oriented analysis displayed by Max Jammer in his fine series of books on the concepts of mass, space, and force. What they will find is a mathematically sophisticated, philosophically oriented analysis of the concept of energy as it is used in classical mechanics, thermodynamics, theories of the electromagnetic field, relativity theory, and quantum theory. The substance of this analysis is sandwiched between two general philosophical chapters which establish the roles that the author assigns to scientific theories and the concepts that appear within them. Along with Rudolf Carnap and others, Theobald argues that human experience is in large measure determined by the language in which we interpret or express it. The purpose of any theory or conceptual framework is to provide a language which can give meaning and coherence to observations, and the scientist is "like a great poet, the creator of a language which enables us to say new things, and which suggests new things that might be said." The unit of the scientist's creation is the concept, a mental invention devised when current language fails to deal adequately with experience.

I am not sympathetic to Theobald's exclusively linguistic model of scientific theory, nor can I agree with his contention that "the historical and psychological factors which play an important part in the genesis of a theory are largely irrelevant in the context of an analytical discussion." Yet, within his self-imposed limits, I think that he has provided an interesting and perceptive discussion.

The value of the book is marred by a few minor but irksome details. For instance, there are several places in which words have been deleted, tenses of the verb changed in mid-sentence, and parentheses forgotten in mathematical expressions. Furthermore, the figures in the text have not been titled, and at least one figure (2.4) is not referred to explicitly in the text and is not within sight of the textual matter to which it applies. The style is condensed and, in the philosophical chapters, often disturbingly cryptic. But in spite of the distractions, *The Concept of Energy* should be of interest to philosophers of science, philosophically oriented physicists, and anyone who lectures on the concept of energy as it is used in any of the exact sciences.

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The Chemistry of Silicates

Silicate Science. Vol. 4, *Hydrothermal Silicate Systems*. WILHELM EITEL. Academic Press, New York, 1966. 631 pp., illus. $24.

If additional evidence were needed of the recent exponential growth of scientific research, it could be provided by citing Eitel's texts in the field of silicate chemistry. The first, a single volume entitled *The Physical Chemistry of the Silicates*, was published in 1954. In the last three years Eitel has produced the five-volume *Silicate Science*. (In addition to the one under review here, the volumes are 1, *Silicate Structures*; 2, *Glasses, Enamels, Slags*; 3, *Dry Silicate Systems*; and 5, *Ceramics and Hydraulic Binders*.) Additional weight is given to this example when we note that the five new volumes do not constitute revision and updating of the 1954 text but deal almost exclusively with data presented between 1952 and 1962. The use of copious footnotes has permitted inclusion of some references up to 1965.

Although largely an annotated collection of phase-equilibrium data, volume 4 also presents a wide selection of topics ranging from detailed discussions of petrogenesis to diagrams and descriptions of high-pressure apparatus, x-ray diffraction patterns, and crystal-structure diagrams. Almost inevitably with such a wide range of topics and of chemical systems, it is not possible for a single author to make critical judgments and comments on all the material included. In several instances, therefore, comments on a particular system are limited to what resembles a précis of the original author's abstract, accompanied by the most appropriate diagram from the original paper. Such an approach would be disastrous in a textbook, but the disadvantages in this reference book are minimal. The wide range of literature referred to in this volume is extremely impressive. Indeed, perhaps one of the major contributions of all