

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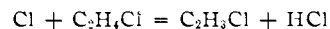
**Gas Kinetics. An Introduction to the Kinetics of Homogeneous Gas Reactions.** By A. F. TROMAN-DICKENSON, Lecturer in Physical Chemistry in the University of Edinburgh. Academic Press, Inc., Publishers, 125 East 23rd Street, New York 10, N. Y. 1955. x + 322 pp. 14.5 × 22 cm. Price, \$8.00.

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.

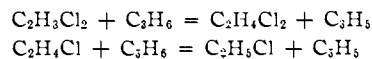
The title provides an inaccurate guide to its contents, which are better fore-shadowed by the Preface: "Investigations in chemical kinetics are undertaken for many reasons, among others, to discover the mechanism of a reaction, to find the best conditions for a synthesis or to determine bond dissociation 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 mecha-

nism given for the uninhibited reaction depends upon a termination step



which must occur to the substantial exclusion of all other termination steps between the three radicals Cl, C<sub>2</sub>H<sub>4</sub>Cl and C<sub>2</sub>H<sub>3</sub>Cl<sub>2</sub>. The mechanism for the inhibited reaction depends upon the steps



being dominant over



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?

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**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