

Additions and Corrections

Syntheses and Optical Resolution of Calix[4]arenes with Molecular Asymmetry. Systematic Classification of All Possible Chiral Isomers Derivable from Calix[4]arene [*J. Am. Chem. Soc.* **1993**, *115*, 3997]. KOJI IWAMOTO, HIROYASU SHIMIZU, KOJI ARAKI, AND SEIJI SHINKAI*

Page 3999–4000: In Tables I–III, the numbers of products are not counted correctly. If regioisomers arising from the arrangement order of different substituents are not counted, the following *O*-alkylation products should be deleted: that is, $A^\alpha B^\beta A^\alpha B^\alpha$, $A^\alpha A^\alpha B^\alpha B^\beta$, $A^\alpha A^\beta B^\alpha C^\alpha$, $A^\alpha A^\alpha B^\alpha C^\beta$, $A^\alpha B^\alpha A^\alpha C^\beta$, $A^\alpha B^\beta C^\alpha D^\alpha$, $A^\alpha B^\alpha C^\beta D^\alpha$, $A^\alpha B^\alpha C^\alpha D^\beta$, and $A^\beta B^\alpha C^\alpha D^\beta$ in Table I, $A^\alpha B^\alpha C^\beta H^\alpha$ and $A^\beta B^\alpha C^\alpha H^\beta$ in Table II, and $A^\alpha B^\alpha H^\beta H^\alpha$, $A^\beta B^\alpha H^\alpha H^\alpha$, and $A^\beta H^\alpha B^\alpha H^\alpha$ in Table III. The asterisk should be given to $A^\beta A^\alpha B^\alpha B^\alpha$ in Table I and $A^\beta A^\alpha A^\alpha H^\alpha$ in Table II.

Book Reviews *

Nuclear Magnetic Resonance. Volume 21. Specialist Periodical Report. Edited by G. A. Webb (University of Surrey). Royal Society of Chemistry: London. 1992. xxii + 594 pp. £145.00. ISBN 0-85186-442-2.

Volume 21 follows the familiar pattern for this series. The period covered is from June 1990 to May 1991. Each chapter is a separate review written by a different author. As is often the case with camera-ready publications, the font, style, and notation vary considerably from article to article. The division of the subject matter is somewhat arbitrary, focusing mainly upon applications rather than techniques, and there is no specific chapter on data processing. The book does contain a listing of NMR books and reviews as well as a comprehensive author index. However, it might benefit from a chapter summarizing the highlights of the year.

Theoretical aspects of nuclear shielding and spin–spin coupling are reviewed by Jameson and Fukui, respectively, while the applications of these parameters are reviewed by Gerathanassis and Kamienska-Trela, respectively; despite incremental progress, there seems to be little significant advance in any of these areas. Continuing this theme, Weingartner, in his review of relaxation, states, "The period under review has seen much continuing activity...but it is notable more for further development...than for complete innovation."

The coverage of solid-state NMR is divided among chapters 7, 9, 10, and 15. Chapter 7, by Groombridge, concentrates on crystalline chemical substances and experimental techniques, while the reviews of natural and synthetic macromolecules, by Parkes and Fawcett, respectively, combine both solid- and solution-state results. Chapter 8, entitled Multiple Pulse NMR contains results from the solution-state only. This is followed by a short review of conformational analysis by C. Jones and a much longer one on NMR of living systems by P. G. Morris. The book is brought to a close by reviews of imaging (MRI) by S. C. R. Williams, oriented molecules by Khetrpal, and heterogeneous systems by Halstead.

The book is a useful guide to the literature, despite the fact there is little critical comment. In many cases the reviews consist of a list of topics with corresponding references. Unfortunately, the price is almost prohibitive for individual purchase.

Christopher J. Turner, *Massachusetts Institute of Technology*

Activity Coefficients in Electrolyte Solutions. 2nd Edition. Edited by Kenneth S. Pitzer (University of California at Berkeley). CRC Press: Boca Raton, FL. 1991. x + 542 pp. \$195.00. ISBN 0-8493-5415-3.

This is a very valuable reference book for anyone interested in chemical reactions involving aqueous electrolyte solutions (geochemists, environmental chemists, chemical engineers, etc.). The book is also a very useful introduction to some of the modern methods of predicting the equilibrium

properties of aqueous mixtures with other phases. Recent work is well covered up to the date of publication (1991). There is very little coverage of nonaqueous electrolyte solutions. Measurements and estimations of standard state properties of aqueous species are outside the scope of this book, although predictions of equilibria require both activity coefficients and standard state properties. Some standard state properties are given in Chapter 7.

The introduction by Prof. Pitzer gives a very nice and concise summary of the early developments in electrolyte solutions. The first chapter by R. H. Stokes gives a short concise statement of the thermodynamic relationships and conventions necessary for calculations in this field. The second chapter by R. M. Mazo and C. Y. Mou gives an introduction to the statistical mechanical theory of aqueous electrolyte solutions. This chapter is, of course, too short for any serious student of the theory of electrolytes, but it does provide a good introduction and appropriate references. Chapter 3 by K. S. Pitzer is a clear, concise discussion of the advantages and limitations of his ion interaction model, together with the necessary equations and a large number of parameters derived from experimental data. Equations for Pitzer and Simonsen's Margules expansion model are given in an appendix. Chapter 4 by J. N. Butler and R. Roy is a very useful symmetry of potentiometric methods, and Chapter 5 by J. A. Rard and R. F. Platford is an excellent and detailed review of the isopiestic technique with a large amount of very useful and practical advice. This chapter is highly recommended for anyone thinking of making this kind of measurement. Chapter 6 by S. L. Clegg and M. Whitfield is a survey of literature calculations of the activities in natural water, mainly at temperatures up to 100 °C. A large amount of literature is covered, and the references are very valuable to anyone interested in this field. Chapter 7 by R. T. Pabalan and K. S. Pitzer on mineral solubility has the objective of demonstrating the successful use of Pitzer's molality based ion interaction equations and his Margules expansion models for calculations of solubility equilibria on a wide variety of chemical systems which are of geochemical or industrial interest at temperatures up to 350 °C. This chapter succeeds admirably in this demonstration. Chapter 8 on ion association at high temperatures and pressures by R. E. Mesmer, D. A. Palmer, and J. M. Simonson is a very thorough review of ion association at higher temperatures and pressures. It does not cover ion association measurements near room temperature, but these are well covered elsewhere. The references are up to date (1991), and this chapter is an excellent sourcebook for anyone interested in association reactions in aqueous solutions at high temperatures and pressures.

The use of Pitzer's ion interaction model to correlate and predict the properties of aqueous solutions in natural waters and mineral solubilities is particularly well covered. However, the book does not attempt to cover all possible approaches, so the serious student would want to consult other references. *The Handbook of Aqueous Electrolyte Thermodynamics*, DIPPR, New York, 1985, by J. F. Zemaitis, D. M. Clark, M. Raffal, and N. C. Scrivner is of particular interest in chemical engineering applications. Geochemists working with reactions in aqueous solutions above 300 °C will be interested in the predictions of standard state

*Unsigned book reviews are by the Book Review Editor.

properties developed by H. C. Helgeson and co-workers (Johnson, J. W.; Oelkers, E. H.; Helgeson, H. C. *Computers and Geosciences* 1992, 18, 899.).

Robert H. Wood, *University of Delaware*

Oxygen Chemistry. International Series of Monographs on Chemistry. By Donald T. Sawyer (Texas A&M University). Oxford University Press: Oxford, U.K. 1991. xii + 224 pp. \$35.00. ISBN 0-19-505798-8.

In his preface, the author describes how the acquisition of a Clark electrode in 1957 resulted in a "thirty-five year odyssey of the electrochemical reduction of dioxygen" that ultimately led to a conviction that "oxygen is the most important element in the realm of chemistry". While others, particularly organic chemists, may not be in wholehearted agreement with Professor Sawyer, this book certainly provides ample evidence for the pivotal role played by oxygen in chemical reactions that occur in the laboratory, in industry, and in nature.

The book opens with an introductory chapter (Why Oxygen Chemistry?) that begins with the first appearance of oxygen in the atmosphere more than a billion years ago as a byproduct of the photosynthetic oxidation of water by blue-green algae. Generation of the stratospheric ozone shield followed the effect of solar radiation on oxygen, paving the way to the beginning of life on the land. Molecular oxygen was independently codiscovered by Joseph Priestly (reported in 1774) and Scheele in Sweden (reported in 1777). In 1777 Lavoisier identified dioxygen as a component in air, named it oxygen, and established that it is the oxidant in fuel combustion and in respiration. In the remainder of the chapter Sawyer develops his theme of the importance of oxygen in chemical and biochemical processes while providing an overview of the aspects of oxygen chemistry to be covered in the remainder of the book. Chapter 2 deals with the redox thermodynamics of oxygen and its reduction products and their dependence on mechanistic pathway, substrate, and solution acidity. In Chapter 3, the nature of the chemical bonds for oxygen and its compounds is discussed from a valence bond point of view. In his forward to the book, Professor R. J. P. Williams calls this approach "idiosyncratic" but is quick to add that "this line of thinking has led Sawyer to look for reaction pathways, especially in non-aqueous media, which others have missed". The chemistry and biochemistry of hydrogen peroxide, alkyl hydroperoxides, and peracids are the subject of Chapter 4. The reactions of oxygen-derived radicals [HO^\bullet , RO^\bullet , $^{\bullet}\text{O}$, HOO^\bullet , ROO^\bullet , and $\text{R}(\text{CO})\text{O}^\bullet$] are discussed in Chapter 5. Chapter 6 is concerned with the reactivity of dioxygen and its activation by metals (in catalysts or metalloenzymes) that makes possible the oxidation of a multitude of organic substrates. Chapter 7 is devoted to the unique chemical and biochemical properties of the superoxide ion, which, depending on the conditions, can function as a Brønsted base, a nucleophile, a one-electron reductant, or a dehydrogenase of secondary amino groups. The final chapter concerns the reactions of the hydroxyl ion as a prototype of all oxy anions.

This book provides a sound background for the student of oxygen chemistry, as well as being an excellent reference source for the expert. It contains a vast amount of chemical data (thermodynamic, electrochemical, mechanistic) on dioxygen and related compounds presented in well annotated tabular form, which will be of particular value to the specialist. The life scientist will also find this book of interest because, in each chapter, chemical and biochemical aspects of the subject matter are integrated. For example, Chapter 6, which deals with the activation of oxygen by metals, contains an extensive discussion of the chemistry of both transition metal chelates as well as metalloproteins and flavoproteins, including cytochrome-C oxidase, cytochrome P-450, and pyrocatechase. Not surprisingly, many of the "pure chemical" sections deal with the reactions of dioxygen in organic solvents, since this is an area of research of special interest to Professor Sawyer. However, as the author has pointed out, the reactions of oxygen species in organic solvents may be more relevant to biological systems than those occurring in water, as the interior of proteins, enzyme active sites, and membranes may indeed be highly hydrophobic. Furthermore, the systems studied by biochemists such as enzymes, proteins, nucleic acids, and membranes are often so complex that it is difficult if not impossible to study their chemistry in any meaningful way. For such systems, small molecular models sometimes have provided clues to the reactions that may occur in more complex systems.

In his excellent preface Professor Williams writes, "There is then in the ongoing chemistry of the surface of the earth, in man's extensive industry from refining down to the most complex drugs, and in living processes the need to utilize dioxygen while controlling adverse factors in that utilization. In this book, Sawyer shows how all this chemistry can be managed and how much of it can be understood through careful considerations of intermediates". Certainly this book should be of interest

to chemists, biochemists, biologists, and biophysicists concerned with any aspect of the reactions of dioxygen and its related compounds.

C. F. Chignell, *National Institute of Environmental Health Sciences*

Laser Chemistry of Organometallics. ACS Symposium Series 530. Edited by J. Chaiken (Syracuse University). American Chemical Society: Washington, DC. 1993. xii + 314 pp. \$74.95. ISBN 0-8412-2687-3.

This book was developed from the symposium sponsored by the Division of Physical Chemistry and the Division of Inorganic Chemistry, Inc., at the 203rd National Meeting of the American Chemical Society held in San Francisco on April 5-10, 1992. After a preface and an introductory chapter by the editor, there are 20 chapters organized under the following headings: Dissociation and Other Photoprocesses; and Laser-Initiated Bimolecular Chemistry. There are author, affiliation, and subject indexes.

High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database. By G. Beamson and D. Briggs. John Wiley & Sons Ltd.: Chichester, New York, Brisbane, Toronto, and Singapore. 1992. \$65.00. x + 295 pp. ISBN 0-471-93592-1.

The goal of this book, as stated in the introduction (section one) is two-fold: It provides an XPS reference source for over 100 readily available organic polymers and promotes the ESCA300 instrument from which the database was acquired. Beamson and Briggs are acknowledged experts in photoelectron spectroscopy and have concisely detailed the physical and instrumental parameters necessary to acquire high resolution spectra. The authors briefly describe the historical goal and benefits of high energy resolution, *i.e.*, structural information such as shake-up and valence band features as well as high resolution core-orbital features that provide much information not available with typical XPS resolution.

Section two describes the essential design components of the ESCA300 spectrometer. The X-ray source (5 or 8 kW) is a rotating anode with aluminum and chromium radial bands illuminated by an electron beam. The monochromator consists of seven toroidally bent α -quartz crystals giving an output energy spread for Al K α radiation of approximately 0.26 eV. The electron lens is a multi-element arrangement including a slit-aperture pair at the entrance to the hemispherical energy analyzer. The lens ensemble allows either high transmission or high spatial resolution. The physical parameters of the hemispherical electron energy analyzer (HMA) are described, but in limited detail. The interested researcher will find this section sparse for quantifiable comparisons with other systems. Photoelectrons are detected using a multichannel detector consisting of an ensemble of microchannel plates, a phosphor screen, and a CCD TV camera. Charge compensation due to the photoionization process was accomplished with two thermoionic emission electron flood guns.

Sections three, four, and five reveal the performance characteristics of the ESCA300 spectrometer. The working spectroscopist will find the ESCA300's performance impressive with the exception of the count rates. The width at the Ag Fermi edge is 0.30 ± 0.02 eV, corresponding to a resolution of 0.28 eV.

Section six gives the experimental protocols of sample preparation and mounting, data acquisition parameters, and charge correction methodology. The sample preparation and mounting methods are interesting because of their simplicity and broad utility.

Section seven describes the curve-fitting algorithm, the physical functions, and the constraints imposed upon the fitting routine. This section ought to be more comprehensive in its physical description of the fit function parameters, *e.g.*, a physical justification for varying the Gaussian-Lorentzian mixing ratios for the same element within the same monomer.

Section eight provides an empirical comparison with a qualitative explanation of the differences between aliphatic and aromatic line shapes. The difference in observed asymmetry is attributed to C-H stretch vibrations during photoionization. Relaxation of the aliphatic core-hole proceeds via σ electron density transfer toward the positive charge. Less vibrational excitation is likely to result from π electron density movement; thus, the aromatic core-hole will manifest much less asymmetry in the line shape.

Section nine offers a fine description and explanation of the major shake-up/shake-off features associated with the core-level spectra of aromatic and unsaturated polymers. Most useful is a lucid and concise description of the effect of shake-up/shake-off processes on core-orbital intensities.

Section ten details the utility and problems associated with acquiring valence band information by XPS. This section is notable for the paucity of interpretive information. By the authors' admission, high resolution valence band spectra could reveal a wealth of chemical bonding information.

Sections eleven and twelve deal with sample impurities and X-ray induced degradation. The impurity section offers a fine example of thorough experimental technique and should be carefully read by the user. The X-ray degradation section by itself provides the reader with a valuable database on the relative degradation rates of various polymers.

The database is arranged starting with hydrocarbon polymers followed by oxygen-, nitrogen-, fluorine-, chlorine-, and sulfur-containing polymers. Two pages are devoted to each polymer with one page containing spectra and the other listing the core-orbital component binding energies, full-width at half-maximum (FWHM), fractional area of each component, Gaussian-Lorentzian mixing ratio, and asymmetry parameter. Also included are observational comments, polymer origin and treatment, shake-up and valence band information, and the X-ray degradation index. The spectra page includes a survey scan, valence region, high resolution core level spectra, and in a few cases the Auger region. The core-line spectra display the original data envelope, curve-fit envelope, and curve-fit component peaks. The appendices provide the user with a wealth of information on primary and secondary chemical shifts along with binding energy positions (relative to saturated C 1s) for various chemical structures.

Mark F. Arendt, *The University of Texas at Austin*

Statistical Mechanics of Phase Transitions. By J. M. Yeomans (University of Oxford). Oxford University Press: Oxford, U.K. 1992. x + 153 pp. \$24.95. ISBN 0-19-851730-0 (paperback). \$49.95. ISBN 0-19-851729-7 (cloth).

Magnets, fluids, microemulsions, superconductors, liquid crystals, and colloidal suspensions are but a few examples of systems that undergo phase transitions. Abrupt changes in a system's properties (phase transitions) occur in a bewildering variety of forms. It is one of the triumphs of science that the condensation of a gas to a liquid upon cooling; the self-assembly of surfactant molecules into lamellar, cylindrical, or spherical structures; or a magnet's loss of magnetization upon heating can be described using a common theory. Nowhere is this commonality more striking than near a critical point, where all systems with the same dimensionality and order parameter symmetry behave in the same way, irrespective of differences in other microscopic properties, such as molecular shape or intermolecular forces. This fascinating behavior is commonly referred to as universality.

Universality is in fact the main theme of J. M. Yeoman's *Statistical Mechanics of Phase Transitions*. The effort to emphasize what is common underlies the choice of topics and examples, the selection of references, and of course the vocabulary and style. This gives the book a remarkable clarity of purpose. The renormalization group, for example, serves here both as starting point and as culmination. It is invoked in the introductory, phenomenological discussion of phase transitions and is the subject of the last two chapters, where this powerful formalism, a basic tool in the modern theory of critical phenomena, is presented with commendable conciseness and clarity. The chapters in between fall into two broad categories: fundamentals (thermodynamics and statistical mechanics, models of phase transitions, mean-field theories) and techniques (transfer matrix, series expansions, Monte Carlo simulations). Each of these topics is treated concisely and at an introductory level. Chapters 2-9 contain anywhere from one to seven problems each. These are well chosen, and many challenge the reader to explore in greater depth the consequences of what is implied in the text. Thus, the formal development of symmetry properties and of equivalences between lattice models is given mostly as exercises at the end of Chapter 3. Readers interested in critical phenomena will find this book to be a concise and readable introduction to the topic.

It would be hard to conclude just from reading this work, however, that there is considerably more to the statistical mechanics of phase transitions than critical phenomena. The almost exclusive emphasis on universality results in a narrow perspective on what in reality is a broader subject. Important topics such as the Lee-Yang theory of phase transitions, or the Bethe-Guggenheim and cluster variation approximate techniques for solving cooperative problems on a lattice, are not mentioned. The author's impatience with classical thermodynamics, and with most topics not directly related to criticality, is exemplified in Chapter 2, *Statistical Mechanics and Thermodynamics*, whose objective is to move "...through the large number of reminders and definitions necessary to arrive at the point where we can introduce the idea of universality...". As a result, the differential form of the fundamental equation in the energy

representation, in which entropy is an independent variable, is called the First Law of Thermodynamics, which is unrelated to entropy; the concept of stability is never mentioned, not even when discussing the convexity of the free energy, and the phase rule is not mentioned.

This is an uneven book. It is a good introduction to one important aspect of the statistical mechanics of phase transitions: the modern theory of critical phenomena. As such, it includes a particularly readable introduction to the renormalization group. However, it either leaves out or barely mentions concepts of fundamental importance to any discussion of phase transitions. Its content is narrower than what its title suggests.

Pablo G. Debenedetti, *Princeton University*

Investigations of Surfaces and Interfaces. Physical Methods of Chemistry. Volumes IXA and IXB. Edited by Bryant W. Rossiter and Roger C. Baetzold (Eastman Kodak, Rochester, NY). John Wiley and Sons, Inc.: New York. 1993. xi + 516 pp and xi + 745 pp. \$140.00 and \$175.00. ISBN 0-471-54406-X and 0-471-54405-1.

These two volumes contain a total of fifteen chapters discussing a wide range of experimental methods used to investigate surfaces and interfaces, each written by experts in these areas. The philosophy of the series, described in the preface, is for the authors principally to address a well-trained scientist who is not necessarily an expert on that topic. Therefore, an introduction to the field is to be given along with a brief description of the basic underlying theory followed by a description of experimental apparatuses and examples of applications. The emphasis, however, is to be on the method and not results. While there is some unevenness in scope and level of detail among the chapters, all of the chapters' authors adhered well to the series prescription. Furthermore, substantial bibliographies are uniformly contained to serve as a wide window to the extensive applications of these methods as well as to present an opportunity for the interested reader to dig deeply into the subject. A fairly detailed index is supplied at the end of each volume as well.

The experimental methods primarily focus on the gas-solid and liquid-solid interfaces. Using "g/s, g/l, l/s, or s/s" as shorthand notation for the principal type of interface investigated between gas (or vacuum), liquid, and solid phases, the chapters' topics are as follows: [Volume IXA]—surface tension (l/s), adsorption from solution (l/s), scanning tunneling microscopy or STM (g/s and l/s), electron energy loss spectroscopy (g/s), secondary ion mass spectroscopy or SIMS (g/s), molecular beams (g/s), and laser-induced thermal desorption (g/s); [Volume IXB]—low energy electron diffraction (g/s), Auger electron spectroscopy or AES (g/s), X-ray photoelectron spectroscopy or XPS (g/s), low and high energy ion scattering (g/s and s/s), X-ray fine structure absorption spectroscopy (g/s), monolayer assemblies (g/s and l/s), electrochemical interfaces emphasizing optical spectroscopies (l/s), and surface-enhanced Raman spectroscopy (g/s and l/s). Also, methods such as SIMS, AES, and XPS can be applied to buried solid-solid interfaces through sputter depth profiling; this aspect is included although not emphasized. There is essentially nothing included on liquid-liquid interfaces. While other methods relevant to surface and interface study could have been included, this collection certainly represents many of the most commonly used techniques.

There are few references after 1988, reflecting when the first drafts of these chapters must have been completed. Thus these volumes should not be sought for the very latest developments. This lag between composition and publication does detract, but on the whole these methods were all sufficiently mature at the time of writing that this reference work admirably provides well-conceived thorough presentations which can prove of great value for those wishing a firm practical understanding of the methods. This is true even for methods with a relatively short history, such as STM; this chapter even includes a list of equipment vendors as testimony to its rapid development. While many of the applications presented are associated with the authors' laboratories, this is in keeping with the theme of giving examples only and not attempting to provide comprehensive results. There are instances where the focus on the author's own results is too strong, but even in these cases, the bibliographies are substantial enough to connect with the wider literature. In summary, these two reference volumes will provide a valuable and substantial introduction to many of the most commonly used methods for providing surface chemical analysis and investigating interfacial phenomena.

Christopher H. Becker, *SRI International*