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BOOK REVIEWS

Handbook of X-ray Spectrometry, 2nd ed., Revised and Expanded. Edited by René E. Van Grieken (University of Antwerp) and Andrzej A. Markowicz (Vienna, Austria). Marcel Dekker, Inc: New York and Basel. 2002. xvi + 984 pp. $250.00. ISBN 0-8247-0600-5.

This book is an update of the 1992 volume of the same title. As with the earlier volume, the editors have sought to provide comprehensive coverage of the methods of X-ray spectrometry and the applications of these methods to a wide range of analytical problems. In this, they have succeeded admirably. With this edition, the editors have provided significantly enhanced coverage; the second edition is more than one-third longer than the first. All of the chapters have been updated and, in most cases, expanded. Two chapters have been completely rewritten by new authors, and a new chapter on microbeam X-ray fluorescence has been added. As with any volume involving multiple authors, there is some variability in coverage and quality from chapter to chapter. However, unlike many such volumes, the authors and editors have been successful in merging the chapters into a coherent whole. Rather than repeating introductory information, often with different nomenclature, each chapter in this volume makes frequent reference to the appropriate sections in other parts of the book and, for the most part, uses consistent symbols and nomenclature. As a consequence, this reads like a single-author treatise.

In the past decade, there has been steady, and in some cases pronounced, progress in X-ray spectrometry. Particularly important are the developments in diffractive optics (zone plates and Snigirev refractive lenses) and Kumakhov polycapillary focusing optics and the advances in synchrotron X-ray sources for X-ray fluorescence studies of ultradilute samples. All of these are discussed, and the volume as a whole is quite current. The only omissions that I noted were on flash sources (e.g., laser-driven) and fourth-generation synchrotron sources (e.g., free-electron lasers), both of which are mentioned only in passing. However, their omission is not a concern, as neither has significant analytical application at present.

The coverage is comprehensive, including measurement (wavelength-dispersive vs energy-dispersive), analysis (spectrum evaluation and quantification), excitation sources (X-ray tubes; portable, i.e., radioisotope-based, sources; synchrotron sources,; particle-induced and electron-induced excitation), sample preparation, and various special-interest topics (total reflection, polarized-beam measurements). Each of the 14 chapters starts with a summary of the physics underlying its topic and then progresses to a critical discussion of selected applications. This style makes the volume quite useful for students (and more senior scientists) looking for a single source that covers all aspects of X-ray spectrometry. Although the principal audience may be analytical chemists, this volume will be of interest to anyone who makes use of X-ray fluorescence.

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JA015389K

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Analytical Mass Spectrometry. Strategies for Environmental and Related Applications. By William L. Budde (Cincinnati, OH). American Chemical Society: Washington and Oxford University Press: New York. 2001. xiv + 386 pp. $125.00. ISBN 0-8412-3664-X.

In contrast to other books describing instrumentation and applications in the field of mass spectrometry, William Budde has approached the subject from a perspective formed by years of experience working for the USEPA. During his tenure, developments in the field of mass spectrometry in general, and GC/MS in particular, have played a critically important role in identifying environmental problems and defining the scope of regulatory policy. The interplay between analytical mass spectrometry and environmental issues is a theme running throughout this book.

Budde introduces mass spectrometric approaches to the analysis of environmental samples in a rather unconventional way. Instead of walking the reader through principles of ionization techniques, instrumentation, and mass spectral interpretation, the book is focused on “analytical and mass spectrometric strategies”. The information on “strategies” is coupled with chapters that identify specific classes of compounds, matrixes, and analytical techniques (both general approaches and EPA regulatory methods). The “strategies” are described in three chapters that cover a range of topics from general approaches for electron ionization GC/MS (e.g., consideration of targeted analyte vs broad spectrum analyses and the use and merits of conventional GC/MS—the “killer application of MS”) to advanced MS capabilities (e.g., high resolution, positive and negative chemical ionization, tandem MS, and chemical derivatization). The book concludes with a brief chapter on field or process monitoring. MS techniques extending beyond conventional GC/MS (LC/MS and desorption ionization techniques) are included in one chapter describing approaches to the analysis of polar, thermally labile compounds and another that focuses on inductively coupled plasma/mass spectrometry.

Throughout the book, instrumentation and ionization techniques are deliberately introduced in a simplified manner, and this information is woven into chapters when needed in the context of an analytical strategy or method. The newcomer to mass spectrometry would best be served by also consulting a more conventional text on mass spectrometry to get a more systematic introduction to ionization, instrumentation, and mass spectral information, but Budde’s emphasis complements that of such texts. The book provides an excellent overview of mass spectrometric approaches to both quantitative measurements and

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Unsigned book reviews are by the Book Review Editor.

compound identification. Most importantly, the book provides detailed information and examples illustrating factors impacting instrument performance, options for quantification and standardization, and strategies for unknown identification (including problems that may be encountered through library search routines). The newcomer to mass spectrometry will appreciate this information.

Although the book is less focused upon the specifics of instrumentation and mass spectral interpretation, it is richly detailed regarding the historical evolution of current practices in analytical mass spectrometry, particularly for GC/MS. This book should be particularly interesting to those curious about the interplay between the developments of analytical instrumentation, environmental crises, and regulatory practices. The introductory chapter takes the reader through developments in chromatography and analytical mass spectrometry, starting in the late 1950s, that both informed and were influenced by heightened public and governmental concerns about the anthropogenic compounds in the environment. For example, a section titled “Priority Pollutants, Fused Silica Capillary Columns, and the Love Canal” describes pressures placed on the USEPA that resulted in the development of methods for the analysis of priority pollutants and the role of capillary column GC/MS in environmental monitoring at Love Canal.

This historical approach extends into chapters focused on the analysis of different compound classes, in which the evolution of EPA regulatory methods are described (and rationalized) in the context of environmental problems, regulatory pressures, and instrumental limitations and developments. This information should give the reader a better appreciation and understanding of EPA methods as well as a broader view of options and factors to consider when selecting a mass spectrometric analytical method.

On the down side, this historical perspective has led to the inclusion of much information that may be considered irrelevant to those not interested in understanding the hows and whys of method development, and some issues and information are dated. For example, some of the instrumentation mentioned is no longer commercially available or widely used, and references often cite older materials (for example, a 1976 reference to literature on packed and capillary columns), and much time is spent on the GC vs GC/MS debate. The newcomer to mass spectrometry interested in an efficient summary of the latest and most relevant information may find this approach distracting. Although this historical spin colors many aspects of the book, the book does include an overview of more recent developments in mass spectrometry (capillary electrophoresis/electrospray ionization, for example).

In summary, this book covers a full range of MS applications in the environmental sciences in an innovative way. It provides a good overview and detailed information about quantitative and qualitative mass spectrometric “strategies” that are applicable to a broad range of samples and offers valuable information about different classes of environmental contaminants (inorganic and organic). A newcomer to MS would best be served by also consulting other sources to develop a better understanding of mass spectral interpretation and the principles and practical details of instrumentation; however, this book provides a rich, historical context for many important environmental applications of MS and breathes life into many of the current practices required by regulatory methods. The book has a very limited table of contents with no chapter subheadings, which can make it difficult to locate information and sections within the chapter, but it provides a wealth of information about the strengths and limitations of mass spectrometric approaches to environmental analyses.

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JA0153215

10.1021/ja0153215

Seminars in Organic Synthesis. XXVI Summer School “A. Corbella”. June 18−22, 2001, Palazzo Feltrinelli, Università Degli Studi Di Milano, Gargnano (BS). Società Chimica Italiana. 2002. 696 pp. ISBN 88-86208-18-9.

This book presents the lectures given at the 26th Summer School “A. Corbella” seminars in organic synthesis in Gargnano, Italy, in June 2001. The book opens with the Giancarlo Jommi Memorial Lecture by P. Beak on useful concepts in organic chemistry and groups the remaining 14 chapters under the following headings: “Carbohydrates for the Life Science”, “NMR Spectroscopic Methods for the Determination of Stereogenic Elements”, “Special Organometallic Bases in Organic Synthesis”, “Low Environmental Impact Processes”, “Ethics in Research”, and “Critical Surveys Covering the Year 2000”.

JA025287+

10.1021/ja025287+

Electroanalytical Methods for Biological Materials. Edited by Anna Brajter-Toth (University of Florida, Gainesville) and James Q. Chambers (University of Tennessee, Knoxville). Marcel Dekker, Inc.: New York, Basel. 2002. xiv + 540 pp. $195.00. ISBN 0-8247-0731-1.

This book presents an authoritative and timely review of recent developments in bioelectroanalysis. Even though each chapter is written by different authors, the editors have successfully avoided significant overlaps and do an excellent job in covering a plethora of techniques. The book is focused on the determination and characterization of DNA, peptides, proteins, carbohydrates, and other organic compounds of biological origin. Despite what its title might suggest, the book does not address the analysis of inorganic analytes in biological matrixes, such as the potentiometry of blood electrolytes or the determination of heavy metal ions.

The 16 chapters have been prepared by major players in the field and cover topics ranging from the electrochemistry of DNA and proteins and in vivo electrochemistry to bioelectroanalytical sensors and their application in capillary electrophoresis and chromatography. The majority of the chapters start with an introduction that will allow even a nonelectrochemist to appreciate the level of sophistication this field has reached. However, a solid knowledge of electrochemistry is required for a deeper understanding. In many chapters, the authors concentrate to varying extents on their own work, but rarely exces sively. For example, although Rosenwald and Kuhr present a wide review of the microfabrication of electrode surfaces for biosensors and Wang discusses various approaches to sequence-specific DNA detection, neither of their articles includes a figure that directly addresses their own extensive work.

The index is carefully prepared—I missed only a few entries. With the exception of one chapter, references are completely up-to-date. The many figures are very useful to illustrate the various issues addressed by this book.

In conclusion, this book will be a very valuable addition to the library of anyone interested in the electrochemistry of biological compounds.

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JA0252476

10.1021/ja0252476

Principles of Thermal Analysis and Calorimetry. Edited by P. J. Haines (Oakland Analytical Services, Farnharm, U.K.). Royal Society of Chemistry: Cambridge. 2002. xiv + 220 pp. $44.95. ISBN 0-85404-610-0.

This book covers the principles, techniques, and applications of thermal and calorimetric methods of analysis. It features the following six chapters: "Introduction" by P. J. Haines; "Thermogravimetry and Derivative Thermogravimetry" by G. R. Heal; "Differential Thermal Analysis and Differential Scanning Calorimetry" by P. G. Laye; "Thermomechanical, Dynamic Mechanical and Dielectric Methods" by D. M. Price; "Calorimetry" by R. J. Wilson; and "Simultaneous Thermal Analysis Techniques" by S. B. Warrington. The book concludes with five appendices providing symbols of physical quantities and units; information on nomenclature; other sources on thermal analysis and calorimetry; American and British standard test methods; addresses for ICTAC and its affiliated societies; and addresses of manufacturers, suppliers, and consultancies. A subject index completes the book.

JA0252835

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Free Energy Calculations in Rational Drug Design. Edited by M. Rami Reddi and Mark D. Erion (Metabasis Therapeutic, Inc., San Diego). Kluwer Academic/Plenum Publishers: New York, Boston, Dordrecht, London, Moscow. 2001. xxii + 384 pp. $110.00. ISBN 0-306-46676-7.

The book offers a comprehensive overview of the applications of free energy calculations in drug design. The editors, who are eminent leaders in the field, have done an excellent job of collecting materials from a cross section of researchers in this area; there are some notable absentees, however, such as Karplus, Warshell, van Gunsteren, etc. The book is divided into five well-demarcated sections, each of which contains several chapters, and represents altogether a nice mix of work done in academia and industry.

The overall emphasis is on the theory, scope, and applications of the free energy perturbation (FEP) method originally put forward by Zwanzig in 1954. The topics range from tautomerism in simple heterocyclics to the development of highly sophisticated but relatively fast methods to estimate free energy changes accompanying ligand binding. The book is relatively free of complicated equations except in two chapters where they are absolutely necessary. The authors who discuss the relevant theory have succeeded in introducing the basic concepts in a simple but rigorous way. This approach makes the first half of the book quite readable. Pearlman's account gives a bird's-eye view of the history of FEP methodology. He elaborates on its limitations, especially its dependence on the simulation time, and cautions the reader about the biggest hurdle in calculation-sampling, that is, which portion of the potential energy surface is relevant and how much sampling is needed. Some of the later chapters provide nice examples of this problem, such as ionization of heterocyclic compounds or solvation free energies.

The two chapters comprising Section 3 emphasize the importance of solvation in rational drug design. Theoretical models of this fundamental phenomenon have been developed and tested with reasonable success, and various aspects of ligand binding are explored in this section. The first one, by Rao, deals with enzyme−inhibitor interactions, whereas the second one, by Kollman, concerns DNA−ligand complexes. Both authors emphasize the importance of constraint dynamics in their calculations. Thus, Rao shows that requiring coplanarity of the HIV protease more closely reproduces the experimental results than allowing the protease to be unconstrained. Similarly, a weak harmonic force is applied to avoid the disruption of the terminal base pairs of the DNA molecule in Kollman's study.

In Section 4, Åqvist applies the linear interaction free energy method (LIE) to estimate the ligand-binding affinities of a series of structurally similar molecules. This is an empirical scoring algorithm that was originally developed to be a reliable but fast alternative to the time-consuming FEP method. What is more interesting, however, are his conclusions about cases in which this model failed. He attributes the failures to the use of the same scaling factor for the nonbonded energy in the bound and the unbound molecule. This observation deserves the attention of force-field developers. Closely related to LIE is Kollman's MM-PBSA method, a combination of molecular mechanics and continuum solvent models that is discussed in Chapter 12. Only time will tell if these rapid but less rigorous methods are reliable. In the concluding chapter of this section, Singh et al. employ a quantum mechanics/molecular mechanics approach in combination with FEP to model the proton and the hydride transfers in the dihydrofolate reductase catalytic mechanism. This is one of the few cases in which FEP was used to elucidate a reaction mechanism.

Section 5 contains a collection of studies of drug design from both academia and industry. As usual, inhibition of enzymes is the subject of all the investigations. In Chapter 15, Jorgensen makes use of molecular dynamics, Monte Carlo and LIE to tackle various problems, including calculation of free energies of binding, the results of which are in good agreement with experimental values. Reddy and Appelt give an account of their successful application of FEP methods in the design of an HIV-1 protease inhibitor. Not only was the lead compound designed on the basis of an FEP calculation, but calculations of ΔG for modifications of it, in an effort to optimize the lead compound, led to predictions of the relative efficacies of the analogues;

synthesis and testing of most of these derivatives showed that their relative binding energies agreed closely with the predicted values. Another important observation in this case was that the key determinant of binding was the magnitude of the free energy of desolvation of ligands. Kollman's pictorial representation of free energy components (PROFEC), which is discussed in Chapter 17, is a qualitative method to compare the relative binding energies of a series of inhibitors. An example is given of the use of PROFEC to predict a more potent inhibitor of thymidylate synthase.

A number of force fields were used in various studies in the book, and it would be quite interesting to measure their relative performance in free energy calculations. Another item on a wish list would be an evaluation of the influence of the Ewald summation method in the calculation of the electrostatic component of the free energy.

Overall, the book meets the needs of the novice and will also be useful to the expert. By reading it, one gets an excellent perspective of the structural, conformational, and energetic features of biological molecules in relation to their functions. It is a timely addition to a computational chemist's bookshelf.

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JA025219N

10.1021/ja025219n

Topics in Current Chemistry 219. Cross-Coupling Reactions: A Practical Guide. Edited by Norio Miyaura (Hokkaido University). Springer-Verlag: Berlin, Heidelberg, New York. 2002. x + 248 pp. $169.00. ISBN 3-540-42175-0.

The use of transition metals in organic synthesis has increased dramatically in the last two decades. Transition metal catalysts provide new opportunities for highly selective reactions that are not achievable by traditional synthetic methods, and their application to cross-coupling reactions provides a new avenue to the formation of C−C, C−H, C−N, C−O, C−S, C−P, and C−M bonds. Although numerous books on this topic have been published, this book is notable because it is not only an up-to-date review on the topic but also a useful practical guide. Each chapter follows the same format and includes detailed representative experimental procedures of different cross-coupling reactions (over 50 experimental procedures are given in this book).

The book consists of six chapters, most of which describe palladium-based cross-coupling reactions. Following a concise chapter introducing cross-coupling reactions, the next three chapters cover new advances in the cross-coupling reactions of organoboron, organosilicon, and organotin compounds. The last two chapters cover two new areas of cross-coupling reactions: carbon-heteroatom bond formation and carbon−carbon bond formation via direct C−H substitution.

Generally, most of the chapters are well written, although attentive readers will find several typographical and grammatical errors. With regard to reference citations, there are ∼1080 references and >80% of these are taken from 1995 to 2001. In conclusion, this book has definite value and is a very useful practical guide that will help researchers use transition metal-catalyzed cross-coupling reactions in organic syntheses.

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JA0252532

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Annual Review of Biophysics and Biomolecular Structure. Volume 31, 2002. Edited by Robert M. Stroud (University of California, San Francisco), Wilma K. Olson (Rutgers University), and Michael P. Sheetz (Columbia University). Annual Reviews: Palo Alto, CA. 2002. xviii + 560 pp. $77.00. ISBN 0-8243-1831-5.

As with previous volumes, Volume 31 includes landmark reviews by eminent scientists in the field of biophysics and biomolecular structure. The topics covered range from computational cell biology to the evolution of protein domains to lanthanide-based probes in resonance energy-transfer measurements. The book opens with a lighthearted memoir by Feher entitled "My Road to Biophysics: Picking Flowers on the Way to Photosynthesis" and features such other sample chapters as "The Linkage between Protein Folding and Functional Cooperativity: Two Sides of the Same Coin?" and "Force Exertion in Fungal Infection". There are 19 chapters in all as well as a subject index and cumulative indexes of contributing authors and chapter titles for Volumes 27−31.

JA025284X

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Annual Review of Physical Chemistry. Volume 53, 2002. Edited by Stephen R. Leone (University of California, Berkeley), Paul Alivisatos (University of California, Berkeley), and Ann E. McDermott (Columbia University). Annual Reviews: Palo Alto, California. 2002. xiv + 634 pp. $72.00. ISBN 0-8243-1053-5.

This book contains 19 chapters on a wide array of topics within physical chemistry. A sampling of the range of topics covered includes chapters on the molecular theory of hydrophobic effects and quantum mechanical methods for enzyme kinetics as well as STM studies of the electronic properties of single-walled carbon nanotubes, to name a few. Author and subject indexes as well as cumulative indexes of contributing authors and chapter titles for Volumes 49−53 complete the book.

JA025285P

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Nano-Surface Chemistry. Edited by Morton Rosoff (Long Island University). Marcel Dekker, Inc.: New York and Basel. 2002. xii + 678 pp. ISBN: 0-8247-0254-9.

The book is a timely review of the principles, methods of characterization, and applications of surface science in the emerging discipline of nanoscale science and technology. The editor has assembled a team of international authors who have made an important contribution by summarizing the field and their respective expertise as it relates to surface and interfacial phenomena at the nanoscale. The title "Nano-Surface Chemistry" is appropriate, because it reflects the importance of surfaces and interfaces in investigating nanomaterials and nanoscale phenomena.

The book primarily describes the regimes of solid–liquid, solid–gas, liquid–liquid, and liquid–gas interfaces, as opposed to ultrahigh vacuum (UHV) environments involving the solid–solid and solid–gas interface. Understanding the balance of forces, the statistical mechanics, and the thermodynamics at this scale is essential for equipping the interested scientist with a road map for manipulating inorganic and organic molecules for new materials and applications. In reading this book, one also gains an appreciation of the challenging issues to understanding phenomena at the mesoscopic and nanoscopic scales.

The book starts with a review of surface forces, adhesion, capillary forces, and monomolecular and supramolecular ordering, to name a few, as they relate to the nanoscale. Importantly, some of the more fundamental aspects of surface science are reviewed to provide a basis for appreciating the role of forces and ordering in this science. For example, two chapters are devoted to the principles and measurement of surface forces using the surface force apparatus and atomic force microscopy, that is, defining the subtle balance of attractive and repulsive forces involved in self-organization. A chapter is also devoted to the interesting technique of scanning polarization force microscopy for investigating wetting and capillary phenomena, and several chapters are focused on monolayers, multilayers, supramolecular ordering, superlattice structures, etc. Historically, these investigations, although not termed nanoscience at the time, have given us very important groundwork for understanding complexity at this scale. In this vein, the popular technique of forming Langmuir monolayers and Langmuir–Blodgett multilayers is revisited here, especially in the preparation of nanoparticle films, arrays, and hybrid multilayers. There is also a chapter on supramolecular organic layer engineering, emphasizing its application to devices and sensors. Some mention is made of the popular alternate electrostatic layer-by-layer deposition method, but this account is not fully developed as a chapter (which could have been a book by itself). These assembly techniques are easily adapted for the manipulation of materials such as nanoparticles, nanocrystals, colloidal particles, amphiphiles, and polymers, whose size and shape could be considered simple templates for creating new nanoscale materials and defining molecular ordering.

Several chapters are devoted to mesoscopic and nanoscopic ordering of biomolecules and understanding biological phenomena. These interestingly designed biological systems, especially those inspired by nature, are important tools and materials for investigating nanoscale applications in biotechnology. In particular, DNA, proteins, enzymes, lipids, membranes (S-layers), and other biomolecules of increasing complexity have found dramatic applications as nanomaterials. Their ordering phenomena made a "programmed assembly" approach to materials feasible and gave rise to the term "nanobiotechnology". Examples have been demonstrated in the preparation of patterned films and arrays, drug delivery, biodioagnostics, biosensors, biophotonic devices, and even data storage. Since one cannot speak of interfacial science without also discussing colloidal phenomena, several chapters are devoted to the study of physical properties and ordering of colloidal particles. Their organized assembly as two- and three-dimensional lattices has seen applications in photonics and display materials. A chapter is devoted to mono- and multilayer films of these spherical particles, and interesting protocols are reviewed for the preparation of hollow capsules and core–shell colloidal particles by templating. The phenomena of micelles, polyelectrolytes, electrophoretic transport, membranes, etc., are also reviewed in relation to their enhancing possibilities for new nanoscale applications. Last, a chapter is devoted to the preparation and investigation of nanocomposite materials made from clay and polymers.

In conclusion, the references cited in the book are up-to-date and comprehensive. Unfortunately, the quality of the contributions is variable, with some chapters that are well-developed and others that are not. The authors have made every effort to relate classical topics in interfacial chemistry to nanoscience and nanotechnology. A reader who is acquainted with interfacial phenomena will see things from a different view by reading this relevant and comprehensive book.

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Information Retrieval: SciFinder and SciFinder Scholar. By Damon D. Ridley (University of Sydney). J. Wiley & Sons: New York. 2002. 252 pp. $45.00. ISBN 0-470-84351-9.

SciFinder Scholar is arguably one of the most powerful database interfaces available to scientists today. Although this search tool is intuitive to use and the program is well-documented, the process of information retrieval is a complex, yet invaluable skill best developed by active explanation and demonstration. Damon Ridley's book aims to develop the skill of information retrieval through SciFinder by teaching through example. His book will undoubtedly be a valuable aid in courses that cover the use of scientific literature, but it will equally serve the needs of individual researchers who want to improve their command of SciFinder. The book is written from a practical rather than theoretical approach; its pages are filled with numerous examples that illustrate the variety of ways that SciFinder can be used to uncover scientific information. All of the examples are taken from actual queries posed by the author. The examples are cleverly chosen to explain the algorithms behind SciFinder, revealing why various approaches yield different answer sets. The topics covered in these examples are of a broad range and of current interest, helping to make the book enjoyable to read. The presentation is well-suited to an advanced undergraduate or graduate level course.

Ridley's style is to encourage the searcher to think creatively and to apply the scientific method to the process of information retrieval. He motivates his readers by appealing to the intellectual challenge and opportunities for discovery available through the power and sophistication of SciFinder. The book does a good job demonstrating the utility of SciFinder functions, such as "analyze" and "refine". The numerous problems that appear at the end of each chapter are a very useful aspect of the book. These problems cover a wide variety of topics from chemistry to life sciences, and they span a range of difficulty.

They are certain to be very valuable for classroom instruction and discussion.

The book is logically organized around the different ways that SciFinder explores information retrieval. It has a fairly complete index and extensive appendices that contain useful information. Plenty of SciFinder screen shots are shown throughout the text to help familiarize the inexperienced searcher with the SciFinder program. The text does have a few typographical and cross-reference errors. Much of the detailed information presented in lengthy tables throughout the book is unlikely to be appreciated by the typical student reader. Aside from these minor points, this book is very effective at conveying the practicalities of scientific information retrieval using SciFinder.

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JA025244T

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Topics in Current Chemistry 220. New Aspects in Phosphorus Chemistry I. Edited by Jean-Pierre Majoral (Laboratoire De Chemie De Coordination Du CNRS, Toulouse). Springer-Verlag: Berlin, Heidelberg, New York. 2002. x + 244 pp. $169.00. ISBN 3-540-42246-3.

This volume, the first in a series, provides both a general and a detailed review of the foremost developments in phosphorus chemistry. All of the chapters contain references up to the year 2000, with some having an occasional reference in 2001. Numerous references to unpublished work and to papers submitted attest to the timeliness of the individual chapters. Each chapter contains a detailed index of topics (with page numbers), and several also include a list of abbreviations and symbols. An author index for Volumes 201−220 is provided at the end of the book.

In the first chapter, Bertrand and Bourissou detail the synthesis, structure, and reactivity of diphosphorus-containing unsaturated three-membered heterocycles and compare the neutral, cationic, and radical species of these ring systems with the analogous nitrogen and carbon systems; the authors emphasize the specificity of phosphorus relative to these other systems. This chapter is superbly written, and the system used for numbering structures makes it easy to follow the comparison arguments. This is by far the best presentation of this topic that I have seen. It will be of interest to organic, inorganic, structural, and physical organic chemists.

Carmichael and Mathey focus their contribution on phosphametallocene chemistry. New structures and reagents based upon main group complexes containing η^5-phospholyl ligands (groups 1−4), the incorporation of phospholyl ligands into transition metal paramagnetic metallacenes (groups 6, 8−10), and the application of transition-metal phospholyl complexes in homogeneous catalysis (for asymmetric catalysis) are reviewed with current timely examples.

In Chapter 3, Majoral et al. describe the use of η^2-benzyne-zirconocene and the parent η^2-phosphabenzyne-zirconocene in phosphorus chemistry. New synthetic methodologies for phosphorus heterocycles and phosphorus ligands are described, as are strategies for C−H and M−H (M = N, O, P, and S) bond activations. The extraordinary regiospecificity of reactions involving the η^2-zirconocene species is illustrated. Insertion of phosphorus-alkyne, vinylphosphine, or 2,3-dihydrophosphole exclusively gives the regioisomer in which the phosphino substituent is located on the α-position of the five-membered zirconacycle. This is the result of a strong interaction between the phosphorus lone pair and zirconium.

Next, Brunel and Buono highlight advances regarding new chiral organophosphorus catalysts for asymmetric synthesis and detail the kinetic resolution of secondary alcohols, the enantioselective borane reduction of ketones, and the asymmetric carbon−carbon bond formation with the introduction of asymmetric two-center catalysts. The review is current and well-written, with numerous schemes and tables illustrating the main themes noted above.

The coordination chemistry of white phosphorus is the subject of Chapter 5, authored by Ehses, Romerosa, and Peruzzini. They attempt to provide a homogeneous picture of the present knowledge of the metal-assisted P_4 activation from the viewpoint of the stepwise demolition of the P_4 tetrahedron. Consequently, the authors focus less on aspects of structure than on mechanism. As a mechanistic tool, a useful formalism is presented to sort the P_x fragments according to the number of bonds cleaved in the P_4 molecule. Workers in this area will find these mechanistic schemes a stimulating and exciting approach for understanding the multiform compounds produced along the degradation pathways of P_4. An outline of the general trends of the ^{31}P NMR chemical shifts for the several degradation products formed from P_4-metal activation is provided. This ^{31}P tabulation provides the worker in this field with useful information about the ^{31}P NMR properties of P_4 ligands and the range of chemical shifts exhibited by polyphosphorus complexes as a function of the P_x ligand ($x \leq 4$).

In the following chapter, McWilliams, Dorn, and Manners detail recent progress in the development of linear inorganic polymers in which phosphorus is contained in the polymer chain. Particular emphasis is placed on new polymer systems and on the synthesis of hybrid systems that incorporate phosphorus and nitrogen together with other elements in the polymer chain. For example, polycarbophosphazenes can be regarded as derivatives of “classical polyphosphazenes” in which every third phosphorus atom is replaced by a carbon atom. Similarly, in polymetallaphosphazenes, every third phosphorus atom from a classical phosphazene is replaced by a metal atom (M = Mo, W). Incorporation of a sulfur or oxygen atom, or both, results in polythiophosphazenes and polythionylphosphazenes. These new polymers are conveniently prepared by using ROMP routes or novel methods of polycondensation.

Synthetic approaches to P-chiral oligonucleotide analogues, including synthesis of isotopomeric phosphates and various nucleotide and oligonucleotide conjugates, are reviewed by Guga, Okruszek, and Stec. They give special emphasis to the application of oxathiaphospholane methodology for synthesis of P-chiral biophosphate analogues in a stereocontrolled manner. The endocyclic P−O and P−S bonds of 1,3,2-oxathiaphospholanes differ substantially, and effects of ring-strain are the major driving force of the ring-opening process as the result of nucleophilic attack at phosphorus followed by fast and irreversible elimination of episulfide. These factors are responsible for the chemoselectivity and stereospecificity observed in the ring-opening of 1,3,2-oxathiaphospholanes, providing the basis for stereocontrolled transformations of diastereomerically pure oxathiaphospholane derivatives.

The review of carbonylphosphonate chemistry by McKenna and Kashemirov in the final chapter is focused on α-keto- and β-keto-phosphonates, including two classes of trifunctional carbonyl phosphonates, α-ketophosphonoglyoxylates, and carbonylbisphosphonates. These compounds exhibit distinctive, multiple chemical properties reflecting in part the mutual interaction of their neighboring carbonyl and phosphonate groups. Special problems in synthesis are presented as well as useful applications ranging from metal chelation to medicinal chemistry. Recent (since 1995) advances are emphasized. This is a fascinating chapter, and the recent coverage of this exciting topic by these authors is excellent.

In summary, this is a volume that covers current advances in the hot topics in phosphorus chemistry. Overall, the chapters are well-written, timely, and relatively free of errors. I found the presentations exciting and stimulating and would recommend this volume to those with a preexisting interest in phosphorus chemistry as well as to those with a synthetic and mechanistic interest in the comparison of phosphorus, nitrogen, and carbon chemistry. This volume provides an excellent model for future additions to this phosphorus series.

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The Chemical Bond in Inorganic Chemistry: the Valence Bond Model. By I. David Brown (McMaster University). Oxford University Press: New York. 2002. xii +278 pp. $130.00. ISBN 0-19-850870-0.

This monograph is one in a series co-published by the International Union of Crystallography that addresses a variety of important topics in solid state science. The present volume nicely complements the others. In particular, this is the first monograph to explore the bond valence model and its theoretical foundation.

This volume consists of four main sections, each one subdivided into several chapters spanning numerous topics. In describing the bond valence model, the author compares it to other more familiar types of chemical bonding, namely, ionic and covalent. Because of recent advances in structure determination, the bond valence model is shown to be more quantitative, intuitive, and predictive. This model can be used successfully to describe the bonding properties of simple molecular structures as well as more complex extended networks. Of importance to synthetic chemistry, the model can also be used to analyze molecular interactions in aqueous or nonaqueous media. The bond valence model is also applicable to several scientific disciplines, such as physics, chemistry, materials science, and biology.

Through the use of a wide variety of examples, the author shows the reader how to apply the bond valence model and what its implications are. He intentionally steers the reader away from a pure mathematical treatment and adopts a more conceptual approach, making it more readable than most texts. The book contains five appendices and an extensive list of references, including those of historical importance. Owing to the wealth of topics and its overall readable format, anyone interested in chemical crystallography will find this book of value.

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Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry toward Heterocycles and Natural Products. Edited by Albert Padwa (Emory University) and William H. Pearson (University of Michigan). The Chemistry of Heterocyclic Compounds. Volume 59. Series Edited by Edward Taylor and Peter Wipf. John Wiley & Sons, Inc.: New York. 2002. xii + 940 pp. $425.00. ISBN 0-471-38726-6.

This is the second volume in the popular Wiley series to review 1,3-dipolar cycloaddition chemistry, the first appearing in 1984. Cycloadditions of this class provide the most versatile approach to five-membered ring heterocycles, and the field has attracted great attention during the intervening 18 years. Therefore, the current volume is timely. The editors are well-known for their extensive and high-quality contributions to the field, and they have assembled an outstanding group of contributors.

The book is divided into 10 chapters by class of dipolar species followed by two chapters of a “special topics” nature. The intention was to focus on synthetic applications to heterocycle and natural product synthesis, as opposed to theory and structure. Each of the contributing authors has adhered well to this principle, and the chapters are presented with the clarity and thoroughness one would expect of such an update. The chemistry of carbonyl ylides and nitronates was omitted in 1984, and the current review summarizes important new developments in these areas.

In such a high-quality collection, one hesitates to single out individual chapters for special mention. However, to this reviewer, the chapters on “Effect of External Reagents” by Kanemasa (Chapter 11) and “Asymmetric Reactions” by Gothelf and Jorgensen (Chapter 12) were particularly informative, since these areas have undergone impressive growth in the past decade. In addition, the chapters on nitronates by Denmark and Cottell, carbonyl ylides by McMills and Wright, and azides by Sha and Mohanakrishnan stand out because of their extensive discussions of 1,3-dipolar cycloadditions applied to the synthesis of natural products. The structural diversity of the target compounds is remarkable.

As with any undertaking of this magnitude, there are a few minor glitches and some unavoidable cases of overlap. For example, because Chapters 11 and 12 cover multiple classes of 1,3-dipoles, it is not surprising that some of the cited examples also appear in earlier chapters. In fact, this reviewer found such reinforcement helpful. As a minor criticism, the placement of schemes was sometimes distracting. Often these were well-removed from the pertinent discussion and occasionally in different sections altogether (in Chapter 11, the absence of compound numbers magnified this difficulty, because it was necessary to translate IUPAC names to structures before locating the appropriate schemes).

In general, this volume is very well written, informative, and perhaps most pleasing of all, not simply a compilation of reactions. The book is certain to be of value to all practitioners of organic synthesis as well as to members of the pharmaceutical community. Although the relatively high price will discourage addition to most private libraries, it will be a "must" purchase for all institutions involved in the chemical sciences.

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Dispersive Kinetics. By Andrzej Plonka (Technical University of Lodz, Poland). Kluwer Academic Publishers: Dordrecht, Boston, London. 2001. vi + 234 pp. $80.00. ISBN 0-7923-7128-3.

This book represents an impressive effort by a single author. A wide variety of theoretical topics are discussed, and the results of a diverse number of experiments are used to illustrate the important points. In the arrangement of the book, a little less than one-third discusses the phenomenological approach to dispersive kinetics. Approximately two-thirds of the book covers examples of kinetics in condensed media, and a small introductory section and a short section on the approximation to classical kinetics complete the book.

The chapter on the phenomenological approach to dispersive kinetics might best be described as an annotated reading list. This chapter primarily gives results from different approaches to the theory of dispersive kinetics; however, without looking up the original papers, the reader will not understand where the results came from, and, in some cases, the significance of the result will also not be clear. This approach to writing a book makes it possible for the author to cover a considerable amount of material. Some topics are introduced with little discussion to link the topic to dispersive kinetics. For example, there is a page dedicated to the Sierpinski gasket, but there is no discussion of what this tells one about dispersive kinetics. Occasionally, terms are used without definition ("ultrametric structures" is an example).

In the discussion of kinetics in condensed media, experimental results from many different topics are discussed. The topics include nonhomogeneous kinetics in radiation chemistry, reactions of electrons in glasses, solvation, spectral relaxation, micellar systems, and semiconductors, to name a few. Data appear to have been reanalyzed, and the graphs are well done and uniform in appearance. In general, the discussion seems relatively readable. There is a tendency, however, for the discussion to veer off when it should be completed with a summary.

The usability of this book as a reference is somewhat limited by (1) the absence of a symbol index and (2) a less-than-complete index. For example, "ultrametric structures" and "Sierpinski gaskets" do not appear in the index.

The major problem with this book, at least for this reviewer, is that the author is so familiar with the topic that he does not recognize what a reader with less knowledge needs to understand it. In conclusion, this book could be useful to a reader who wishes to learn the topic and has access to a good library.

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