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.

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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

development is one of logical deduction without pretense of excessive mathematical rigor. The partition function is introduced and the properties of the monatomic perfect gas derived. The free energy (Helmholz) is defined in terms of the partition function, and its properties and usefulness derived and discussed. Equilibrium and the equipartition of kinetic energy are the subjects of the next two chapters. The simple crystal, the ideal diatomic gas, phase equilibrium, dielectric constant of a gas, and chemical equilibrium are then taken up, and the book finishes with a short chapter on Fermi–Dirac and Bose–Einstein distributions.

The author assumes a knowledge of elementary calculus on the part of the student, and as much knowledge of physics and chemistry as might be held by a bright high school graduate, or a more average student who has had freshman courses in these two subjects.

It is inevitable that a reviewer well acquainted with the field should contemplate how he himself would have presented the material, and where he feels that the author had made an omission of logical step, or a mistake in emphasis. In the first chapter the reviewer would have preferred to state the conservation of mechanical energy, potential plus kinetic, as a consequence of the fact that no frictional forces exist on a molecular scale, rather than as a consequence of the Newtonian Laws, which it is not. So also the derivation of the equipartition of kinetic energy seemed to this reviewer to omit one important and necessary step in view of the knowledge expected of the student. It does not follow from the quadratic dependence of the kinetic energy on the velocities, but on the quadratic dependence on momenta. The one example of Guggenheim presumption in the book, the assertion that there is no ground for the statement that thermal expansion depends on non-harmonic terms in the vibrations, seems to be gratuitous. Although Guggenheim has cleverly, and quite rightly, avoided discussing the non-harmonic terms, his tacit assumption of a dependence of frequency on volume in the crystal requires the existence of such terms. This reviewer would have justified the use of the logarithm of the largest term of a sum of positive terms for the logarithm of the sum by comparing numerically the logarithm of the number of terms with that of the largest term. However, the admirable brevity and conciseness of such a meaty, and truly tiny book, requires that steps which some might consider essential must be omitted, or treated extremely shortly.

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Catalysis. Volume III. Hydrogenation and Dehydrogenation. Edited by PAUL H. EMMETT, Gulf Research and Development Company's Multiple Fellowship, Mellon Institute, Pittsburgh, Pennsylvania. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1955. vii + 504 pp. 16 × 23.5 cm. Price, $12.00.

The third volume of this treatise on "Catalysis" passes from the realm of basic underlying theory treated in the first two volumes to particular catalytic reactions. Hydrogenation and dehydrogenation reactions are the processes here reviewed. The choice is a logical one since it includes reactions which have been the objective of the most intensive study in the recent scientific development of catalytic research. This arose from the great technical importance of ammonia synthesis, the production of methanol, the hydrogenation of fats and of hydrocarbons with dehydrogenation of the latter from petroleum sources to yield butadiene and styrene as raw materials for synthetic rubbers. Furthermore, the hydrogen–deuterium exchange, the hydrogenation of isotopic hydrogen, whose study became possible early in the 1930's, made possible for the first time studies of the action of a catalyst surface in opening up the bonds of a chemical molecule. What was thus begun with H–H and D–D bonds has been extended to C–H, N–H, C–C and N–N bonds and the list is lengthening yearly both with respect to bonds and the surfaces which activate them.

The authors selected, including veterans such as Frankenburg and Natta and younger workers such as Eley, Trapnell, Bond and a group of Dutch workers, guarantee an approach to the problems with both authority and fresh outlook. Trapnell's initial chapter on parahydrogen conversion and hydrogen–deuterium exchange while very nearly exhaustive in coverage is not conclusive even in this the simplest case of bond activation. Bokhoven and his colleagues in Holland reviewing the research on ammonia synthesis since 1940 themselves reach a similar conclusion, admiration for ingenuity displayed and inability to provide "an unambiguous answer to the questions facing us" . . . but with "a few bright spots" . . . an increase in our understanding of fundamentals, but "many problems are still unsolved" and "many new problems have arisen." Natta is somewhat more optimistic concerning methanol synthesis. Kearby gives a very revealing analysis of a phenomenal technical development of World War II which made possible butadiene production in partial vacuum-type systems and the alternative of butene dehydrogenation in presence of diluent steam. It was an incalculably vital contribution to the war effort at a critical period. In the hydrogenation of unsaturated hydrocarbons, Eley on ethylene and Bond on acetylenic compounds give excellent surveys of the basic science while Corson and Feuge take up the practical problems with olefinic hydrocarbons and glycerides, respectively. In these latter cases selectivity is a practically important and theoretically baffling problem. So there are still problems for the neophytes even in these well-tilled areas of catalytic science.

DEPARTMENT OF CHEMISTRY
PRINCETON, N. J. HUGH TAYLOR

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