Book Reviews

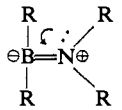
Heteroatom Ring Systems and Polymers. By H. R. ALLCOCK, Department of Chemistry, The Pennsylvania State University, University Park, Pa. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1967. xi + 401 pp. 16 × 23.5 cm. $16.50.

"Heteroatom Ring Systems and Polymers" embraces those compounds having, as skeletal backbones, regular alternating arrangements of pairs of the following atoms: B, C, N, O, Al, Si, P, S. Thus aminoboranes, metaphosphates, siloxanes, polyaldehydes, phosphonitriles, triazines, and thiazenes, to name a few examples, are described. The material is arranged under the following chapter titles: (1) Definitions, Scope and Nomenclature; (2) Bonding Theory; (3) Aromaticity and Delocalization; (4) The Oligomer-Polymer Relationship; (5) Synthesis of Heteroatom Compounds; (6) Polymerization of Monomers and Cyclic Oligomers; (7) Reactions of Heteroatom Compounds; (8) Heteroatom Polymers; and two appendices, one summarizing recent developments (to mid-1966) and the other listing bond angles and bond lengths for a number of compounds.

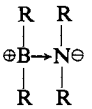
The author has undoubtedly performed a service in bringing together a vast amount of data and literature on these systems. The organizational problems in a book encompassing such a topic are formidable, and it is perhaps not surprising that the system adopted has resulted in closely related material concerning a group of compounds being presented, sometimes with considerable repetition, in several locations in the book. Thus data (with references) on cyclosilazanes (despite what the index indicates) are found on pages 64, 107, 146–150, and 196–199, and closely related discussions on polymerization are found in Chapters 4, 6, and 8.

Much of the early, more theoretical work on bonding and delocalization is unevenly written, elementary and specialized material being randomly admixed. The chapter on synthesis and reactions of heteroatom compounds contains vast amounts of data, concisely given, but with little of the systematic comparison between classes that the book claims to make. Thus reactions of each class of compound are briefly considered under the headings: general hydrolytic stability, thermal behavior (also covered again in the next chapter on polymerization), nucleophilic-type substitution reactions of halogen derivatives, Friedel–Craft-type substitutions, halogenation, hydrohalide additions, skeletal bond-cleavage reactions, and miscellaneous reactions.

The structures given throughout the book have a number of stylistic peculiarities which are at times distressing and would be particularly so, I believe, to the nonchemist reader. Thus arrows and partial charge distributions are sometimes used in the normal manner to designate inductive effects (*e.g.*, IX, p 44) but more frequently complete charge separation is shown (*e.g.*, XXIIa, p 50) also associated with arrows. This leads to confusion as to whether the arrows are designating inductive effects or dative bonding, for which purpose they are also used (XLVII, p 65). To further confuse the situation, in some cases where "fish hook" type arrows are used, the electrons involved are shown both at their origin and also in the bond they create by their designated movement, in the same structure. Thus i is considered as a π-electron-delocalized form of



i



ii

ii, both being representations of R_2BNR_2. In many cases, only one of the two lone pairs is shown for O or S atoms in a formula (*e.g.*, structures on pp 63 and 65 but not p 61).

Numerous errors, some quite serious, were also observed. On page 164, the author appears to have forgotten that it is the energy of activation which governs the rate of interconversion of a compound to an intermediate, and not the enthalpy difference between the species and the intermediate. On page 183, a novel type of aldelyde polymer RCHOH–$(CROH)_n$–COR is said to arise from aldol condensation; on page 113, the mechanism written for the first step of formation of melamine is incorrect; on page 41 the bond length of benzene is given as 1.44 Å; on both pages 75 and 82–83 the author states that, because of the loss of π-bond energy, the polymerization of carbonyl or thiocarbonyl systems should in general involve a decrease in enthalpy. The author does not make clear that the breaking of a double bond in such a reaction results in two single bonds being formed. In fact, for aldehydes using the data given in Table 4.1, the polymerization would actually involve an increase in enthalpy.

This book may be a distinct contribution to the literature, particularly in view of the extensive assemblage of data on a field not previously covered in a single volume, but the enthusiasm with which it can be recommended, in this nonexpert's opinion, is certainly limited by the errors and stylistic peculiarities noted.

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Carbohydrate Chemistry. By EUGENE A. DAVIDSON, Duke University. Holt, Rinehart and Winston, Inc., 383 Madison Ave., New York, N. Y. 1967. vi + 441 pp. 16 × 23.5 cm. $11.95.

This book fills a long-neglected niche, that of a textbook for a course in carbohydrate chemistry at the senior college or graduate level. Not a reference book, it appears to be strongly beefed-up from lecture notes for such a course. This reviewer intends to adopt the book as a text for his course.

The author successfully meets his goal of correlating organic theory with carbohydrate chemistry. This is the principal achievement of the book. To accomplish this end, conformational formulas are used almost exclusively. Many tables and figures add much to the presentation.

Sections dealing with nuclear magnetic resonance and infrared spectroscopy are adequate introductions to these fields. The correlations with biochemistry add interest. In general they concern the steric fit of substrate with enzyme. In this the author does not go beyond what is included in a good biochemistry text.

The index is brief (3 pp), and the Table of Content does not provide a sufficient guide to the subject matter of the book. An unfortunate error is the confusion of the half-chair conformation with the skew, on pages 44 and 49. The treatment of polysaccharides is necessarily brief in a book this size, and the author misses an opportunity to chide carbohydrate chemists for having learned so little about the natural forces which govern size and structure of these substances.

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Organoboron Chemistry. Volume 2. Boron-Nitrogen and Boron-Phosphorus Compounds. By HOWARD STEINBERG, Vice President and Director of Research, and ROBERT J. BROTHERTON, Research Supervisor, U. S. Borax Research Corp. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1966. xx + 568 pp. 16 ×23.5 cm. $25.00.

Volume 2 of "Organoboron Chemistry" is the most comprehensive summary available on the chemistry and physical properties of organoboron compounds which contain bonds between boron and one of the group V elements: nitrogen, phosphorus, arsenic, and antimony. Over 90% of this volume is devoted to boron–nitrogen compounds, which reflects the limited amount of information available concerning compounds which contain bonds between boron and one of the remainder of the group V elements. Literature is reviewed through 1964. The bibliography not only contains journal citations, but also refers to U. S. and foreign patents, doctoral dis-

sertations, and government reports. In addition to a comprehensive bibliography at the end of each chapter, all reported compounds are listed in tables and, where available, physical properties are presented also.

This work should prove to be an invaluable aid to active workers in the areas covered. However, the nonspecialist probably will not find it of much use with respect to understanding or assimilating in an organized way the facts discussed. The text is not only terse, it effectively neglects principles or generalizations which might help collect and organize information. Furthermore, results are in general presented in an uncritical manner with little attempt to evaluate or correlate observations. Nevertheless, this volume is a most welcome contribution to the literature of boron chemistry and will be greatly appreciated by experienced investigators.

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Advances in Structure Research by Diffraction Methods. Volume 2. Edited by R. BRILL and R. MASON. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1966. 166 pp. 16 × 24 cm. $9.75.

All the articles in this volume are concise and well written by leading research workers in their respective fields, continuing the high standards set by Volume I.

G. E. Bacon reviews a unique application of neutron diffraction inaccessible by X-ray methods—the study of magnetic structures. P. Corradini discusses some of the recent work on high polymers, naturally emphasizing the work of the Italian school which has pioneered in this field. Very reasonably he limits his discussion to synthetic polymers; perhaps a future article will discuss the larger and untidier field of natural polymers. The article by R. Mason and G. B. Robertson on diffraction methods and quantum chemistry devotes about half of its space to each of the two aspects. I would have preferred to see a far larger proportion of the article devoted to the accurate X-ray methods necessary. The quantum chemistry is covered in several books and reviews already, while the X-ray diffraction methods tend to be scattered in journal articles.

For me, the outstanding contribution is that on the determination of protein structures by David Phillips. No other review of this subject approaches this very concise but high-level discussion.

The only error I noticed is a trivial one: the illustration of the α helix in the Phillips article has three consecutive carbon atoms in part of the peptide chain. However, since this diagram has appeared in many places already, I can hardly blame Phillips or the editors.

A much more serious criticism can be leveled at the publisher. The Phillips review is the only one carrying a date, though I estimate from the termination dates of the references in the others that they were submitted at a similar time. The date on the Phillips article is May 1964. The volume was published in 1966. It is, however, relatively inexpensive by present-day standards. Perhaps the fact that it was published in Germany and printed in Poland is the common cause of both the publication delay and the relatively low price. Let us hope that the delay can be reduced with future volumes without a price increase.

This series is highly recommended.

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Spectroscopic Gas Temperature Measurement: Pyrometry of Hot Gases and Plasmas. By RICHARD H. TOURIN, Manager, Control Instrument Division, The Warner and Swasey Co., Flushing, N. Y. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1966. xi + 139 pp. 14.5 × 23 cm. $10.75.

Tourin's book "Spectroscopic Gas Temperature Measurement" is basically a summary of methods for spectroscopic gas pyrometry, based primarily upon the author's own experience. The reader must keep this fact in mind when approaching this book. Most of the material covered is presented in a relatively condensed form, leaving it to the reader to obtain a detailed understanding of the assumptions, principles, and subleties inherent in the methodology of gas pyrometry by using the extensive body of literature quoted.

The principal chapters deal with thermodynamic and spectroscopic principles, radiometric and spectrometric methods of gas pyrometry, spectroscopic measurements of temperature profiles, spectrocopic pyrometers, spectroscopic pyrometry of combustion gases, transient gas temperatures, and measurements of plasma temperatures. A brief exposition of the general subject and of the accuracy of temperature standards is given in the general introduction to the book. The individual chapters contain brief topical introductions aiming at the definition and the clarification of principles and of methods discussed.

The authors' style is that of a practitioner relating his practical knowledge to other practitioners in his field of research. The uninitiated readers, engineers, and scientists alike, who want to use this book as a guide to methods for the solution of particular measurement problems, should be on their guard against overlooking underlying concepts and assumptions implicit in the methods presented. Thus, a novice is not likely to perform a successful measurement without considerable reading of the cited references.

For readers with a thorough background in spectroscopic methods, the book presents a useful additional source of reference including material to the beginning of 1966. At the same time, these readers may be irritated or stimulated by the authors' treatment of temperature as a concept, its relation to spectroscopic observables, and its accessibility by spectroscopic observations under mundane conditions. Unfortunately, the author does not give a careful exposition of this subject in the chapter on thermodynamic and spectroscopic principles, and he does not emphasize the primary importance of methods by which the experimenter can check the existence of a spectroscopically accessible temperature.

The existence of a temperature is implicitly assumed throughout the book, and this fact should not be overlooked, for example, on page 29, where the author states in essence that the emission–absorption method is independent of *a priori* information about the hot gas. Similar flaws, which are caused by not stating all of the assumptions made or by not giving precise definitions, and which should be eliminated in a future edition, are phrases like: "thermodynamics deals with the steady-state properties of matter" (p 6), "each degree of freedom . . . can be regarded as a thermodynamic system, and each such system has a temperature" (p 9), "the distribution of an assembly of gas particles with respect to available internal energy states is given by the Maxwell–Boltzmann formula" (p 10), "chemical equilibrium is a state in which the species concentrations in a mixture remain constant" (p 11), or definitions like the spectral radiance and related intensity quantities (pp 13, 14) and the absorption and transmission (pp 14, 15) as functions of a temperature before thermal radiators are considered on page 16. A more expository and didactic treatment in the general introduction and in the introductions to the topical chapters would considerably enhance the value of this book for newcomers to the field of spectroscopic gas pyrometry.

The author is to be commended for his considerable efforts in presenting a generous and pertinent collection of references from which the reader can extract details about the methods and the techniques discussed or mentioned in the text. His inclusion of appendices about the peaking function method for temperature contour determinations, and various methods for the determination of radial radiance profiles from lateral radiance profiles, is most welcome as an expedient dissemination of techniques, which are often only heard of among the users of gas pyrometry.

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Principles of Defect Chemistry of Crystalline Solids. By W. VAN GOOL, Scientific Laboratory, Ford Motor Company. Academic Press Inc. 111 Fifth Ave., New York, N. Y. 1966. x + 148 pp. 16 × 23 cm. $7.00.

Although Wagner and Schottky demonstrated the existence of point defects in solid compounds in 1931, the thermodynamics of lattice defects in solids has been largely ignored in formal chemical thermodynamics courses despite the fact that the presence of defects may have pronounced effects on the thermodynamic properties of a compound. One of the reasons for the neglect of this topic

may have been the lack of an elementary systematic introduction to the field from a chemist's standpoint. This little volume should fulfill that need.

A more appropriate title for the book might have been "Chemical Thermodynamics of the Defect Solid State." After a short introductory chapter on some chemical and physical aspects of defect solids, the following two chapters on the thermodynamics of lattice defects introduce the types of point defects which may be present in a solid compound, discuss applications of the mass action law, and define the thermodynamic and electrochemical potentials of lattice defects. The next five chapters treat various aspects of high-temperature equilibria: pure compounds, impure compounds, equilibrium constants, general aspects, and quenched samples. The final two short chapters briefly discuss the effects of defects on some properties of solids and outline some approaches to future work in defect chemistry. Thus, over 80% of the book is devoted to thermodynamics and chemical equilibria, and while electronic properties and catalysis are succinctly discussed, other topics relevant to the "defect chemistry of crystalline solids" such as diffusion, ionic conduction, chemical reactivity, structural transformations, and nonthermodynamic experimental techniques for detecting defects and impurities have been either completely omitted or only briefly mentioned. However, as an introductory text on the chemical thermodynamics of defects (rather than on defect chemistry, in general), this book does an admirable job.

The first few chapters are especially clear expositions of the application of thermodynamic principles to lattice defects. The systematic presentations of nomenclature, definitions, and rules for formulating reactions involving defects will be of value to the working scientist as well as to students. For example, in the formation of defects, the necessity of taking changes in the total number of sites into consideration is emphasized, and defect formation (or elimination) is expressed in terms of real and virtual quantities. These distinctions are sometimes overlooked by investigators in the field of solid-state chemistry. A later chapter on defects in samples quenched from high-temperature equilibrium conditions including a discussion of the subtle problems which may arise in explaining the electronic behavior of quenched materials also should be of particular interest to the research worker.

Most of the chapters contain a well-chosen set of problems illustrating the concepts presented in the chapter. The author points out that a few of the problems represent simplified versions of actual research subjects that have not yet been solved. Several include references to the literature. These features should be especially useful in training students.

There are several instances in the book where clarity, and even accuracy, appears to be sacrificed for the sake of brevity. The descriptions of Hall and Seebeck effects are much too condensed to be of value to anyone unfamiliar with these effects. In defining the Fermi function, reference is made to the number of energy levels with a definite energy, E, rather than to the number of levels over a narrow range of energies, $E + dE$. On page 108, it is stated that a condition for equilibrium is that the free energy of electrons must be equal in different parts of a system, and the Fermi level is described as the free energy of electrons in a solid instead of the partial molal free energy or electrochemical potential. The Fermi level is correctly defined earlier in the book (p 37), however. Although frequently mentioned, the important concepts relating nonstoichiometry and lattice defects in *pure* compounds are not sufficiently developed. Throughout the book, deviations from stoichiometry are almost always discussed in terms of impurities, and the term "deviation from stoichiometry" is algebraically defined (p 117) relative to the amount of impurities present such that the definition becomes essentially meaningless for pure compounds.

There are approximately two dozen typographical-type errors, most of which are not serious. However, the partially wrong answer in the first problem of Chapter 4 and a wrong temperature in the answer to the first problem of Chapter 5 may tend to bewilder the student attempting to solve these problems. Also confusing, is the use of capital X on page 103 to represent both the mole fraction and one of the components of the crystal. On page 74, an algebraic error leads to an incorrect conclusion regarding the relative amounts of gallium interstitial and gallium substitutional impurities in cadmium sulfide. The gallium interstitial concentration varies inversely with the total gallium concentration and is not directly proportional to the third power of this latter quantity as indicated in Eq. (5.30).

Despite its shortcomings (most of which can be easily remedied in a second printing), I can strongly recommend this book not only to students and newcomers as intended by the author, but also to instructors of chemical thermodynamics and undergraduate physical chemistry courses for inclusion of some of the subject matter into their course content. In addition, for the reasons mentioned above, I believe most chemists working in the area of the defect solid state would find it advantageous to have a copy of the book readily available.

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Dehydrobenzene and Cycloalkynes. By REINHARD W. HOFFMANN, Organisch-Chemisches Institut der Universität Heidelberg. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1967. xi + 386 pp. 16 × 23.5 cm. $14.50.

Scarcely half a dozen references to the literature prior to 1953 are needed to trace the history of dehydrobenzene (benzyne) as a recognized chemical species. Since that time, and especially since about 1960, research papers dealing with this reactive compound have been published at an ever-increasing rate. Several important reviews have appeared, but Reinhard Hoffmann's book is the first attempt to deal with the subject comprehensively, to bring together all of the synthetic chemistry that has evolved, as well as all of the mechanism studies. This attempt has been generally successful, and the book will be an extremely useful reference work.

After a brief introduction, the author discusses in detail the numerous reactions that have been found to generate dehydrobenzene. There follow two chapters devoted to "polar additions to dehydrobenzene" and to reactions with "nonpolar partners." These three chapters comprise two-thirds of the book and contain references to nearly a thousand papers. The organization of this large body of material has posed many problems, and not every one has been solved effectively. That feature of the book which most invites criticism follows from the classification of experimental results into reaction types. The products of a single preparative experiment may be reported in different sections, without cross-referencing, and without taking advantage of the opportunity which such experimental results offer for discussing the factors which influence the product distribution. For example, the reaction of dehydrobenzene with 1,3-cyclohexadiene forms three products of known structure, as the author points out on page 249. In the tabular data of Chapter 3, one of these products appears in Table 3.2 ("Ene Syntheses") and one in Table 3.5 ("Diels–Alder Additions"), and the other does not appear in the tables, possibly because it eludes classification. Unsatisfactory as this may appear, other obvious ways of organizing the material would have created a different set of problems. If, here and there, the reader finds the presentation inconvenient, he might place less blame on the author than upon dehydrobenzene itself, which has never yet failed to react, usually in more than one way.

A chapter on "Structure and Reactivity of Dehydrobenzene" is concerned with the selectivity of this species, the spectroscopic characterization of gaseous benzyne, and a molecular orbital treatment of two benzyne models, the latter section written in cooperation with H. E. Simmons. The last three chapters deal with the formally analogous 1,3- and 1,4-dehydrobenzenes, dehydroheterocyclic intermediates, and cycloalkynes.

The reviewer is unaware of any significant published work on benzyne chemistry which has been overlooked in this treatise. There are, furthermore, numerous references to unpublished work. One might question the wisdom of citing so much unpublished material, in view of the difficulties in critically appraising such experiments. In a work of this type, however, the chief value does not lie in its critical comment, but in its encyclopedic coverage, which provides the research worker with an efficiently organized key to prior work in this field. Under these circumstances one can defend including mention of all pertinent work which has come to the author's attention.

Most readers in this country will be grateful to Dr. Hoffmann for writing in English. One hopes that sales of the book in America will compensate him for persevering in a task which required the writer to bear his own burden and the readers' as well.

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BOOKS RECEIVED; *April 1968*

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