

BOOK REVIEWS

Contributions to the Theory of Chemical Kinetics. A Study of the Connection between Thermodynamics and Chemical Rate Processes. By THOR A. BAK. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1963. 101 pp. 15 × 23 cm. Price, \$5.50.

It is a pleasure to note that Dr. Bak's most interesting book on chemical kinetics is now accessible to the broad audience it deserves. The problems discussed are of significance, and the treatments are elegant and lucid. The book is not a general introduction into the theoretical aspects of chemical kinetics; rather, a limited number of topics are treated rigorously and in detail. Students in advanced courses in thermodynamics, statistical mechanics, and kinetics will find this book excellent supplementary reading, and the specialist will find the book and its bibliography (through 1958) quite useful.

Bak first discusses the application of the principle of minimum entropy production in steady states; diffusion, nucleation, sets of consecutive first-order reactions, and LeChatelier's principle are treated. He then turns to the question of oscillating reactions, often thought to be of biological interest, and employs the methods of Krylov and Bogoliubov to investigate the qualitative behavior of solutions to nonlinear rate equations which may show oscillatory behavior. The theory of electrodiffusion in steady and alternating fields is then presented, and application is made to systems in which electrodiffusion is coupled to chemical reaction. The mathematical treatment of electrodiffusion is adapted to the analysis of chromatography, which is briefly discussed. The next portion of the book is concerned with the problem of the presence of irreversibility in a world whose equations of motion are reversible. Bak shows how such irreversibility appears for certain limiting cases; the general problem remains to inspire and baffle the theoretician. The last chapter of the book deals with the statistical mechanical treatment of chemical reactions by methods similar to those employed by Kramers. The reaction system is treated as a canonical system in contact with a lattice (the thermostat), and the Liouville equation for the entire system (including the lattice) is then examined.

I was pleased to see that the editors have retained the Danish flavor of the book. It is to be regretted that the price of the book, a short paperback, is such as to make it unavailable to most students.

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Chemical and Biological Aspects of Pyridoxal Catalysis. Proceedings of a Symposium of the International Union of Biochemistry, Rome, October, 1962. Edited by E. E. SNELL, P. M. FASELLA, A. BRAUNSTEIN, and A. ROSSI FANELLI. The Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. xv + 599 pp. 16 × 23.5 cm. Price, \$20.00.

Anyone interested in reading this book to gain a complete analysis of how pyridoxal phosphate functions as a coenzyme in enzymatic reactions will be disappointed to learn that almost as much remains to be learned as is already known about this subject. Although there is general agreement among researchers in this field that the Braunstein-Snell theory of the mechanism of action of pyridoxal is fundamentally correct, there remain disagreements concerning the details of the chemical events associated with the functioning of this compound. Also, a number of experimental observations have been made that cannot yet be explained to everyone's satisfaction. These uncertainties exist largely because of the complexities of the problems with which the experimentalist is confronted. The development of new experimental techniques, such as the temperature-jump method already being used (see the chapter by Fasella and Hammes in the book), offers renewed hopes for a more complete understanding of this subject.

Certainly, it must be said that the subject of vitamin B₆ has been thoroughly covered in this book. The title, "Chemical and Biological Aspects of Pyridoxal Catalysis," is used in its broadest sense, because not only is the subject of the mechanism of

catalysis with pyridoxal covered, but also much information is included on such allied subjects as antimetabolites of pyridoxal, purification and properties of enzymes, physiological effects associated with the presence or absence of the vitamin, and the metabolism of pyridoxal.

The book contains 46 separate papers, the first eight of which deal with the mechanism of catalysis with pyridoxal studied in model reactions. Generally speaking, these eight papers were written in clear and concise language, and enough experimental data were included so that the reader can clearly follow the reasoning of the authors in arriving at conclusions. The findings reported in these chapters mostly seemed significant in providing bases for an understanding of the mechanism of catalysis of pyridoxal, although a complete picture is still not available.

The next eight papers present a clear view of what is known about the chemistry of pyridoxal phosphate catalysis in enzymatic transamination. The major portion of the remaining chapters is devoted to discussions of individual enzymes that are either known to contain or suspected of containing pyridoxal phosphate as a prosthetic group. Some of these investigations make significant contributions to knowledge of the mechanisms of action of these enzymes. However, a number of the papers contain mostly descriptions of purification procedures and general properties of enzymes and, thus, are of little value to the reader interested in understanding the mechanisms of enzymatic action.

In assessing the plus values of the book, one could probably agree that there is some merit in having all of the knowledge of vitamin B₆ compiled into a book and presented with data so that one can critically evaluate the conclusions of the authors. The discussions at the close of each chapter were in some cases very spirited and in most cases interesting and valuable. The first and last chapters of the book deserve special mention because they provide excellent summaries of the history of pyridoxal catalysis (first chapter by E. E. Snell) and the current state of knowledge of the subject (last chapter by A. Braunstein).

In general, the book makes a favorable impression and should certainly be a welcome addition to the biochemistry sections of science libraries, although the relatively high cost is a factor that may influence individuals in deciding whether or not to add the book to their private libraries.

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Inorganic Complexes. By CHR. KLIXBÜLL JØRGENSEN, Cyanamid European Research Institute, Cologny, Geneva, Switzerland. Academic Press, Inc., Ltd., Berkeley Square House, Berkeley Square, London, W1, England. 1963. 220 pp. 16 × 23.5 cm. Price, \$7.50.

The classical valency theories provided principles that allowed the deduction and classification of the compounds capable of existence; their aim was not to elucidate the nature of chemical bonds. Modern theories of valency are of a different character because of our belief that all chemical phenomena are the consequences of the known laws of physics, and much effort is being spent in showing that certain chemical phenomena can indeed be derived from these laws. Among theoretical chemists, Chr. Klíxbüll Jørgensen is outstanding for his intense interest in chemical reality and for his efforts towards its classification. His concepts of the nephelauxetic effect and optical electronegativities are the results of surveying a large body of experimental facts and have grown out of the same type of reasoning as the atomicity concept of Kekulé and the coordination principle of Werner.

What Jørgensen believes to be the most fruitful theoretical background for a comprehension of inorganic complex chemistry has been made the content of his book "Orbitals in Atoms and Molecules" (Academic Press, 1962). The book to be discussed here may be described as a confrontation of these theoretical principles with chemical reality. Inorganic complexes are defined as clusters MX_N or MX_aY_{N-a} of a central atom M surrounded by

ligand atoms X or Y, whether they occur as parts of separate ions in salts and solutions or within the endless structures of crystalline solids or glasses, acting there as spectroscopical units, *i.e.*, as chromophores. M may be any element of positive oxidation number, comprising not only all the metals, but also hydrogen, the heavy halogens, and even some of the noble gases (*e.g.*, in the xenon compounds). The ligands range from fluorine all the way down the electronegativity scale to certain metallic elements in intermetallic compounds. Only the true organometallic compounds with alkyl and aryl groups σ -bonded to metals are outside its scope.

The author is, of course, particularly interested in the spectroscopic and magnetic behavior of these complexes. He gives innumerable positions of absorption bands and their interpretation. When the spectra have not been taken, at least the color of the compound in question is stated. Furthermore, the book gives an interesting account of the solution stabilities of complexes, including chelates, polynuclears, and even simple ion pairs, not only in water, but also in strong HCl (chloro complexes) and nonaqueous solvents. Whenever possible, the kinetic characteristics are also stated. Related phenomena of solid-state chemistry and physics are also discussed. The many literature references make up a bibliography with 1176 citations.

In only 180 pages, this book contains an almost complete review of that part of inorganic chemistry that has been the outstanding field of research during the past 20 years. In spite of the condensed form of presentation of a huge amount of experimental facts, the text is easy and entertaining to read. Every chemist will profit in doing so.

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Radiolysis of Hydrocarbons. Edited by A. V. TOPCHIEV, Director, Petroleum Institute, U.S.S.R. Academy of Sciences, Moscow. English Edition edited by R. A. HOLROYD, Mellon Institute, Pittsburgh, Pa. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York 17, N. Y. 1964. xii + 232 pp. 15.5 × 23 cm. Price, \$11.00.

This book, organized in seven chapters, is the English translation of a report of the Radiation Chemistry Laboratory of the Institute for Petrochemical Synthesis in Moscow. Academician Topchiev, who directed and edited this notable effort, died shortly after its completion. Although it may not be his *opus magnum*, it will certainly contribute to his good reputation.

It cannot be denied that language difficulties make for poor scientific communication between the U.S.S.R. and the rest of the western world. Thus, a book of this type serves two useful functions. Its bibliography reveals to us which of their own national works the Russians consider important in a particular field. On the other hand, it also reveals, by its omissions, a failure to appreciate or to understand, or even to know of the existence of, pertinent non-Russian literature. For Americans, this book is a very good introduction to texts which we might otherwise have overlooked.

The book itself is concerned to a very high degree with the radiation chemistry of heptane and closely related aliphatic hydrocarbons in the liquid and solid states. The mechanistic portion of the interpretation of the chemical facts is largely free-radical orientated, a not unnatural situation in view of the dominant position of Semenov in Russian reaction kinetics. Certainly, many fresh ideas are introduced, but the impression is given in the early chapters, at least, that the pertinence of the literature on the reactions of ions and excited species is not fully appreciated. However, it is clearly apparent that the essentially theoretical portion is intended to be sufficiently broad in its conception and presentation to cover the behavior of charged and excited species.

Certain facts emerge clearly from the presentation. In the work of the Institute, much attention was addressed to establishment of the chemical nature of the products which they presumed to identify. Also, there seems to have been some considerable use of e.s.r. techniques, in a preliminary way to be sure, in the identification of free-radical species present, particularly in solid systems. Further, as indicated mainly in the last chapter, the members of the Institute are very much concerned with the practical employment of radiation chemistry—

for example, in what they identify as radiation thermocracking. In the experiments in the latter area, they have examined a number of compounds and mixtures not too closely related to heptane. It is also clear that the people doing the actual practical work concerned with the practical utilization of radiation chemistry have been very much supported in their efforts by people with primarily theoretical interest—although certainly it is difficult to understand how the theorists have permitted survival of an almost religious faith in the log-log method (pp. 55 and 56) for the establishment of precise reaction order.

Theoretical concern shows in the extensive use of free-radical theory in the interpretation of the kinetics, in the limited remarks on the radiation chemistry of hydrocarbons adsorbed on catalysts and on energy transfer in the radiolysis of hydrocarbons, and, very importantly, in Chapter 6 entitled "Some Aspects of the Theory of Hydrocarbon Radiolysis." The theoretical conceptions attempt to be rather general. There is an effort toward mathematical rigor which can encompass the behavior of a wide variety of chemical species. The treatments provide an excellent introduction to papers which are not generally read or whose existence is not even appreciated in this country. Although they reveal to some extent a lack of appreciation of some of the concepts which have been current outside Russia, the freshness of approach resulting from that fact is itself very stimulating to the reader. One gathers the impression that Russian scientific workers are rather generally acquainted with many of the ideas current in the United States, and even with the terminology employed—but not necessarily acquainted with the details or the authorship.

In Chapter 6, there is a clear attempt to develop all-encompassing generalized statistical theory of reaction kinetics applicable to the special case or cases of radiation chemistry. There is heavy emphasis on the theory of collective phenomena and a time criterion of a collective effect is clearly stipulated. Much of the discussion is given over to time and distance details of deposition of energy by a fast-moving charge particle.

Topchiev's "Radiolysis of Hydrocarbons" is a book which ought to be readily accessible to anyone working in the field of radiation chemistry, because it will put him in touch with many features of the Russian literature important both in radiation chemistry and in kinetics generally, which he might otherwise miss. On the other hand, the makeup is not esthetically pleasing; the book seems to have been printed by the photo-offset method and it contains a rather large number of typographical errors as well as crudities of expression, again a reflection of semantic difficulties, which can result in misinterpretations. *In toto*, however, this book reveals that scientific communication does, in a curious way, surmount language barriers; it, itself, will do much to improve communication and understanding between radiation chemists in the Russian- and English-speaking worlds.

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Physical Properties of the Steroid Hormones. International Series of Monographs on Pure and Applied Biology. Edited by LEWIS L. ENGEL, Associate Professor of Biological Chemistry, Harvard University Medical School. Pergamon Press, The Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. viii + 488 pp. 18.5 × 25.5 cm. Price, \$15.00.

Neither the title of this book nor the editorial note give any indication as to the reader for whom the book was primarily intended. Furthermore, there is no indication that there are any subsequent volumes to follow. It is distinctly surprising, therefore, that a book entitled "Physical Properties of the Steroid Hormones" should include no data and not even a single reference concerning mass spectrometry, circular dichroism, or nuclear magnetic resonance spectroscopy. Understandably, the editor does refer to available authoritative compilations of infrared, optical rotatory dispersion, and specific rotation data for steroids. Apart from a fine chapter on ultraviolet absorption spectroscopy by a group of authors from the Lederle Laboratories (almost half the book), this volume contains mainly data on the less well-studied physical properties of steroids—partition coefficients, chromatographic mobilities, fluorescence spectra, and absorption spectra in concentrated sulfuric acid. Thin layer chromatography receives minor mention. The choice of topics does give the reader access to information which is not gathered