BOOK REVIEWS

Isotope Effects on Reaction Rates. By LARS MELANDER. Nobel Institute of Chemistry, Stockholm. The Ronald Press Company, 15 East 26th Street, New York 10, N. Y. 1960. vi + 181 pp. 14 × 21 cm. Price, $6.00.

This little volume, written by an active worker in the field, deals both with theoretical and experimental aspects of isotope effects on chemical rates. In the earlier chapters the theory of isotope effects based on transition state theory is presented and the evaluation of relative isotopic rate constants from experimental data is treated. It is somewhat unfortunate that some of the more recent theoretical methods for the treatment of isotope effects are not discussed. Subsequent chapters deal with isotope effects observed in various systems. The emphasis is very heavily on hydrogen and carbon isotope effects in organic systems. First the experimental magnitudes of these isotope effects and the theoretical predictions of these magnitudes are discussed for simple systems. Subsequently isotope effects are discussed from the point of view of learning about reaction mechanisms in more complicated systems. In general the book is well written, although there are one or two obscure passages. The book should form a valuable addition to the libraries of those interested in the application of kinetic isotope effects to problems in organic chemistry.

CHEMISTRY DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY MAX WOLFSBERG
UPTON, LONG ISLAND, NEW YORK

Preparative Methods of Polymer Chemistry. By WAYNE R. SORENSON, Research Chemist, and TOD W. CAMPBELL, Research Manager, Pioneering Research Division, Textile Fibers Department, E. I. du Pont de Nemours and Co., Inc. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1961. viii + 337 pp. 16 × 23.5 cm. Price, $10.50.

If one decides actually to *do* some polymer chemistry (as distinguished from reading or talking about it) he quickly finds that the information he needs for carrying out polymerization reactions is scattered through the original literature, patents and industrial lore which never appears in print. Even when he has found what he wants, he finds it very difficult to evaluate the merits of different procedures. Sorenson and Campbell's book should go a long way toward resolving this dilemma, and, in these days of multiple-authored compendia, it is a pleasure to encounter a volume which sets itself a specific goal and proceeds to reach it clearly, concisely, and with adequate but not unnecessary detail.

The authors start with a brief account of the general properties of polymers and equipment and techniques for polymerization and polymer handling, together with a very helpful definition and discussion of the terms used in polymer chemistry. The main part of the book, however, consists of some 275 specific sets of laboratory directions for polymerization reactions (including a number of preparations of commercially unavailable monomers). These procedures are divided into polycondensations (83 examples), vinyl polymerizations (106 examples, including radical, carbonium ion, carbanion and "Ziegler" processes), ring opening polymerizations (41 examples ranging from cyclic ethers to sulfur), "non-classical routes to polymers" (20 examples including some strange and wonderful reactions), and synthetic resins (25 examples). Each section begins with a clear and sensible discussion of the general principles involved, and ends with an extensive bibliography of the original literature. The individual directions appear to contain just about the right amount of detail, and the authors state that most have been checked, either by themselves or their associates.

In addition to its utility for practicing polymer chemists, this book should provide a splendid basis for a laboratory course in polymer chemistry (or as a source of individual experiments in an organic chemistry course) and the authors thoughtfully provide a list of recommended experiments for the purpose in the introduction. Even for the non-polymer chemist, this book should make fascinating reading if he has any curiosity about how these things are actually done, which play such an important part in chemical technology and which support so many of his friends and former students.

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The Theory of Brillouin Zones and Electronic States in Crystals. By H. JONES, Professor of Mathematics, Imperial College, University of London. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1960. ix + 268 pp. 16 × 23 cm. Price, $9.50.

The chemistry and physics of crystalline matter depend heavily on the band theory of solids: the theory of the electronic structure of perfect crystals. Professor Jones has presented a carefully written introduction to this subject.

The announced purpose of the book is to give an account of the mathematical methods for the approximate solutions of the one-electron Schroedinger's equation for crystals. The emphasis is placed on the use of symmetry, or group theory, for displaying the nature of the solutions independent of models for the potential. This policy is started in the first chapter on the one-dimensional periodic potential, where notation and symmetry theory applicable to the three-dimensional case are introduced. In chapter 2 the direct and reciprocal lattice and the translation group are introduced using a notation which is both clear and useful in later chapters. Bloch functions and Brillouin zones are then introduced followed by a discussion of constant energy surfaces and some examples of three-dimensional zones.

The next two chapters, which take up about half of the book, are devoted to the development of group theory for the classification of electronic states. The division into two chapters is based on the distinction between space groups having or not having glide planes and screw displacements. In each chapter, examples of the symmetry properties of states within the Brillouin zone are worked through in helpful detail. For instance, the ten pages devoted to the α-uranium structure begin with a detailed description of the direct and reciprocal lattices and the Brillouin zone. The groups of the wave vectors at several points in the zone are derived and the wave functions and energy bands for the case of free electrons are developed in some detail.

There follows a chapter on nearly free electrons and the extended zone scheme. The value of band theory as an approximation method is brought out in this chapter in the discussion of perturbation theory and in the applications to alloy phases.

The chemist will be on familiar ground when reading chapter six in which specific models for the potentials are chosen; much space is given to the LCAO method. Other commonly used approximations and their strong and weak points are also discussed. This chapter is a concise and valuable critique of these methods.

The final chapter is a short account of the modifications which must be made to include effects of spin–orbit coupling. The double groups are shown to follow from the invariance of the Schroedinger equation with spin, and examples of spin–orbit splitting in crystals are worked out.

This book is unique among all other books treating band theory because of its emphasis on the use of symmetry. To this reviewer's mind the use of group theory is a great advantage; it enables one to distinguish clearly between the parts of the subject which are indisputably correct such as selection rules and those which depend on approximations. Physical chemists on the average are more used to thinking in terms of group theory than are physicists, and this book should appeal especially to them for this reason. It is unfortunate that the unsystematic notation for representations used by solid state physicists was used instead of the Mulli-

ken notation which has become well established in molecular physics and chemistry. However, anyone conversant with point groups can easily make the changes.

Although the book is mainly a mathematical text, physical facts are brought in to illustrate important points and to maintain interest in the mathematical results. The book does not give a discussion of the limits of validity of the one-electron band theory nor of exciton levels.

In the reviewer's opinion, a student who has had no previous exposure to the theory of point groups would have difficulty with this book; however, a relatively simple briefing on groups of symmetry operations and their use in constructing symmetrized functions should be sufficient introduction. The book is highly recommended to serious students of chemistry who wish to gain an appreciation of the electronic structure of crystalline solids.

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Physiko-chemische Grundlagen und Tabellen zur Qualitativen Analyse (Mit Ausnahme der Gasanalyse). By W. D. TREADWELL. Nach dem Tode des Verfassers herausgegeben von Prof. Dr. O. Gübeli, Zürich, und Dr. W. Prodinger, Wien. Verlag Franz Deuticke, Helferstorferstrasse 4, Wien I, Austria. 1960. xi + 236 pp. 17.5 × 24.5 cm. Price, ost. S 168.—.

"By their fruits you shall know them" remains an infallible standard by which one may measure accurately the capacity and usefulness of an individual in any sphere of activity. Against a background of multitudinous analytical methods and much chemical triviata, the researches of W. D. Treadwell are a convincing reassurance that the analytical researcher need not be merely a sharpener of tools but may possess inherently a distinct approach to chemical problems.

Unmistakably, Treadwell's "Qualitative Analysis" indicates the direction which can be given to the solving of analytical problems by an adequate accumulation and integration of descriptive material. Perhaps a rearrangement of the title to emphasize analytical aspects would more appropriately describe the content of the book. With a total of 231 pages, approximately 54 pages are concerned with explanations for some three dozen physical chemical terms as well as tables of such physical constants as activity coefficients, solubility products, dissociation constants, and optimum acidities for precipitation, etc., of chemicals related to analytical procedures. The remainder of the book, in five sections, deals with methods of approach and preliminary examinations of materials with a view to qualitative separations of the common elements extended to include such metals as uranium, gold, titanium, molybdenum, etc. The procedure, preceded also by a detailed description of the physical and chemical properties of the elements involved, is largely the classical chloride–sulfide–carbonate separation with the final methods of identification involving a few of the more effective recently developed reagents. A similarly complete qualitative scheme for anions is included.

For those metals not included in the qualitative schemes, the author has supplied a supplement. In this section the physical properties, precipitants, methods of dissolution and separation are listed for the alkali metals, lanthanide series, and the rarer metals of the sulfide group. Momentarily, one's enthusiasm for this book is tempered by the contents of the final page. One cannot associate the proved competence and thoroughness of the author's work, here and elsewhere, with the antiquated procedure for the separation of the noble metals of column VIII. Neither the author nor any one else has yet succeeded in separating ruthenium by heating in oxygen at 700°. This small section of the volume is of little value.

Furthermore, the book may not be acceptable to those who, for either pedagogical or practical purposes, require some integration of the empirical separational procedures such as chromatography or ion exchange techniques. It would seem that the author could profitably have made some concession to the more effective ion exchange methods, even at the expense of reduced instructional value. This would have improved the out-dated section dealing with the separation of the lanthanide metals.

This is a book of chemical data and analytical methods, largely without detailed prescriptions. Most of the methods are classical with a small admixture of recently reported reagents; one must not expect a compilation of the latest precipitants or color reagents.

In this Reviewer's opinion the book is a useful contribution to analytical literature, an excellent classical text for qualitative courses at the university level, and a distinct asset to any chemical library.

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Advances in Organic Chemistry. Methods and Results. Volume II. Edited by RALPH A. RAPHAEL, The University, Glasgow, Scotland, EDWARD C. TAYLOR, Princeton University, Princeton, New Jersey, and HANS WYNBERG, Rijksuniversiteit, Leiden, The Netherlands. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1960. vii + 504 pp. 16 × 23.5 cm. Price, $15.00.

This second volume of what promises to be a most useful and stimulating series on new developments in organic chemistry continues the high standard of excellence set by Volume I. The objective of the editors is a series of volumes containing articles providing a critical appraisal and evaluation of new aspects of organic chemistry ripe for further development and of novel extensions to well-established methods, ideally by the originator of the method described or a practitioner expert in its use. This objective is very well realized in Volume II.

The topics covered and the authors are the following: Alkenylmagnesium Halides (65 pp.) by H. Normant (Paris); Dialkoxydihydrofurans and Diacycloxydihydrofurans as Synthetic Intermediates (49 pp.) by Niels Elming (Copenhagen); Ethynyl Ethers and Thioethers as Synthetic Intermediates (96 pp.) by J. F. Arens (Utrecht); Ketene in Organic Synthesis (51 pp.) by R. N. Lacey (Hull, England); Nuclear Magnetic Resonance in Organic Structural Elucidation (64 pp.) by Harold Conroy (New Haven, Conn.); Hydrogenation–Dehydrogenation Reactions (38 pp.) by L. M. Jackman (London); Ultraviolet Photochemistry of Simple Unsaturated Systems (59 pp.) by Paul de Mayo (London, Canada); The Chemistry of Muscarine (29 pp.) by C. H. Eugster (Zurich).

Alkenylmagnesium halides represent a most useful addition to synthetic methods involving the Grignard reagent; this brief review is timely. Dialkoxydihydrofurans and Diacycloxydihydrofurans are of more limited value but deserve the attention this review will focus on them. The chapter on ethynyl ethers and thioethers, the most exhaustive review in this volume, is an important survey of all of the work on these compounds and admirably illustrates their general utility. Ketene is an old chemical but new aspects of its chemistry make its inclusion here appropriate; the sections on isopropenyl acetate and β-propiolactone are especially interesting.

Nuclear magnetic resonance is probably the most important new development included in this volume. The theoretical part is somewhat too condensed to be easily understood but the examples are well chosen to illustrate the scope of the method.

Only a small portion of the field of hydrogenation–dehydrogenation reactions is covered in the sixth chapter—that dealing with homogeneous hydrogen transfer between organic molecules without catalysis by inorganic derivatives. Short sections on catalytic, photochemical and biochemical hydrogen transfer are barely illustrative.

Probably the most provocative topic is ultraviolet photochemistry of simple unsaturated systems. Photolysis promises to be of increasing importance in organic chemistry and the examples reviewed suggest much further work.

The final chapter on the chemistry of muscarine presents a concise review of the application of modern and older methods to structure elucidation of a simple but intractable molecule. A better choice might have been made to illustrate the application of modern techniques to such problems, but the chapter is well written and interesting.

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