BOOK REVIEWS

Kinetics and Mechanism. A Study of Homogeneous Chemical Reactions. Second Edition. By ARTHUR A. FROST and RALPH G. PEARSON, Professors of Chemistry, Northwestern University. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1961. ix + 405 pp. 15.5 × 23.5 cm. Price, $11.00.

This is a second edition of a well-known introductory text to chemical kinetics first published in 1953. The general theme of the first edition is preserved, which is an emphasis on the basic concepts of chemical kinetics and the methods of interpreting experimental data in terms of reaction mechanism. As before, the material is limited to homogeneous reactions, and is supplemented at the end of each chapter by several problems selected from the literature.

Although a good deal of the text is a verbatim reprint of the first edition, the additions and changes are numerous. Throughout, the typography has been improved and the references revised to take into account new work. The new material in the chapter on reactions in solution consists of a discussion of the electrostatic contribution to the enthalpy and entropy of activation. In the chapter on homogeneous catalysis, the discussion of linear free energy changes has also been expanded.

Most revisions and changes involve the section dealing with elementary gas phase reactions. The discussion of unimolecular reactions has been brought up to date with a brief discussion of the theory of Slater; a new subchapter has been added on the effect of pressure on unimolecular reactions, which includes a survey of the latest results on the isomerization of cyclopropane and the reactions of excited methylene radicals. The chapter on chain reactions has new subchapters on chain transfer reactions and bond dissociation energies. The subchapter on inhibition has new material dealing with the action of inhibitors in autoöxidation. An up-to-date discussion of the pyrolysis of acetaldehyde has been added as an illustration of the Rice–Herzfeld mechanism.

A new chapter entitled "The Study of Rapid Reactions" has been added. It first deals with the principles of flow methods, steady-state methods and encounter-controlled reactions, and then goes on to outline briefly the basis of experimental techniques involved in the quenching of fluorescence, polarography and flash photolysis, and in the rotating sector, magnetic resonance, mass spectrometer, shock tube and relaxation methods. This is a departure from the policy the authors adhered to in the first edition of excluding discussion of experimental techniques.

The final chapter, which discusses in detail the evidence for the mechanism of several reactions in solution and the gas phase, has been revised in the light of recent work.

The addition of new material has brought about, perhaps inevitably, some awkward situations. For example, the effect of pressure on unimolecular reactions is discussed in Chapter 6, while unimolecular reactions are discussed in Chapter 4. The inhibition by nitric oxide and propylene is dealt with in Chapter 6, while inhibition in general is relegated to Chapter 10, with no cross-reference. One might also question the logic of including a brief account of flash photolysis but not of ordinary photolysis, although photochemical evidence is used in several instances. Finally there is the strange omission (common with the first edition) that throughout the book (except for a paragraph on p. 115) there is scarcely a hint of the troubles with heterogeneous effects that commonly beset the investigations and interpretations of supposedly homogeneous reactions. A word of caution to the unwary would have been useful. However, these are only minor reservations.

Despite the numerous additions, the book has grown only about 50 pages in length, which still keeps it reasonably compact for use as a textbook and reference text. The book thus preserves the virtue of the first edition which was a lucid exposition uncluttered by unnecessary detail. The price, however, has gone up almost 100% compared with the first edition, and is quite high even by today's standards for a volume of such modest size. As a result, it is very likely that the book will be found mainly in institutional libraries rather than in personal libraries where it belongs and where it would be most useful. Unfortunately it would be overly optimistic to expect that publishers will wake up to the possibilities of paperbacks in this field, or that they will recognize that expensive binding is an unnecessary frill for technical books, most of which become obsolete in five years.

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Radiation Chemistry of Gases. ACS Monograph No. 151. By SAMUEL C. LIND, Oak Ridge National Laboratory, Operated by the Union Carbide Corporation for the Atomic Energy Commission, with Collaboration of CLARENCE J. HOCHANADEL, Oak Ridge National Laboratory, and JOHN A. GHORMLEY, Parma Research Laboratory, Union Carbide Corporation, Parma, Ohio. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1961. x + 313 pp. 16 × 23 cm. Price, $12.50.

This is the second of two authoritative monographs on radiation chemistry published in the United States, both authored by Samuel C. Lind. The first (ACS Monograph No. 2) was published in two editions (1921 and 1928). The present volume is both a revision and a substantial enlargement of the 1928 edition. It is presented under two section headings: Part I—Physical Principles, Part II—Gaseous Reactions. Part I includes two chapters on the use of radon as a source of ionizing radiation in studies of the radiolysis of gases, a brief chapter by Ghormley on other sources of ionizing radiation and on some aspects of dosimetry, and a brief chapter by Hochanadel on interactions of ionizing radiation with matter. The material on radon is substantially the same as in the 1928 monograph, but these experimental techniques and methods for calculating dosages and kinetics data continue to be valuable to radiation chemists using gaseous radionuclides other than radon. Ghormley briefly presents useful information on characteristics and properties of a variety of radionuclides and electrical sources of vital interest to chemists, *e.g.*, availability, useful chemical forms, maximum available intensities, shielding problems, etc. The discussion of dosimetry is concerned almost entirely with methods for measuring energy deposition in condensed phases. Measurements with liquid and solid dosimeters are, of course, not directly applicable to determination of dosages in gases exposed to penetrating radiation from an external source. A statement of and discussion of problems in determining energy absorption from external sources would have been a valuable complement to the chapters on the use of radon as an internal source. Hochanadel's discussion of mechanisms of interaction of various kinds of ionizing radiation with matter is a model of conciseness and includes a number of illustrative and otherwise valuable tabulations and figures. All of the chapters of Part I are supplied with valuable references to definitive articles in the literature.

Part II seems to be as close an approach as is presently possible to a critical survey of all published work on gaseous reactions from its beginnings to July, 1960. Experimental results, including extensive tabulations of experimental data in many instances, are presented under the headings: Reactions of One Component, Oxidation, Hydrogenation, Polymerization, and Nitrogen Oxides. A brief chapter on the chemical effects of nuclear transformations, *e.g.*, Szillard–Chalmers reactions and reactions induced by isomeric transition, is also included. Much of the work reported under these headings is again discussed and correlated in chapters on the effects of foreign gases and the effects of various experimental parameters, *e.g.*, temperature, intensity, phase, etc. The work of Essex and others on radiation chemistry in electrical fields is reported in a separate chapter. Recent studies of reactions between charged and neutral species (ion-molecule reactions) are