

the preface of the author is dated September, 1961, all references except one (which is from the January, 1961, issue of *Analytical Chemistry*) refer to publications through 1960, and this cannot be accidental. My impression is that the manuscript was compiled late in 1960 or early in 1961, and it took more than one year until it was published. In this respect, I would like to refer again to my earlier remarks in the previous book review: If fast publication is necessary in a general textbook, it is even more important in a short handbook.

Despite certain limitations, the book of Dr. Knox contains much valuable information and gives a good compilation of different questions, the knowledge of which is necessary in the everyday work; therefore, the book belongs in the library of the practical gas chromatographer.

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**Biochemical Mechanisms.** By LLOYD L. INGRAHAM, Department of Biochemistry and Biophysics, University of California, Davis, California. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1962. x + 108 pp. 15.5 × 23.5 cm. Price, \$5.75.

This book represents a birds eye view of biochemical mechanisms, albeit from a considerable height. The first part of the book consists of a review of atomic orbitals, bonding, conjugated systems, ligand field theory, transition states, ionic reactions, displacement reactions, concerted reactions, metals as acid catalysts, charge transfer complexes and "high energy" bonds in the course of 30 pages, presumably to enable the reader to grasp the second part, which consists of a more detailed discussion of specific mechanisms of different types of reaction. The usefulness of the first part for the average biochemist is open to question, especially in the case of more recent developments. Thus, for example, the treatment of charge transfer complexes occupies less than one page.

The reaction mechanisms put forward are lucidly explained and alternate possibilities are pointed out, although for an introductory treatment of this type perhaps too many of the proposed schemes are of a speculative nature. It is interesting to consider how even within a single year after publication, some of the proposed mechanisms have been disproved and others confirmed. Thus the mechanisms for rearrangements catalyzed by vitamin B<sub>12</sub> discussed on pp. 100, 101, and 102 cannot be correct since it has now been shown that these reactions are not accompanied by deuterium uptake from a D<sub>2</sub>O medium (Barker, *Fed. Proc.* 20, 956 (1961), and Overath, *et al.*, *Biochem. Z.*, **335**, 500 (1962)). Similarly, on p. 63 the view is expressed that the decarboxylation of prephenic acid, if concerted, would require a *trans* configuration for the COOH and OH groups. Plieninger (*Z. Naturforsch.*, **16b**, 81(1961)) has now shown, however, that the stereochemical relationship between these two groups in prephenic acid is *cis*. On the other hand, Lindberg, *et al.* (*Biochemistry*, **1**, 182 (1962)) have confirmed the mechanism of the decarboxylation of mevalonic acid 5-pyrophosphate described in the same section.

It is also regrettable that there are a considerable number of what are presumably printing errors in the labeling of formulas and in the equations; *e.g.*, on p. 69 the equation contains 2 Fe on one side and 3 on the other, and on p. 71, the second reaction is obviously meant to lead to the formation of a ferryl ion and not FeO<sup>+</sup>.

Perhaps the most valuable part of this presentation are the references, quoted in connection with each reaction mechanism, which will lead the conscientious student to a more thorough contemplation of the subject.

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REINHOLD BENESCH  
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**L'oxydation des métaux. Tome I. Processus fondamentaux.** Sous la direction de JACQUES BÉNARD, Professeur à la Faculté des Sciences de Paris. Avec la collaboration de JEAN BARDOLE, FLORENT BOUILLON, MICHEL CAGNET, JEAN MOREAU et GABRIEL VALENSI. Gauthier-Villars et Cie., 55, Quai des Grands-Augustins, Paris 6, France. 1962. 465 pp. 16.5 × 24.5 cm. Price, NF. 55.

The rapid development of ideas and theories in the field of oxidation of metals has led to the publication, in 1962, of two important books dealing with this subject matter: the one under review and a second, thoroughly revised edition of Kubaschewski's and Hopkins' standard monography. The reviewer has read both with infinite pleasure and found them to be complementary. Both should be consulted frequently by any one interested in the mechanism of gas-solid reactions.

The book edited by Prof. Bénard, whose fundamental work on many aspects of oxidation is universally appreciated, is the result of the coöperation of many authors. But they have clearly worked as a team, comparing results and exchanging ideas, so that there is little duplication and the unavoidable heterogeneity of a collective enterprise has been reduced to a minimum.

This is not an encyclopedia, a work of compilation, and the book should complement rather than replace older ones.

The classical theories of Wagner, Mott and Cabrera, and others are adequately summarized but more stress is laid on recently discovered facts and on new ideas. Each author dealing with his own subject puts forward his own views resulting from first-hand knowledge acquired by carrying out extensive experimental research. The authors have steered a midway course, avoiding two common pitfalls: they have resisted the temptation of considering only too simplified models, and they have not restricted themselves to purely descriptive statements. One finds in every chapter a sound and constructive criticism of experimental methods, a number of reliable data, which are classified and interpreted and a fresh and original outlook on many well known facts.

Every single chapter has its merits, but the reviewer has been particularly struck by the following ones.

*Chapter II to V dealing with the adsorption of oxygen* (by J. Bénard): The influence of chemisorption of oxygen on the surface structure of metals, and the importance of adsorption as a first step in the formation of an oxide layer, is clearly shown. This aspect has never been treated so exhaustively.

*Chapter VI. Nucleation in oxide films* (by J. Bénard): Nucleation is interpreted as resulting from the local crystallization of a primary film. Nucleation is shown to be a very general phenomenon, representing an intermediate stage between the formation of thin continuous layers at low temperatures, and thick ones, kinetically controlled by diffusion, at high temperatures.

*Chapter VIII. Orientation of reaction products at the surface of a metal* (by J. Bardolle): This orientation results from a superposition of *lines* rather than *planes* of maximum atomic or ionic density.

*Chapter XI. Quantitative theory of the kinetics of metal oxidation* (by G. Valensi): Thermodynamics of irreversible processes are applied far more thoroughly and rigorously than is usual in this field, so that this chapter should be invaluable to many readers.

*Chapter XV. Various modes of oxidation of alloys* (by J. Bénard and J. Moreau) and *Chapter XVI. Internal oxidation of alloys* (by J. Moreau): The importance of dissolved oxygen is discussed, and certain conclusions might be extended to the oxidation of pure metals.

*Chapter XVII. The real structure of oxidation layers* (by M. Cagnet): The importance of the mechanical properties of the oxide layer and of their variation with temperature is pointed out.

Finally it must be stressed that process of oxidation is followed in a logical sequence: adsorption, nucleation, thin films, thick films, oxidation of alloys, so that the book should be read from cover to cover. It is well worthy of an English translation.

As is frequently the case with French books, the printing and binding might be better, but illustrations, including microphotographs, are reasonably good, and there are few misprints.

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**Physical Organic Chemistry. Second Edition.** By JACK HINE, Professor of Chemistry, Georgia Institute of Technology. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1962. x + 552 pp. 16 × 23.5 cm. Price, \$11.50.

The appearance of a new edition of this well-known and widely-used textbook is an event to be welcomed. I still believe it is the best available general introduction to organic reaction mechanisms. Its judicious tone and its excellent balance between rigor and clarity inform the student without prejudicing him, and without teaching him blatant oversimplifications that he must unlearn later. This is not to say that all experts will agree with everything in the book, but all will certainly agree that Dr. Hine tries his best to be fair in controversial matters. There are times when he is a bit too reticent about expressing an opinion. I wondered, for example, just what views he does hold on hyperconjugation and on mechanisms of borderline displacement reactions.

Among the new features of this edition are the problems at the end of each chapter. Though obviously intended to meet the competition, they are by no means perfunctory, and offer ample intellectual stimulus even to the experienced worker. Another improvement is more extended coverage of kinetics and catalysis. Especially to be commended is Chapter 4 on "Quantitative Correlations of Reaction Rates and Equilibria." There is an ex-

cellent chapter on methylenes, an area in which Dr. Hine has made major research contributions.

Inevitably, anyone covering such a broad field will slight some important subjects, and give a somewhat distorted emphasis on others. Along this line, I regret the impression given by Dr. Hine that the steric effect of the leaving group is a generally accepted explanation of Hofmann-rule orientation in elimination reactions. Certainly many workers in the field, probably a majority, ascribe the major role to electronic effects. Some subjects that seem to me to deserve more emphasis than they get are Winstein's work on ion pairs, Cram's work on the stereochemistry of electrophilic replacements, and studies on the stereochemistry of free-radical additions. Some important advances in these fields may have come after the deadline for the manuscript, however. By way of minor quibbles, the stereo formulas for the bicycloheptane system (p. 324) are such complex jumbles of lines and circles that they are more likely to confuse the student than help him.

These are all minor faults, and I am sure Dr. Hine himself is not laboring under the illusion that he has written a perfect book. He has written a very good one that will be useful both as a textbook to the student and as a source of ideas and leads to the practicing organic chemist.

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WILLIAM H. SAUNDERS, JR.

**Inorganic Isotopic Syntheses.** ROLFE H. HERBER, Editor  
W. F. Benjamin, Inc., 2465 Broadway, New York 25, N. Y.  
1962. vii + 249 pp. 16 × 23.5 cm. Price, \$7.50.

In accordance with the stated intention of its editor, this volume is an excellent guide to the preparation of isotopically labeled inorganic compounds. A brief introductory chapter reviews radiochemical technique in general and radiochemical terminology. Each of the following eight chapters is devoted to a particular nuclide and is written by a separate author whom the editor considers to be an authority for that nuclide. The isotopes discussed are: H<sup>2</sup>, H<sup>3</sup>, N<sup>15</sup>, O<sup>18</sup>, P<sup>32</sup>, S<sup>35</sup>, Cl<sup>37</sup> and I<sup>131</sup>.

Over 300 syntheses are described. Some preparations are given in great detail, sufficient to enable the reader to proceed without further recourse to the literature. For other cases, when sophisticated equipment is required or the preparation is quite involved, the discussion is intended only as a guide and the reader must resort to the original publication. References to the original publications and related material are given for almost all but the most trivial syntheses. In all, almost 1000 references are listed.

This reviewer believes that this book would be a valuable edition in any laboratory, since today every laboratory is interested in isotopic syntheses to some extent.

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**Introduction to Ligand Field Theory.** By CARL J. BALLHAUSEN, Professor of Chemistry, University of Copenhagen, Denmark. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1962. ix + 298 pp. 16 × 23.5 cm. Price \$11.75.

In the borderland between physics and chemistry, one of the most fruitful applications of quantum mechanics is found in crystalline or ligand field theory, which is the key to understanding the magnetism, optical properties and coordination chemistry of solids containing ions of the transition groups. A review article written by the late Professor W. Moffitt and Dr. Ballhausen aptly concludes: "It will be a long time before a method is developed to surpass in simplicity, elegance and power that of crystalline field theory. Within its extensive domain, it has provided at least a deep qualitative insight into the behavior of a many-electron system. No other molecular theory, to our knowledge, has provided so many useful members which are so nearly correct. And none has a better immediate prospect of extending its chemical applications."

The broad outlines of crystal field theory were developed in the 1930's, but the subject has come into its own only in the last decade or so. New experimental techniques, such as microwave spectroscopy and better facilities for preparing single crystals of exotic compounds, have made it possible to put the theory on a more quantitative footing. In addition, the advent of the maser and laser has given it important technological repercussions.

In view of the current wave of interest in crystalline or ligand field theory, it is to be expected that a number of books would be written recently on the subject. In addition to numerous review articles, there are four such volumes of which the writer is aware. One of them is by a physicist (Low's "Paramagnetic Resonance in

Solids"), and the other three by chemists. All three of the latter omit the rare earths almost entirely. In size, price and amount of mathematical analysis, Professor Ballhausen's volume is intermediate between Orgel's "Transition Metal Chemistry," which contains not a single equation, and Griffith's "The Theory of Transition Metal Ions," which develops such mathematical refinements as fractional parentage and parity in half-filled shells. Ballhausen's book is, however, more complete than the other two in giving historical perspective and especially in references to the literature. For example, proper credit is given to the often overlooked pioneer work of Penney in 1940 on the stabilization of binding energies in the solid state by crystalline Stark splittings. Almost a thousand papers are cited, the bulk of them within the last few years, an indication of the rapidity with which the field is growing.

By ligands are meant the cluster of atoms about a central ion. Ballhausen and other modern writers use the term crystal field theory for mathematical analysis in which one treats the transition ion as a one-atom problem with the effect of the surrounding ligands represented by a static potential field of some particular symmetry type. The term ligand field theory is then employed for a more general treatment based on the method of molecular orbitals in which electrons can wander from the central ion to the ligands and *vice versa*, and various degrees of covalence thus are obtained. The reviewer was shocked recently to learn that one aptitude test question given to pupils in a suburban New York school was to distinguish between physicists and chemists by whether they are interested in atoms or molecules. If such outmoded compartmentalization is employed, crystal field theory is physics and ligand field theory is chemistry! Actually the two fuse together closely. Ballhausen's book combines both the basic central core of crystal field theory, roughly the first half of the book, and the modern ligand field ramifications. Recent work in paramagnetic and nuclear resonance has shown that even in the most ionic cases, except in the rare earths, the wandering or incipient covalence tendency is larger than was supposed in the early work.

As the pages unfold, the character of the book properly changes considerably. After a brief historical introduction, there are chapters on the theory of atomic spectra and on symmetry, which serve substantially as digests of Condon and Shortley type of material, and the results of group theory. Then two chapters give the mathematical development appropriate to crystalline fields of different symmetry types. The next chapter is on spin-orbit interaction, and the comparison with experiment becomes more frequent. The following one on molecular orbitals introduces the more general ligand field theory. Chapter 8 treats vibronic interactions and the Jahn-Teller effect, a subject to which the author naturally gives particular attention because of his original contributions in this field. After a short chapter dealing mostly with rotary dispersion, there is a long final one, almost devoid of equations and replete with references to the literature, on "electronic structures of selected inorganic complexes."

Professor Ballhausen has struck a good compromise between readers who would like to see everything proved mathematically and those who want merely the results of analysis. In a book of its dimensions, it is impossible to derive everything, and occasionally he could delineate a little more sharply between what he has and has not proved.

The English and literary style are excellent, though the author is not writing in his native tongue.

In summary, Professor Ballhausen is to be congratulated in writing a valuable, comprehensive and authoritative volume on a timely subject.

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**The Opium Alkaloids. Selected Topics.** By DAVID GINSBURG, Israel Institute of Technology, Haifa, Israel. Interscience Division, John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1962. 111 pp. 16 × 23.5 cm. Price, \$6.50.

This is a pleasant, personal little book written by an author who is indeed expert in the field about which he writes. It is the child born of the author's research interest, developed from a series of lectures, and intended as a teaching tool to assist organic chemistry graduate students. It cannot serve as an alternative to the various compendia on the opium alkaloids (Small, Bentley, Manske and Holmes), and, of course, Ginsburg does not purpose to do so. The chief, and considerable, value of this book is that it reflects the author's personal interest both in research and teaching.

"Selected Topics," is part of the title and this is indeed the case. Selection is the book's virtue from the pedagogic standpoint. A tasty mixture of classical and recent topics in opium alkaloid chemistry is presented, flavored by the author's own