

lates the distribution coefficients of simple and complex ions of all of the elements. It also describes how these distribution coefficients can be applied to predict separations. An example of a qualitative separation scheme for a mixture of 10 elements from various groups is given. The Introduction is followed by more detailed descriptions of methods for separating the elements of each of the groups. One of these sections describes the separation of the actinides and compares their order of elution with that of corresponding members of the rare earths series.

Chapter 16, "Chromatographic Separation of Anions," is also new although part of its content was included in the first edition. It considers the more common anions; separation of the metal complex anions was covered in Chapter 15.

Chapter 17, "Inorganic Qualitative Analysis," appears in both editions but has been somewhat expanded in the latter. It is not apparent why the author retained this chapter in the new edition rather than presenting the material in earlier chapters where it would appear to fit. The description of the use of exchangers in "Spot Tests and Indicators" in this chapter is new and summarizes numerous publications describing these applications which have appeared since the first edition.

In conclusion, "Ion Exchange Separation in Analytical Chemistry" appears to be a well-organized presentation of the use of exchange resins for chemical separations. It should be of considerable value to analytical chemists and is a good general reference for all chemists.

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Progress in Solid State Chemistry. Volume 1. Edited by H. REISS, North American Aviation Science Centre, Canoga Park, Calif. The Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. vii + 536 pp. 16.5 × 24 cm. \$17.50.

It is not so long since the phrase "solid state" automatically implied a branch of physics; in retrospect this is a puzzling act of surrender on the part of chemists who have been concerned with the solid state since the inception of their subject. As pointed out by Professor Tompkins in the preface, the division of the subject between physicists and chemists—in so far as workers in either of these groups accept *any* division—is that physicists are interested mainly in the theory of the subject and an understanding of its implications; for the chemist, however, the subject is a much wider one, being concerned with the correlation of structure, energetics, reactivity, etc.—in short, almost the whole of physical chemistry.

This series sets out to provide at regular intervals a series of reviews on topics of current interest. In this first volume there are a large and varied number of articles. The Reviewer does not pretend to be knowledgeable on more than a few of these and, therefore, his remarks are restricted to a few articles in particular and to providing a summary in general of the book. In all there are eleven contributions. In a brief Chapter I, H. P. Kirchner discusses "The Thermal Expansion of Ceramic Crystals." Much original experimental data are provided and such theoretical understanding as is available is introduced. A good chapter is provided by M. F. C. Ladd and W. H. Lee dealing with "Lattice Energies." The latest experimental data are given and the variations between these values are discussed. A. Kjekshus and W. B. Pearson discuss phases with nickel arsenide structures in a long chapter in which structural data and magnetic and electrical properties are brought together. D. Grieg discusses "Lattice Imperfections and the Thermal Conductivity of Solids," while in the fourth chapter D. W. G. Ballentyne surveys briefly "Photoluminescence, Electroluminescence and Structure." "Ferroelectricity in Crystals" is surveyed by C. F. Pulvan in a long article in which a considerable amount of original work is presented. J. C. Woolley discusses alloy semiconductors; naturally most of the attention is devoted to the (post-) transition elements of interest in transistor work. Some aspects of organic semiconductors are examined by H. A. Pohl; there are no less than 176 references to this subject even though most of the work has been carried out in the past 10–15 years. L. V. Azaroff discusses "X-Ray Diffraction Studies of Crystal Perfection," and the "Applications of Nuclear Quadrupole Resonance" are reviewed by G. A. Jeffrey and T. Sakurai. I found the latter chapter very stimulating; one hopes that perhaps this technique will help in the assignment of structure in the solid state in the future as n.m.r. has done for liquids and solutions. The final chapter by

D. K. Huggins and H. D. Kaesz discusses the use of "Infra-red and Raman Spectroscopy in the Study of Organometallic Compounds." A wealth of original experimental data are presented and, although the limited space available prevents detailed discussion, the authors are able to show how widely applicable these techniques are for structural assignments.

This book is one which libraries will need to make available to chemists, but later volumes will prove more useful if fewer, but longer articles are provided. In articles such as these, it seems to the reviewer that the writers should be given scope to develop *ideas* as much as to present *facts*. One looks forward to Volume II wondering whether the Editor will be able to continue the superb impetus of Volume I.

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Mammalian Protein Metabolism. Volumes I and II. Edited by H. N. MUNRO, Department of Biochemistry, The University, Glasgow, Scotland, and J. B. ALLISON, Bureau of Biological Research, Rutgers, The State University, New Brunswick, N. J. Academic Press Inc., 111 Fifth Ave., New York 3, N. Y. 1964. 16 × 23.5 cm. Vol. I: xv + 566 pp. \$18.50. Vol. II: xv + 642 pp. \$21.00.

This two-volume treatise by a distinguished international group of authors will be of considerable value to the advanced student or investigator interested in mammalian protein metabolism. Volume I contains an excellent introductory historical chapter and Part I, "Biochemical Aspects of Protein Metabolism," comprising 10 chapters which cover all aspects of the field. These chapters include: digestion and absorption (two chapters), free amino acids and peptides in tissues, metabolic fate of amino acids, protein biosynthesis (two chapters), metabolism of plasma proteins, regulation of protein metabolism (two chapters), and elimination of nitrogen from the body. Volume II contains Part II, "Nutritional Aspects of Protein Metabolism," in six chapters and Part III, "Pathological Aspects of Protein Metabolism," in six chapters; this volume will be of particular interest to those concerned with problems in human metabolism and nutrition.

It would be unjust to single out for special mention specific chapters in a treatise by more than 30 authors. In general, the work is authoritative and clear in presentation. Some chapters are succinct in presentation summarizing major aspects of very large and general fields, but all chapters contain adequate references to other reviews as well as to specific papers. Other sections of the work, mainly in the more specialized areas of mammalian protein metabolism, are more complete in coverage. Fortunately for the progress of science and unhappily for authors, the interval between writing and publication of bound volumes inevitably leaves some gaps between the printed page and the actual state of knowledge in rapidly developing areas of investigation. The present work is no exception, but fortunately only a few chapters appear somewhat dated.

The volumes display careful editing and each contains complete author and subject indexes.

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Molecular Complexes in Organic Chemistry. By LAWRENCE J. ANDREWS and RAYMOND M. KEEFER, Department of Chemistry, University of California, Davis, Calif. Holden-Day, Inc., 728 Montgomery St., San Francisco, Calif. 1964. vii + 196 pp. 18 × 25.5 cm. \$8.75.

This book was read with the bias of one who from 1953–1957 had occasion to determine many association constants by the spectrophotometric method using a modification of the Benesi-Hildebrand treatment proposed by the authors of the present text; who found that the constants obtained frequently varied with the wave length of measurement and the concentration ranges of the components; who observed cases where the spectrophotometric method gave values in disagreement with those obtained by other physical methods; who noted instances where the treatment appeared to indicate the presence of complexes where none in fact existed; and who was led, finally, to question the significance of many of these spectrophotometrically determined values. In all of these

experiments the Andrews and Keefer treatment appeared to be giving results of precision—excellent linear plots with all experimental points apparently on the line.

This apparent precision was in part, at least, a delusion, for a more searching and penetrating analysis would reveal a considerable area of uncertainty in the values obtained. Since 1957 progress in this field has been explosive, and the basis for a more rigorous treatment of experimental data is available. In this connection it is, perhaps, pertinent to cite the following references:

- (1) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).
- (2) E. Grunwald and W. C. Coburn, Jr., *ibid.*, **80**, 1322 (1958).
- (3) N. J. Rose and R. S. Drago, *ibid.*, **81**, 6138 (1959).
- (4) M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).
- (5) P. R. Hammond, *J. Chem. Soc.*, 479 (1964).
- (6) N. B. Jurinski and P. A. D. de Maine, *J. Am. Chem. Soc.*, **86**, 3217 (1964).
- (7) W. B. Person, *ibid.*, **87**, 167 (1965).

Of the foregoing references, ref. 1 and 4 are cited in the text, "Molecular Complexes in Organic Chemistry," by Professors Andrews and Keefer, ref. 7 appeared after publication of the book, and ref. 5 and 6 were probably published after it was written. If I find myself somewhat dissatisfied with this text, it is not, however, because of the authors' failure to include a particular reference or references. It is rather that the authors' treatment of experimental methods in this field is unduly optimistic, and their discussion of the results obtained is consequently devoid of healthy scepticism. This reaction was particularly prevalent during my reading of Chapter IV which discusses the experimental methods for determining association constants and the stabilities of the complexes in solution. Here it would have been of real service to organic chemists to stress the many difficulties in these measurements and more clearly mark the numerous pitfalls that await the inexperienced investigator. The neophyte in this field will surely profit from a reading of this book, but I would strongly urge the seven references cited as supplementary reading.

Of the remaining five chapters in the book, Chapter II, which describes the spectra of complexes, Chapter III, which details the complex geometry, and Chapter VI, which discusses the relationship of complexes to reaction mechanism, will prove of most interest to organic chemists. The coverage in all three chapters is detailed and comprehensive. Where divergent views exist, they are given with little or no editorial comment. My own preference would be for a more critical even if less objective discussion.

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Thermodynamics of Irreversible Processes. By PIERRE VAN RYSELBERGHE, Stanford University. Blaisdell Publishing Co., 501 Madison Ave., New York, N. Y. 1964. 165 pp. 17 × 23.5 cm. \$7.50.

Since there have been a number of books published recently on irreversible thermodynamics, the first question which comes to mind is what features, if any, of the present book set it apart from previously published books on the subject. The material which is presented in the major books on irreversible thermodynamics falls into three major categories: (1) equilibrium thermodynamics and the calculation of entropy production rate, (2) the theoretical basis for and derivation of Onsager's reciprocal relations, and (3) applications of the theory. Both the present book and Prigogine's book of the same title include material in category 1, but Van Rysselberghe includes little material of category 2. On the other hand, he discusses many more applications of the theory than Prigogine. DeGroot's books jump almost immediately into a discussion of the theoretical basis without including a section on equilibrium thermodynamics. The present book is written on a somewhat more introductory level than the other books mentioned. Thus the book should find its place as an introductory text for those who are more interested in applications than in the development of the theory.

Van Rysselberghe's book is taken from his lecture notes for a course which he has given. The general outline of the book is similar to Prigogine's book, but the treatment is different. In terms of the number of words, Van Rysselberghe's book is approximately three times larger. Roughly the first third of the book is devoted to a discussion of those parts of equilibrium thermodynamics which are required for the remainder of the book. Thus the first and

second laws of thermodynamics and terms such as entropy, enthalpy, affinity, activity, uncompensated heat, and the chemical potentials are defined and discussed. Entropy production rates are calculated for a number of different types of systems.

Onsager's reciprocal relation is introduced as a postulate with very little mention of its theoretical basis. There is little explicit discussion of the restrictions on the fluxes and forces which are required to make the Onsager relations apply. The remaining two-thirds of the book is devoted to a discussion of various applications of the theory. These include electrochemical reactions at the electrodes in galvanic cells; transport processes between two homogeneous phases, including a discussion of the Knudsen effect and thermosmosis; fluid motion; diffusion in isothermal systems, in systems having temperature gradients (Soret and Dufour effects), and in systems having mobile charge carriers (relations between electrical mobility and diffusion coefficient); thermoelectricity and thermo-electrochemistry; chemical reactions at constant affinity and states of minimum entropy production; and viscous fluid flow. The book concludes with a short discussion of thermodynamic time.

The author's style is rather terse with a high ratio of mathematical expressions to text. There is no index; however, the Table of Contents is quite detailed.

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Applications of NMR Spectroscopy in Organic Chemistry. Illustrations from the Steroid Field. By NORMAN S. BHACCA, Varian Associates, Palo Alto, Calif., and DUDLEY H. WILLIAMS, Churchill College, Cambridge. Holden-Day, Inc., 728 Montgomery St., San Francisco, Calif. 1964. ix + 198 pp. 19 × 26 cm. \$7.95.

All persons interested in the use of n.m.r. spectroscopy for obtaining structural information of organic molecules should own this book.

In such a rapidly developing field as n.m.r. spectroscopy, the major books written on this subject 2 to 6 years ago are now seriously outdated. This timely book by Bhacca and Williams is a welcomed sight, and it is hoped that others covering different aspects of the subject will be forthcoming.

The book emphasizes proton magnetic resonance spectral correlations with the structures of steroids. Much of the material presented should be extended readily to conformationally more mobile molecules. A large part of the presentation follows closely the style of a review article. As such, the discussion in parts tend to be lacking in depth; however, this unattractive feature is offset partly by the fairly thorough and up-to-date (through mid-1964) literature references provided.

The authors' approach is to present and tabulate well-documented empirical correlations of n.m.r. parameters with structure along with a minimum of theoretical discussion. This is followed generally by carefully selected illustrations of the applications of these correlations to evaluate various structural features of steroids. The authors emphasize the numerous variables that cumulatively affect proton chemical shifts and coupling constants and they stress, often with illustrations, the potential dangers of extracting proton coupling constants from apparent first-order spectra. Examples are given that illustrate the various techniques (*e.g.*, double and triple resonance, "tickling" experiments, selective deuterium labeling, and effects of solvents) that are useful for obtaining the maximum information from complex spectra.

Particularly noteworthy are (1) the authors' review in Chapter 5 of long-range H,H and H,F spin-spin couplings, and (2) their discussions in Chapter 7 of the "reaction field" solvent effects and of the effects of benzene solvent on proton chemical shifts. Most of Chapter 7 derives from the authors' unpublished work.

The book is organized well, the spectral reproductions and drawings are clear, and only a few typographical errors are apparent ($4.5 \cos^2 \phi$ should read $4.5 \cos 2\phi$ in eq. (3-6) on p. 49). It should serve as an excellent reference source. Because of its somewhat limited general coverage and its deficiency in presenting the fundamental aspects of the topics discussed, this book alone would not be suitable as a text for an introductory course in n.m.r. spectroscopy for the organic chemist.

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