BOOK REVIEWS

Organic Syntheses. Volume 35. T. L. CAIRNS, Editor-in-Chief. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1955. vi + 122 pp. 15.5 × 23.5 cm. Price, $3.75.

Volume 35 of "Organic Syntheses" contains directions for the preparation of thirty-six organic compounds. The editing and presentation of the experiments in this latest addition to the annual series are very good and follow the pattern of previous volumes. Without doubt this is a work of considerable value to the practicing organic chemist.

Actually, one wonders how the editors manage so well to meet the requirements of a new volume each year without including many over-specialized preparations which would seriously weaken the series.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER V. BOEKELHEIDE
ROCHESTER, NEW YORK

High Vacuum Technique. Theory, Practice, Industrial Applications and Properties of Materials. Third Edition. Revised. By J. YARWOOD, M.Sc., F. Inst. P., Head of Department of Mathematics and Physics, The Polytechnic, Regent Street, London W. 1. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1955. viii + 208 pp. 14 × 22 cm. Price, $5.50.

The salient feature of this book is conciseness. The type and illustrations are clear, the paper robust, and the book well suited for travel between work bench and office desk. Although likely to be acquired by most operators in high vacuum, it will appeal particularly to the student or technician and the occasional user of vacuum methods, where the crisp, didactic style will provide answers uncomplicated by qualifications or alternatives.

The subject-matter is presented functionally rather than historically, much of the information being derived from catalogs. This leads to curious inversions of authority. Burch, inventor of the oil diffusion pump, receives one reference, Langmuir 3, Gaede 9, Distillation Products, Inc., 5, and W. Edwards Co. 29. One result of this preoccupation is a valuable summary of pumps, mechanical, diffusion and ejector, obtainable commercially throughout the world. Throughputs, energy consumption and ultimate vacuum are listed comparatively (pp. 49–57).

The chapters on gas kinetics and measurement of pump speeds are excellent. The lesser methods of leak detection are well recounted, but the important mass spectrometer type is dismissed as too expensive to warrent inclusion. A similar lapse is noted in connection with the vacuum furnace, which is not treated.

The 6th and last chapter gives a compilation of chemical data and physical constants—a Critical Table in miniature—which will save the vacuum technologist much searching through larger reference volumes. Chapters 4 and 5, on "gettering" and application of vacuum to industry, provide a token initiation which should at least encourage the student to read elsewhere.

In summary, it may be said that within the limits set by the author, this is an admirable small textbook for the occasional worker in high vacuum which will be welcomed in its third edition by the American reader.

136 PELHAM ROAD
ROCHESTER 10, NEW YORK KENNETH HICKMAN

Diffusion in Metallen. Platzwechselreaktionen. Volume 3. By WOLFGANG SEITH, Professor für physikalische Chemie an der Universität Münster and Theodor Heumann, Dozent für physikalische Chemie an der Universität Münster. Springer-Verlag, Reichpietschufer 20, Berlin W 35 (West-Berlin), Germany. 1955. vi + 306 pp. 16.5 × 24 cm. Price, Ganzleinen geb. DM 39,—.

The field of metallic diffusion has shown a remarkable growth in the 15 years since the appearance of the first edition of "Diffusion in Metallen." The quality and quantity of experimental data has increased tremendously, due in large part to the widespread availability of artificially produced radioisotopes; notable progress in understanding the mechanism of the diffusion process has resulted from both the theoretical and experimental attacks; a start has been made toward putting the problem of "structure-sensitive" diffusion on a rational and quantitative basis. It is not surprising, therefore, to find this second edition to be thoroughly revised and greatly expanded.

The first third of the book, dealing largely with experimental aspects, is mainly an updating of corresponding chapters in the first edition. An extensive, well-arranged and very useful tabulation of experimental results is included. However, the organization of this section does not seem to be the most desirable. For example, after the discussion of experimental techniques and tabulation of results, there is a chapter on general theory and mechanism, after which the authors return to discuss the measurement of concentration-dependent diffusion coefficients.

The middle third of the book is almost entirely new. Included here are discussions of the Kirkendall Effect and its implications, Darken's phenomenological treatment of diffusion in binary systems, diffusion in systems with intermediate phases, and grain boundary and surface diffusion.

A series of nine special topics occupy the last third. These subjects range from the influence of third components on the diffusion of solutes, to the theories of precipitation and sintering, to diffusion in liquid metals. This portion is again essentially a revision of the last half of the first edition. As might be expected in a book dealing with the broad subject of diffusion in metals, these special topics are not covered in any great depth.

The appendix includes pertinent mathematical tables and a table of experimental results that were published after the preparation of the manuscript.

Perhaps the best recommendation for the book is that it gives a fairly comprehensive survey of the important literature of the field. (The excellent thermodynamic treatment of diffusion in alloys by Bardeen and Herring is a notable exception.) As such, it will serve as a useful addition to the libraries of those who desire a handy source book. On the other hand, those who wish a discriminating critique of the present state of knowledge will probably do better to look elsewhere.

GENERAL ELECTRIC RESEARCH LABORATORY
THE KNOLLS R. E. HOFFMAN
SCHENECTADY, NEW YORK

Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra. By E. BRIGHT WILSON, JR., Professor of Chemistry, Harvard University, Cambridge 38, Massachusetts, J. C. DECIUS, Associate Professor of Chemistry, Oregon State College, Corvallis, Oregon, and PAUL C. CROSS, Professor of Chemistry, University of Washington, Seattle 5, Washington. McGraw-Hill Book Company, Inc., Publishers, 330 W. 42nd Street, New York 36, N. Y. 1955. xi + 388 pp. 16 × 23.5 cm. Price, $8.50.

No authors could have been more competent to undertake a work on this subject and within the limits they have set for themselves, this book is highly successful. Most of the published infrared and Raman spectra have their origin in molecular vibrations and in this work the authors develop all of the essential elements of the theory of such vibrations.

Except for some very important new methods in the Chapter "Advanced Applications of Group Theory," most of the material presented is available in the literature. However, the original papers are widely scattered, and the importance of the present work is that it takes up its subject from the beginning, develops the frequently obscure mathematical techniques in an extremely lucid way without making any strenuous demands on the mathematical background of the reader, and includes most of what is relevant to cur-

rent research in this area. In addition, it has a definite "how to do it" flavor; there are numerous examples to illustrate the working of the theory and a whole chapter on methods of solving the secular determinant from which the vibrational frequencies of a molecule are calculated. A complete sample analysis of the benzene molecule is given. It is, therefore, a book which should certainly be in the hands of every student beginning work in molecular spectroscopy.

The main criticism of this excellent work is that the chosen subject is in some ways too narrowly limited. The analysis is formal and very little attempt is made to give physical feeling for the problems. Furthermore, very little consideration is given to the problem of proceeding from observed spectra to the calculations. Since in spectra the molecular vibrations always occur in vibration-rotation bands, it may be impossible to assign these bands correctly or even to obtain the correct vibrational frequencies without understanding the rotational fine structure. In this connection a comparison with Herzberg's well known book is inevitable. Fortunately, the two are valuable supplements to each other, the present work giving a clearer and more comprehensive treatment of the problems of symmetry and vibrations, Herzberg giving a broader view of the problems of infrared and Raman spectra.

Both of these books suffer from a lack of discussion of the principles involved in the interpretation of the spectra of molecules which are too large or complicated to be treated formally. Such a discussion does not yet seem to be available anywhere in the literature, yet most published spectra are in this category, and this lack may decrease the value of this book to "practical" spectroscopists.

Nevertheless, this is a masterful presentation of the problem of molecular vibrations and the utilization of symmetry through group theory. It should be on the reference shelf of every molecular spectroscopist and ought to be required reading for anyone beginning to use molecular spectra.

METCALF RESEARCH LABORATORY
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Gas Kinetics, An Introduction to the Kinetics of Homogeneous Gas Reactions. By A. F. TROTMAN-DICKENSON, Lecturer in Physical Chemistry in the University of Edinburgh. Academic Press, Inc., Publishers, 125 East 23rd Street, New York 10, N. Y. 1955. x + 322 pp. 14.5 × 22 cm. Price, $8.00.

In the present unsatisfactory state of reaction kinetics, the preparation of a short summary is a thankless task. We must, of course, have books, even though we have not learned enough to produce good ones. It is important to recognize this basic fact before we consider how the volume under review disappoints our hopes.

The title provides an inaccurate guide to its contents, which are better fore-shadowed by the Preface: "Investigations in chemical kinetics are undertaken for many reasons, among others, to discover the mechanism of a reaction, to find the best conditions for a synthesis or to determine bond dissociation energies. This book, however, is not primarily concerned with any of these topics, rather the investigations that are discussed have been selected because they throw light on the fundamental question of why elementary reactions occur at the rate they do." As a consequence of this attitude, the author is content to devote five lines to the hydrogen–oxygen reaction, and four to the oxidation of hydrocarbons, while completely ignoring the fascinating subject of explosion limits. There is also a more serious consequence, in that the author gives the impression of hurrying through the mechanistic complexities of the reactions he discusses to reach the precious core of information on elementary reactions. While the basic work on some sketchily presented reactions appears sound, other reactions with highly speculative mechanisms receive similar treatment. This attitude will encourage errors in the initial researches of the advanced undergraduate—beginning graduate group to which the book is directed.

This criticism may be illustrated by the discussion (pp. 147-149) of the decomposition of 1,2-dichloroethane, both alone and inhibited by propylene. The chain mechanism given for the uninhibited reaction depends upon a termination step

$$Cl + C_2H_4Cl = C_2H_3Cl + HCl$$

which must occur to the substantial exclusion of all other termination steps between the three radicals Cl, C_2H_4Cl and $C_2H_3Cl_2$. The mechanism for the inhibited reaction depends upon the steps

$$C_2H_3Cl_2 + C_3H_6 = C_2H_4Cl_2 + C_3H_5$$
$$C_2H_4Cl + C_3H_6 = C_2H_5Cl + C_3H_5$$

being dominant over

$$Cl + C_3H_6 = HCl + C_3H_5$$

It seems improbable that chlorine atoms can assume such varied importance as a chain-breaking reactant in the two regions. The author totally ignores the existence of these problems. The serious student will be further confused by the occurrence of three major misprints in the steady-state equation (p. 148).

The author has embraced recent work of N. B. Slater on unimolecular reactions as representing a uniquely realistic theory of these processes. His enthusiasm in this matter must be somewhat surprising to Slater himself, who is still wrestling with the mathematical problems involved in development of his theory. For example, the first quantum theory treatment was published after the book under review had gone to press. The physical problems in obtaining structure data needed to make full use of the Slater theory are perhaps even more difficult. The pioneer theories of unimolecular reaction, which were developed nearly 30 years ago, at a time when information on energy levels of polyatomic molecules was virtually nonexistent, elicit gentle mockery. Yet these theories were frankly based on a simplified model, with a small number of empirical parameters being used to summarize the relevant information in scores of unknown vibration frequencies and transition probabilities, and the more one accepts the Slater theory as representing ultimate reality, the more he must be impressed with the merit of the early intuitive model.

It is embarrassing to discuss these personal matters, but your reviewer feels strongly that good models and simple calculations can still contribute vitally to the progress of chemistry and physics. In all past ages, David has competed with Goliath. Shall we now tell our students that the chemist with only a pencil must acknowledge as master the wave equation with an I.B.M. machine?

UNIVERSAL OIL PRODUCTS COMPANY
DES PLAINES, ILLINOIS LOUIS S. KASSEL

Boltzmann's Distribution Law. By E. A. GUGGENHEIM, M.A., Sc.D., F.R.S., Professor of Chemistry in the University of Reading. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1955. 61 pp. 12.5 × 18.5 cm. Price, $1.50.

This excellent little booklet furnishes two hours interesting and thought provoking reading for the expert, or five times this much serious study for the undergraduate novice. The contents derive the mechanistic basis for many of the simpler laws of physical chemistry. The author says in the preface that for eight years he has hoped that it might be written by someone more experienced than he is in elementary teaching, but that he had now lost this hope. To this reviewer, at least, it appears very doubtful that one more experienced in elementary teaching could have done better. Since the reviewer has also long shared the conviction that the elementary laws of physical chemistry are most simply understood in terms of the mechanism of interaction of molecules, he was prejudiced to approve the book after reading the preface. This hope was not disappointed by the text.

The first chapter presents the elementary facts of quantum theory, namely, that there exist quantum states of molecules of discrete energy, and that these are spaced by the Bohr relation. The examples of the particle in a box and of the harmonic oscillator are discussed in detail. In the second chapter the concept of temperature is introduced and the statement of the Boltzmann distribution law is made that the relative numbers of molecules in two quantum states is given by $\exp -\Delta E/kT$. From there on the