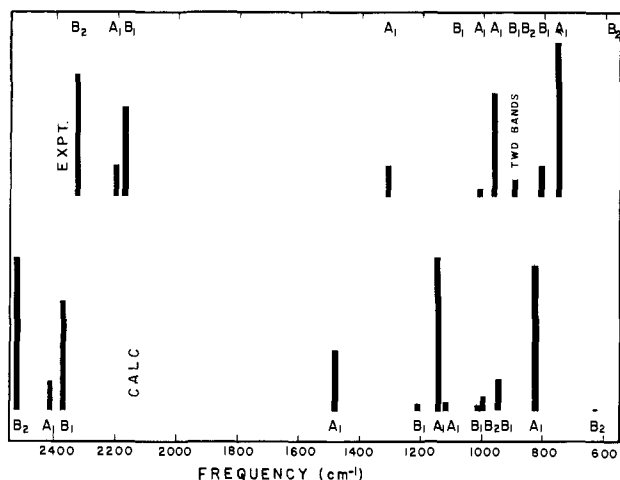


**Ab Initio Theoretical Frequencies and Intensities in the Interpretation of Infrared Spectra** [*J. Am. Chem. Soc.* 1984, 106, 4348]. B. ANDES HESS, JR.,\* L. J. SCHAAD,\* and PRASAD L. POLAVARAPU\*

Page 4351: Figure 5 was accidentally modified in printing. It should appear as follows.



**Design and Reactivity of Topologically Unique, Chiral Phosphoramidates. Remarkable Diastereofacial Selectivity in Asymmetric Olefination and Alkylation** [*J. Am. Chem. Soc.*, 1984, 106, 5754–5756]. STEPHEN HANESSIAN,\* D. DELORME, S. BEAUDOIN, and Y. LEBLANC

Page 5755, right column, line 5 from bottom: *pro*-R should be *pro*-S.

Page 5756, right column, line 4 from top: *pro*-R should be *pro*-S.

Page 5756, ref 19, line 5: *pro*-R should be *pro*-S.

**Mechanisms of Stereochemical Control in Propylene Polymerizations with Soluble Group 4B Metallocene/Methylalumoxane Catalysts** [*J. Am. Chem. Soc.* 1984, 106, 6355–6364]. JOHN A. EWEN

Page 6361, right column, Scheme III, eq 4: The rate constant should be  $k_{2,2}$ .

Page 6363, left column, 37th line: The line should read—methine and methylene groups.

Page 6363, Appendix: The left sides of eq 3 and 4 should be M—S.... The right side of eq 4 should be M—R—S....

## Book Reviews

**Chemical Thermodynamics.** By Peter A. Rock (University of California, Davis). University Science Books, Mill Valley, CA. 1983. xiii + 548 pp. \$29.00.

This is an introductory textbook, of fourteen chapters and four appendices, written for undergraduates. The first four chapters develop the fundamental concepts of thermodynamics: purpose and scope, temperature, internal energy and the first law, and entropy and the second law. Chapter 5 reviews the partial differential calculus and its applications to thermodynamic state functions. Chapter 6 deals with absolute entropies and the third law. The thermodynamics of chemical reactions (e.g., determinations of  $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$ ) is discussed in Chapter 7, while Chapters 8 and 9 deal with chemical potential, phase rule and phase equilibria, and the activity function. Equilibrium constants are discussed in Chapter 10. Chapters 11 and 12 treat activities of solution species and the thermodynamics of ions in solution. Phase equilibria in solutions are handled in Chapter 13, while a cursory examination of statistical thermodynamics is the topic of the final chapter.

In general this is a carefully constructed and well-written text. It is especially good in enunciating the very crucial concepts of work, heat, thermodynamic properties, and the mathematics governing them as they are defined and used in thermodynamic science. Many books are not sufficiently clear on these points. In this reviewer's opinion any physical science undergraduate should be able to comprehend these ideas clearly and completely after reading about them in Rock's book. The author combines a fine writing style with a reasonable economy of words. However, this latter aspect, while generally admirable throughout the text, does on occasion lead to some shallowness in the presentation of certain topics. For example, this reviewer feels that the basic *concepts* of activities are too superficially covered, and therefore there may be some vagueness and unanswered questions in the mind of an average student. It is unfortunate that the author fails even to mention the "fugacity" of a gas in connection with the ideas of activity, preferring, rather, to develop activity in a more general sense. This is not improper, but this reviewer believes that the student is somewhat short changed in this regard by at least not being made *aware* of the existence of a thing called "fugacity". It has been with us a long time, and will more than likely continue so.

The only major disappointment for this reviewer is that Rock eschews the contemporary approach to the description of chemical equilibrium in terms of the degree of advancement variable,  $\xi$ , which leads to  $dG/d\xi = \Delta G^\circ + RT \ln Q$  at constant  $T, P$ , etc. Rather, the author writes this in the older form,  $\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT \ln Q$  etc., which, unless carefully

and properly interpreted, can be quite misleading and confusing. Because of this the author has missed a golden opportunity to illustrate the manner in which total  $G_{T,P}$  of a system declines with increasing  $\xi$  for a spontaneous reaction until equilibrium is attained for minimum  $G$  at  $dG/d\xi = 0$ . Some subtle complications and confusion concerning *units* also arise from the application of this older approach. For example, in applying the older form of the equation to exercises on pp 307–8, the author obtains answers for  $\Delta G_{rxn}$  and  $\Delta G^\circ_{rxn}$  in units of kJ, rather than the proper units of kJ/mol, which automatically result when using the equation in terms of  $dG/d\xi$ ,  $\xi$  having the unit of mol (of reaction). In this reviewer's opinion this represents a step backward in the progress of the development of thermodynamic rigor and conceptual understanding.

In spite of these flaws, this reviewer highly recommends the present text for the clientele for whom it is intended. It is well written. There are but very few errors and errata. There are ample, well-selected, and instructive examples and problems. The author obviously knows his subject quite well and puts it across in a better than average manner. The only caveat is that some areas may require greater amplification on the part of an instructor. On a scale of 1 to 10, if 5 is average, then this reviewer would award Peter Rock's book a rating of about 7.5.

James L. Copeland, Kansas State University

**Biological Magnetic Resonance. Volume 5.** Edited by Lawrence J. Berliner (Ohio State University) and Jacques Reuben (Hercules Incorporated). Plenum, New York. 1983. xix + 303 pp. \$45.00.

This volume of the series consists of five chapters. The first chapter by R. L. Baxter, N. E. Mackenzie, A. I. Scott is a concise review of the applications of CMR ( $^{13}\text{C}$  NMR) to study metabolic pathways, *in vivo*. The power of CMR as a probe in the analysis of metabolic pathways at the level of cells and whole organs by following the fates of  $^{13}\text{C}$ -enriched precursors is well documented. The second chapter is a comprehensive survey of  $^{15}\text{N}$  NMR of molecules of biological interest by F. Blomberg and H. Ruterjans. The authors provided not only extensive tables for the values of chemical shifts and coupling constants of various compounds but also compact sections for the properties of  $^{15}\text{N}$  NMR and experimental considerations to overcome the low sensitivity of the  $^{15}\text{N}$  nucleus. The third chapter, by B. D. Nageswara Rao, describes the application of  $^{31}\text{P}$  NMR to enzyme systems. This chapter starts with the basic considerations pertinent to the problems in  $^{31}\text{P}$  NMR of enzyme systems followed by sections containing examples of several enzyme systems, and of computer simulations of the spectra. M.-D. Tsai and K. Bruzik summarize the use of oxygen isotopes ( $^{18}\text{O}$  and  $^{17}\text{O}$ ) in  $^{31}\text{P}$  and  $^{17}\text{O}$  NMR

studies of phosphate compounds of biological importance and their application in biochemistry. This chapter includes the tables for the  $^{18}\text{O}$  isotope shift in  $^{31}\text{P}$  NMR of various biophosphates, and for the  $^{17}\text{O}$  chemical shift and coupling constants of P-O groups. The list of applications of oxygen isotope effect on  $^{31}\text{P}$  NMR for the stereochemistry of enzyme reactions is also provided. The last chapter by P. F. Devaux presents extensive discussions on both EPR (including saturation-transfer EPR) and NMR ( $^1\text{H}$ ,  $^2\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$ ) data pertinent to the biological problems related to lipid-proton interactions. Principles and experimental considerations are briefly given on the techniques presented. The author describes the information available by these methods and their various limitations.

Magnetic resonance spectroscopy is one of the most common techniques used in biochemical and biophysical research. The salient feature of this series of publication is its coverage of topics in both NMR and EPR in a thorough and pedagogical fashion. This volume continues this series at its high level. This series is a necessity for biomedical and chemistry libraries, and essential reading for researchers in biochemistry and biophysics.

Masao Ikeda-Saito, *University of Pennsylvania School of Medicine*

**The Phthalocyanines. Volumes I and II.** By Frank H. Moser (Consulting Chemist, Holland, Michigan) and Arthur L. Thomas (Hull and Co., Greenwich, Connecticut). CRC Press, Boca Raton, Florida, 1983. Volume I: v + 227 pp. \$84.00. Volume II: V + 157 pp. \$75.00.

According to Drs. Moser and Thomas, phthalocyanine was the first organic molecule to undergo complete X-ray analysis. The electronic properties and the thermal and chemical stability of metal phthalocyanines have given rise to the widespread industrial use of these compounds as pigments and catalysts. The present two-volume set updates an earlier monograph which Moser and Thomas published in 1963 and provides a review of phthalocyanine chemistry covering the years 1963-1975. Approximately 3500 references are cited.

Volume I deals with the physical and chemical properties of phthalocyanines and Volume II with synthesis and commercial uses. The first volume describes extensively the optical and magnetic spectroscopy of phthalocyanines, areas in which there was significant progress in the 12 years reviewed by the authors. This volume also contains a short but interesting chapter on the use of phthalocyanines in laser design. These compounds are finding application in Q-factor modulation and Q-switching as well as in wavefront multiplication.

Volume II describes the preparation of over 50 different metal phthalocyanines. The chapter on industrial applications describes traditional uses in oxidative catalysis and pigment preparations as well as newer applications in the design of semiconductors and in Xerography. A chapter on phthalocyanine polymers provides a glimpse of an exciting area which will develop in the future.

Except in their choice of topics, the authors give little evaluation of those developments in phthalocyanine chemistry which they consider most important. Furthermore, they do not offer the reader any critical guidelines concerning the results they cite. Nevertheless, these volumes provide an extensive bibliography to the recent literature and as such are very useful.

Pierre LeBreton, *University of Illinois at Chicago*

**Chemical Reaction Equilibrium Analysis: Theory and Analysis.** By W. R. Smith and R. W. Missen. John Wiley and Sons, New York. 1982. xvi + 364 pp. \$42.95.

The subject of equilibrium calculations has long presented a number of pedagogical difficulties at the early undergraduate level, even though the solutions generally involve the conceptually simple procedure of solving  $n$  mass/charge balance equations for  $n$  unknowns. The complexity arises from nonlinearity introduced by the equilibrium constraints. To minimize computation in dealing with pH, the student is traditionally presented with a number of approximate equations, each of which applies to a certain situation. The relationships between the equations are vague, and the transition regions where one approximation blends into another are usually avoided. Complex ion equilibria are treated even less satisfactorily. Lip service is paid to stepwise formation, but the examples given are often those where the fully saturated complex is assumed to form in one fell swoop. No wonder generations of chemists have been taught to consider equilibria a mystery. This situation need not persist. All one needs to set up the rigorous equations that pertain to a given situation is a feeling for simple stoichiometry. Present-day computing power, even in hand calculators, reduces the computational difficulties to trivial levels. In the book under review, the authors, one a mathematician and the other a chemical engineer, present a thorough discussion of rigorous solutions to equilibrium problems and discuss and provide

listings of several algorithms which have been developed.

In the early chapters of the text, stoichiometry, equilibrium theory, and thermodynamics are reviewed. The discussion is at an advanced level and presented in the context of matrix algebra. In an interesting treatment, even stoichiometric equilibrium relationships are obtained by using matrix rank analysis.

In the middle sections, rigorous approaches for simple equilibrium systems are introduced. Numerical methods useful for solving these types of equations are surveyed, and the concepts are combined with those introduced earlier to provide the tools for more complicated systems. The final discussion is devoted to deviation from ideality, sensitivity of results to parameter values, the influence of initial estimates, isotopic and isomeric computations, and problems involving constraints other than constant  $T$  and  $P$ . The final third of the book provides valuable program listings. These are given in three languages: BASIC, FORTRAN and the programming language for the HP41C calculator.

The book is not aimed at chemists. Numerous examples illustrating the principles are worked out in each chapter. The major thrust concerns industrial applications, while complex-ion equilibria and equilibria pertinent to biochemistry receive minimal attention. The authors prefer to obtain equilibrium distribution by minimizing free energy functions, rather than employing the equilibrium constant expressions that are more familiar to chemists. Finally, a serious omission is the total neglect of the elegant contributions to this area of chemists who have been interested in solution interactions.

This text would not be suitable for use in an undergraduate course on equilibrium unless the students have had a good course on matrix algebra. However, anyone interested in this subject should become familiar with this work as one source, among several.

Daniel L. Leussing, *The Ohio State University*

**Studies in Organic Chemistry. Volume 5. Comprehensive Carbanion Chemistry. Part B: Selectivity in Carbon-Carbon Bond Forming Reactions.** Edited by E. Bunce (Queen's University) and T. Durst (University of Ottawa). Elsevier Science Publishing Co., Inc., New York. 1984. viii + 304 pp. \$83.00.

The five photocopied manuscripts in somewhat different typescripts are (1) Formation of carbon-carbon bonds via  $\pi$ -allyl complexes of transition metals by L. S. Hegeudus, (2) The syn effect and the use of enolate equivalents in synthesis by R. R. Fraser, (3) The formation and transformation of allenic- $\alpha$ -acetylenic carbanions by R. Epsztajn, (4) Stereoselective aldol condensations by C. H. Heathcock, and (5) Techniques in carbanion chemistry by T. Durst. An adequate index is included and structures are professionally drawn. Chapter 1 contains no references to work after 1980, while Chapter 4 was written in December 1980-January 1981 and is covered in other more recent reviews published in 1982-1983. Chapter 5 concerns the preparation and reactions of organolithium reagents and is more representative than comprehensive although it does contain references from 1982 to 1983.

Glen A. Russell, *Iowa State University*

**The Foundations of Chemical Kinetics.** By Sidney W. Benson. Robert F. Krieger Publishing Company, Malabar, Florida. 1982. xvii + 723 pp. \$39.50.

When the first version of this book appeared in 1960, it met the goal of its title by providing a thorough and complete foundation for chemical kinetics. This 1982 version bears the same title but is described as an updated and corrected edition. The updates, however, consist of a few modifications of certain sections and the addition of several very helpful Tables in Appendix C and Appendix D under the titles "C. Some Thermodynamic Data for Atoms, Molecules, and Free Radicals in the Gas Phase" and "D. The Estimation of Thermodynamic Properties of Simple Molecules in the Ideal Gas State." If the Tables of Contents of the two books are compared, there are few differences, even to having the same page listings. A careful reading, however, reveals the small modifications which were made as improvements.

It is unfortunate that the updating did not include many of the topics which are presently at the forefront of kinetics research, such as results from surface reactions and the whole area of molecular beams. One could conceivably argue that once the foundation is reasonably well described, the extension to new areas of research will utilize the same foundation. There are new concepts which should be addressed, however, and the use of the new Benson book as a text for a graduate kinetics course will require supplements and recent literature references to provide a modern introduction to the topic.

James W. Taylor, *University of Wisconsin—Madison*