Book Reviews

Valence Bond Theory and Chemical Structure. By D. J. Klein (Texas A&M) and N. Trinajstic (Rugjer Boskivic Institute). Elsevier: Amsterdam. 1990. xii + 630 pp. $215.50. ISBN 0-444-88186-7.

Given the continued growth in molecular mechanics level molecular modeling (explicitly based on a localized description of bonding), high-T_c superconductors (where electron–electron interactions are the essence of the effect), and the general acceptance of the importance of static as well as dynamic electron correlation effects in chemical bonding, this is a timely book. In the introduction the authors discuss rather nicely the criticisms presented over the years regarding the comparitive worth of molecular orbital theory and valence bond theory. The book then continues with discussions of the methodology involved, the modern algorithmic implementation of the methodology, and applications to larger molecules and concludes with applications in polymers, metals, alloys, intermetallic compounds, and high-T_c superconductors. The discussions of the algorithmic development are particularly useful for someone considering implementing a valence bond approach for inclusion of electron correlation. This book is certainly recommended for libraries and for researchers in the area of electronic structure as well as physical chemists wanting an exposure to some important developments in electronic structure theory.

Anthony K. Rappe, *Colorado State University*

Detection-Oriented Derivatization Techniques in Liquid Chromatography. Edited by H. Lingeman (Leiden University) and W. J. M. Underberg (State University of Utrecht). Marcel Dekker, Inc.: New York and Basel. 1990. xvi + 389 pp. $99.75. ISBN 0-8247-8287-9.

Fifteen authors with expertise in the field of liquid chromatography (LC), derivatization methods in chromatography, and pharmaceutical analysis have contributed to this book. The book is Volume 48 of the Chromatographic Science Series. Its objective is to provide the interested reader with the fundamental and practical aspects of derivatization reactions and techniques used in liquid chromatography with emphasis on "the quantitative determination of drugs and drug metabolites in pharmaceutical formulations and biological fluids".

The book can be divided into two interrelated sections: (i) an introductory section grouping four chapters that describe the basic elements for selecting the appropriate derivatization techniques and procedures to enhance detectability in LC separation, and (ii) a section of six chapters each of which emphasize specialized detection-oriented derivatization procedures concerning either a group of compounds, e.g. enantiomeric and enzymatic derivatizations, or a particular detection technique such as absorbance, amperometric, chemiluminescence, and fluorescence detection.

Chapter 1, by H. Lingeman and W. J. M. Underberg, on derivatization in LC, introduces the reader to the rationale of derivatization and provides a comprehensive description of the optimum conditions for derivatization reactions and the proper choice of suitable derivatization reagents. It also covers the necessary equipment and the chromatographic systems used in combination with derivatization reactions.

Chapter 2, by A. N. Fruijtier, H. Lingeman, J. H. Beijnen, and W. J. M. Underberg, is an overview of the most important derivatization reactions in LC as well as the factors that effect the reaction rate, e.g. solvent, temperature, concentration, and substituent effects.

In most chemical analyses an enormous amount of effort and time may be spent on sample pretreatment. This is the subject of Chapter 3, by H. Lingeman and U. R. Tjaden. It is a rich source of information on many methods for extracting the analytes from various matrices.

Thereafter, the book furnishes the steps required for separation and derivatization in post chromatographic format in Chapter 4 by G. J. de Jong, U. A. Th. Brinkman, and the late R. W. Frei. This chapter discusses the fundamentals and applications of a wide variety of post column reactors including open tubular, segmented stream, and solid-state reactors.

An overview on enantiomeric derivatization is provided in Chapter 5 by S. Gorog. After a brief discussion on chromatographic separation of enantiomers, the author provides a comprehensive survey on chiral and achiral derivatizations. Thereafter, enzymatic derivatization techniques are treated in Chapter 6 by F. C. Van Krimpen and M. A. J. van Opstal. This chapter familiarizes the reader with the basic principles of enzyme-catalyzed reactions and discusses briefly the various enzyme reactors that have been developed for selective detection by HPLC and especially those based on enzymatic immunoassay methodology.

The book ends with a series of four chapters that treat specialized derivatization techniques. These are ultraviolet–visible derivatization (Chapter 7, by J. A. P. Meulendijk and W. J. M. Underberg), electrochemical derivatization with emphasis on amperometric detection and its advantages and disadvantages with respect to other techniques (Chapter 8, by J. A. Lisman, W. A. Underberg, and H. Lingeman), fluorescence derivatization with an overview of derivatization reagents, methods, and applications (Chapter 9, by J. Goto), and chemiluminescence derivatization (Chapter 10, by K. Imai).

In summary, the book is well-organized, well-illustrated, and concisely written. The 1200 bibliographic citations and 120 diagrams and photographs make the book a handy reference for students and researchers new to the field as well as for experienced investigators. The strengths of the book outweigh its weakness. As do all types of monographs, it suffers from the inevitable delay between the writing and publishing, and as a result, it references literature up to 1988. Although some recent advances have been made in the field of derivatization for LC, much of the early work is also significant and their comprehensive coverage by this book can be regarded as one of its many strengths. The book is highly recommended for every library and for individuals whose research activities involve chemical analysis with high sensitivity and selectivity.

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Theoretical Foundations of Radiation Chemistry. By Jaroslav Bednár, translated by the author (Institute of Nuclear Research, Řež, Czechoslovakia). Kluwer Academic Publishers: Dordrecht, Boston, and London. 1990. 281 pp. $96.00. ISBN 90-277-2668-X.

As pointed out by the author, radiation chemistry deals with all aspects of the action of high-energy radiation on atomic, molecular, and more organized matter. This includes energy-loss processes of charged particles; ionization, excitation, dissociation, and other fast physical and physicochemical processes occurring on time scales of 10^{-15} to 10^{-12} second; and subsequent relaxation processes, solvent polarization, diffusion, reactions of ions, excited states, and radicals, etc. which lead to intermediates and products on time scales from picoseconds to milliseconds, and longer. Accordingly, in attempting to write a book on theoretical foundations of radiation chemistry, Bednar has set himself a difficult task.

The organization of the book is rather conventional. There are four chapters on fast physical processes such as energy loss by charged particles, excitation, and ionization; a chapter on primary radiation chemical yields; a discussion of track effects; and a chapter relating theory with experiment. A 6-page addendum summarizes work which appeared while the book was in production. By contrast, Bednar's approach to his subject is rather unusual. He intentionally avoids discussion of specific chemical systems throughout much of the book, but instead tries to describe each phenomenon on the most fundamental basis possible. In some instances, this approach results in a discussion which approaches the philosophical. Typically, theories are presented in terms of integrals over functions which are described in broad terms, but which are rarely given explicitly, or numerically evaluated. However, the author is thoroughly familiar with the literature of theoretical radiation chemistry; abstract discussions of the sort described include references to more pragmatic presentations and computations in the literature, when such exist.

Bednar's book does not appear suitable as a text, or for personal study by someone seeking a first introduction to theoretical radiation chemistry. However, it would serve as a good guide to the literature for such an individual. One suspects that the author's main purpose may be to bring to the attention of other experts in the field certain nuances, new approaches, or crucial physical foundations which may have been overlooked previously, but which may ultimately prove fruitful in providing new insights for workers in this field.

Robert J. Hanrahan, *University of Florida*

Introduction to the Theory of Benzenoid Hydrocarbons. By Ivan Gutman (University of Kragujevac, Yugoslavia) and Sven J. Cyvin (University of Trondheim, Norway). Springer-Verlag: New York, 1989. 152 pp. $79.50. ISBN 0-387-51139-3.

This book summarizes the major current developments and theoretical results on benzenoid hydrocarbons, presented from the viewpoints of two of the outstanding practitioners of chemical graph theory. The first two chapters present crucial definitions which clarify the scope of the work.

This scope is generally taken as restricted to the benzenoid hydrocarbons that correspond to a set of polyhexagonal drawings which are termed "benzenoid systems" (more about this later). The third chapter discusses topological and other structural features of the benzenoid system graphs, including classifications based on symmetry, numbers of edges, vertices, internal vertices, etc., and this chapter also gives definitions for the concepts of fjords, coves, and bay-regions in the perimeters of benzenoid systems. Ensuing chapters present summaries of many types of enumeration problems for benzenoids, discussions of resonance theory and the theory of conjugated circuits, an illuminating discourse on the concept and use of the aromatic sextet, and some results on benzenoids with holes (coronoid systems). The concluding short chapter has a very interesting section outlining speculation on the occurrence and abundance of benzenoid hydrocarbons in interstellar space. In fact, two nice aspects of this book are historical and chemical details which are interspersed throughout the text.

However, the highly restricted scope of the ideas and results presented in this book limits its useful lifetime. The main difficulties are the assumptions that planar polyhex figures excisable from the planar hexagonal lattice (defined as benzenoid systems) have a one-to-one correspondence with chemical species known as benzenoid molecules and that the benzenoid molecules are therefore required to be "planar or, to be less exclusive, nearly planar" to use their phraseology. This, in spite of the fact that the larger fraction (e.g., 86% of 14 107 cata and pericondensed systems with 10 rings) of even the systems in their restricted set would represent highly nonplanar mixtures of diastereomers and/or pairs of enantiomers. The authors are certainly aware of this circumstance, and on p 5 (Chapter 1) they refer, for example, to the experimentally established nonplanarities of admissible [4]- and [5]-helicenes and also to the defined exclusion of [6]-helicenes from the class of benzenoid molecules.

The effect of the Gutman-Cyvin definitions and restrictions is to obscure the correspondence of the theoretical results in this book with real chemistry. Nowhere is this more evident than in the numerous discussions and tabular data on point group symmetries of benzenoid systems which form an important part of the discourse. Rather than discuss this matter at length, I will just mention the fact that the only point groups given in figures and several tables throughout the book refer to symmetry species with a horizontal plane of symmetry, whereas the majority of corresponding benzenoids could only possess chiral point groups or inversion centers.

Still, I recommend the acquisition of this book, especially for those who have some interest in the applications of graph theoretical and topological ideas in chemistry. The inclusion of the historical vignettes and interesting chemical facts about benzenoids, combined with the clear expository writing and up-to-date summary of graph theoretical results, make this a book well worth acquiring.

William C. Herndon, *University of Texas at El Paso*

Particles on Surfaces 2: Detection, Adhesion, and Removal. Edited by K. L. Mittal (IBM US Technical Education). Plenum Press: New York and London. 1988. viii + 328 pp. $82.50. ISBN 0-306-43367-2.

This is the second volume documenting the proceedings of a series of symposia devoted to the study of Particles on Surfaces, and it deals with the second meeting, held in Santa Clara, California, July, 1988. This volume contains 25 peer-reviewed papers delivered at the meeting, which was dedicated to the topic of Detection, Adhesion and Removal topics.

Papers are grouped into four parts. Part I is devoted to particle–substrate interaction, deposition, and adhesion. Part II is devoted to particle detection, analysis, and characterization. Part III is devoted to particle prevention and implications. Part IV is devoted to particle removal.

The material is often of a highly technical and applied nature. More fundamental matters addressed include theoretical models for the adhesion of small particles to surfaces and the analysis of particles on surfaces using a variety of surface analytical tools. A number of experimental papers are included that address such matters as particle kinetic energy loss measurements, measurements of adhesion forces, adhesion induced particle deformation, the measurement of the presence of contaminant particles on clean room garments and electronic equipment, the adhesion of drug particles to surfaces, the behavior of wear resistant coatings, and the effect of particle contamination on thin film growth and electron beam lithography. The fourth part of the book is devoted to the removal of particles by methods such as solvent cleaning with high molecular weight fluorocarbon surfactants, Freon, and water. Ultrasonic and hydrodynamic cleaning methods are also discussed.

Surface-analytical methods discussed include X-ray photoelectron spectroscopy (XPS or ESCA), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), ion-scattering spectroscopy (ISS), low-energy electron diffraction (LEED), reflection high-energy electron diffraction (RHEED), scanning electron microscopy (SEM) (the most widely used method), energy-dispersive X-ray analysis (EDX), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, and mass spectrometry. The role of high-performance liquid chromatography (HPLC) is discussed as a means of monitoring cleanliness. The extent of discussion of these approaches varies, but the papers provide useful examples of the role of these analytical methods for particle analysis.

The volume provides the reader with a useful perspective on the current state of research on the interaction of particles on surfaces. It will clearly be most valuable to the highly specialized audience. As with many such collections of papers it does not make light reading. There are substantial differences in content and approach from paper to paper, despite the appropriate grouping of the papers into four sections. This reflects the diversity in the field. Certainly the work allows the reader to appreciate the application of general approaches (such as surface analytical methods) to the area, as well as approaches that are specific to particle problems. The latter includes impact adhesion theory, the particle energy loss measurements, the estimation of particle densities, and studies of particle generation and removal.

Peter M. A. Sherwood, *Kansas State University*

Chemical Kinetics: The Study of Reaction Rates in Solution. By Kenneth A. Connors (University of Wisconsin). VCH Publishers: New York. 1990. xiii + 480 pp. $49.50. ISBN 1-56081-053-X.

Chemical kinetics, like its counterparts thermodynamics and structure, is a topic of universal interest and necessary study for any student of the molecular sciences. Perhaps because of this breadth there have not been many universal texts that can thoroughly introduce the student to this complex and fascinating field of study. The author has accepted this difficulty and chosen to develop an introductory treatise aimed at an advanced undergraduate or beginning graduate student audience interested in understanding kinetic phenomena in the solution phase. In the process, however, a book has been developed which provides an excellent primer for anyone wishing an introduction to the methods, mechanics, and problems of chemical kinetic study.

The book starts with three chapters devoted to the introduction of phenomenological rate processes from simple to complex with careful emphasis on the realistic problems encountered. A refreshing aspect of this treatment is the care taken to detail both elementary methods for the solution of integrated rate forms as well as the more complex methodology required for many realistic chemical mechanisms. In particular, excellent, lucid discussions are made regarding methods of Laplace transforms, eigenvalue or matrix solutions, numerical methods, and Monte Carlo simulations. These treatments are quite effective and are well referenced.

Chapter 4 presents a treatment of fast kinetics focussing on relaxation and nuclear magnetic resonance methods.

Chapter 5 is a treatise of solution reaction rate theory with particular emphasis on transition-state theory and a good introduction to potential energy surfaces. If there is any particular limitation to the topics presented in this book, it lies in the focus of this chapter. Although the material to this point is entirely general in its applicability to all students of kinetics, the theory treatment is entirely devoted to an elementary discussion of the simplest models of microscopic kinetic mechanisms. This limitation can be easily surpassed by reference to the cited literature or, in the case of the instructor, by supplementary lectures regarding non-Arrhenius systems and non-statistical effects in reactivity. The final three chapters ambitiously explore realistic problems of study regarding internal (isotope, charge, and structure effects), as well as external, medium influences on bulk reactivity taken from classical, as well as quite current, literature. Each chapter includes an extensive set of references as well as a modest problem set for which brief answers are provided in an appendix.

This text provides a lucid and quite current introduction to solution kinetics and is a valuable addition to the field. Owing to its superb treatment of kinetic analysis, it promises to find a place in the introductory education of students of kinetic phenomena cross the spectrum of chemical studies.

Mark A. Smith, *The University of Arizona*

Physiology of the Bacterial Cell: A Molecular Approach. By F. C. Neidhardt (University of Michigan), J. L. Ingraham (University of California, Davis), and M. Schaechter (Tufts University). Sinauer Associates, Inc.: Sunderland, MA. 1990. xiv + 507 pp. $43.95. ISBN 0-87893-608-4.

From its beginnings, microbiology has been the field of biology most concerned with the chemical activities of living cells. Early microscopes did not permit the fascination with anatomy that characterized other fields of biology, so investigators have long placed emphasis on the nutrients and end products of microbial growth. The broad acceptance of a small number of bacterial species, such as *Escherichia coli*, as convenient systems for biochemical analysis and the rapid rise of bacterial genetics over the past 50 years have provided an impressive chemical description of the structural and dynamic characteristics of numerous bacteria. Bacterial physiology is a truly molecular science.

In this excellent volume, the structure of typical bacterial cells and the major pathways of biosynthesis and energy-yielding metabolism are clearly and vividly presented. These chapters do not simply repeat the cataloging of such pathways found in many biochemistry texts, however, because aspects unique to bacteria are strongly emphasized, as are careful metabolic cost accounts for the major pathways. The physiology of bacteria, as opposed to descriptive biochemistry, gives the book its uniquely useful focus. Thus, major chapters are devoted to such issues as metabolic regulation, with a welcome emphasis on global or multigene regulatory networks. Likewise, bacterial cell division and growth, responses to environmental stress and ecological competition, and means of genetic exchange receive full attention. The scope of the volume permits little more than a fascinating peek at some of the best-studied systems of prokaryotic cellular differentiation, but that chapter is vividly and thoughtfully written.

The book is very well illustrated and written in pleasing, lively style. The authors not only give us the current picture of the subject, but repeatedly identify the unsolved problems and intriguing vistas for future research. I found much to praise and little to criticize. Inevitably, given the massive use of *E. coli* as the standard laboratory species for biochemical studies over the past 50 years, the book relies heavily on our knowledge of the physiology of that organism. However, the authors have very frequently introduced descriptions of many other microbial species to enrich and broaden the text. I would have wished to see a chapter on macromolecular degradation and intracellular turnover in bacteria to complete the picture of the cells' physiology, but its omission is not a serious flaw. The book concludes with 6 pages of references to the literature. These are as recent as 1989 and come largely from the review literature. There are points in the text when an investigator will wish to have references to the original research papers. This would have greatly cluttered the flow of the narrative, however, so the authors' decision to reference reviews and treatises is understandable.

Physiology of the Bacterial Cell is a truly superb text for advanced undergraduates or graduate students of microbial physiology. A background in general microbiology and biochemistry is required by users of the book. It is also an excellent resource for active researchers in microbial physiology and biochemistry. The authors deserve our praise, not only for this vivid and complete presentation of the excellent past progress and current status of research in molecular physiology of bacteria, but for constantly reminding us of the fascinating and important problems in this field that have yet to be solved.

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Thermodynamics. An Advanced Textbook for Chemical Engineers. By Gianni Astarita (University of Delaware and University of Naples). Plenum Press: New York and London. 1989. xi + 444 pp. $69.50. ISBN 0-306-43048-7.

Traditional books on chemical engineering thermodynamics are largely expositions of the equilibrium properties of fluids and phase, especially vapor–liquid equilibria. However only about 25% of this book is directly devoted to such topics. Substantial attention is given to chemical equilibria, relaxation, and dissipative phenomena, surfaces, polymers, electrochemistry, and electromagnetism. Two chapters are contributed by other authors.

The first half of the book, entitled Macroscopic Theory, develops principles suitable for this wide range of topics. The first and second laws are presented in general forms which extend to non-equilibrium and non-uniform systems. A series of more restrictive versions for various special cases is derived in the next few chapters. These include local versions for equilibrium and non-equilibrium systems.

An extensive treatment of reacting systems is given. It starts with a single reaction proceeding in a homogeneous system, continues to the general case of multiple reactions and phases in equilibrium and non-equilibrium systems, and ends with the continuous descriptions of very complex systems.

In all of these discussions a distinction is made between internal and external variables. External variables represent conditions that can be imposed on a system from the outside at any particular time. Examples are volume, temperature, and pressure and their rates of change. Internal variables represent properties of the system that cannot be externally imposed. Examples are concentrations of components in a reacting system and other measures of dissipation. A distinction is also made between the state and the site of a system. State variables are a particular set of independent external, and possibly internal, variables. They define the state at an instant of time. Site variables are a set of external variables that can be assigned independently of time. Thus, for example volume and its rate of change could both be chosen as state variables but not as site variables. This leads to a general definition of equilibrium as the condition attained by a system when the site has been held constant for a sufficient length of time.

The second half of the book, entitled Engineering Theory, applies these principles to a variety of practical topics.

The multiplicity of symbols used by different textbook authors has plagued teachers and students of thermodynamics since its beginning. To help remedy this situation the International Union of Pure and Applied Chemistry has recommended a basic set of symbols for thermodynamics. These recommendations have heavily influenced textbook writers during the past two decades, even when they have not adopted them entirely. The IUPAC recommendations do not cover the breadth of theory and applications presented in the book under review here. The author's solution is largely to ignore these recommendations. Each chapter is preceded by a glossary that defines the symbols for that chapter. A few symbols are common to all, or most chapters, but most are specific to each chapter. A peculiarity is the inclusion of units as part of the symbol definitions. The units are a mixture of SI units and older metric units. Thus, for example, the calorie or kilocalorie is used for energy and the atmosphere for pressure. But the meter is used for length and the kilogram for mass. Few people will be comfortable with these combinations. However since few numerical examples are presented, either in the text or in the problems at the end of each chapter, the choice of units is nearly irrelevant.

On the positive side the book presents a rigorous and systematic exposition of modern thermodynamic theory and applies it to a wide range of potential interest to chemical engineers. Careful attention is paid to many relationships which are left murky in most elementary textbooks. It *is* suitable only for students who have already mastered elementary thermodynamics and have achieved sufficient sophistication in mathematics.

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Nuclear Magnetic Resonance: Principles and Theory. By Ryozo Kitamaru (Ryokuku University). Elsevier Science Publishers B.V.: Amsterdam. 1990. XIII + 299 pp. $128.25. ISBN 0-444-88185-9.

This book is a comprehensive exposition of the quantum mechanical basis of nuclear magnetic resonance, with emphasis on the general theory worked out by Kubo and Tomita. In the preface, it is stated that most articles and books presenting the basic theory of NMR spectroscopy are written for physicists and this book is directed more toward experimental chemists and engineers. In working toward this goal, the author has begun his work with a first chapter on the framework of quantum mechanics, intended to bring the neophyte up to speed, and then discussed spin operators, nuclear magnetic susceptibility, dipolar broadening, the general theory of Kubo and Tomita, relaxation, and NMR spectroscopy in solids. The presentation is, indeed, very systematic and complete and rehearses in logical succession the development of theory to date. However, it will be a rare chemist or engineer with no previous experience in these matters who will be able to follow the development and benefit by it. This is in part owing to the unrelieved emphasis on the mathematical theory without relation to applications. Some applications are discussed in the final chapter, mainly solid-state studies of polymers. Most experimental engineers and chemists will find this book very tough to read and comprehend and without apparent direct relevance to their interests.

There is, however, an audience who will want to have, and study, this book. Those who are involved with, and interested in, spin dynamics and the complicated and difficult task of understanding exactly what it is that the spins are doing in there, as they are affected by the static field, dipolar interactions with other spins, the motions in the environment, chemical shift tensors, scalar couplings, quadrupole moment interaction with electric field gradient, and other such intriguing factors will want to have and study this book.

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