

Book Reviews

Handbook of Tritium NMR Spectroscopy and Applications. By J. A. Elvidge and J. R. Jones (University of Surrey). John Wiley & Sons: New York, 1985. xiv + 216 pp. \$39.95. ISBN 0-471-90583-6.

Tritium NMR has considerable potential in both stereochemical studies and as a site-specific label for following reaction pathways both *in vitro* and *in vivo*. Tritium NMR is about 100 times as sensitive as deuterium NMR for equal numbers of nuclei and has seven times the resolution. Both of these features indicate that tritium is a much better nucleus for high-resolution studies than is deuterium when the label needs to be detected rather than determining the absence of a proton signal. Many currently available spectrometers can detect tritium with little or no modification. The radiological hazards associated with handling tritium can be eliminated by using the procedures described in this handbook, and a typical NMR sample containing 1 mM tritium in a 0.3-mL sample contains 10 mCi. However, tritium labeling is relatively quite expensive.

The handbook is divided into three sections. The first contains a brief overview of tritium NMR. The second chapter contains the information on preparing tritium-labeled compounds. A minor problem is that many of the references, though a relatively small percentage of the total, are to unpublished work by the authors. However, the extensive bibliography will significantly aid anyone considering tritium labeling of amino acids, nucleic acids, steroids, or many other classes of compounds. The last chapter describes applications of tritium labeling to problems in biochemistry, structure determinations, reaction mechanisms, and other investigations.

The handbook is well-organized and easy to read, and it has most of the information in clearly presented tables. It is very easy to locate the information about labeling a specific compound. This is definitely a good first place to look if contemplating hydrogen isotope labeling. Given the wide range of interest in site-specific labeling, this is a handbook no library should be without.

Philip H. Bolton, *Wesleyan University*

Advances in Physical Organic Chemistry. Edited by V. Gold (King's College, London) and D. Bethell (University of Liverpool). Academic Press: London, 1984. viii + 252 pp. \$50.00. ISBN 0-12-033520-4.

Radicals or radical pairs form the "leitmotiv" of the three reviews grouped in the volume under discussion. The first review is entitled Magnetic Field and Magnetic Isotope Effects on the Products of Organic Reactions, by I. R. Gould, N. J. Turro, and M. B. Zimmt. It is an up-to-date account of work carried out mainly at Columbia University, in Japan, and in the USSR on organic reactions whose product yields are affected by the presence of an external magnetic field (stronger than earth's, usually between 0.2 and hundreds of a kG). A clear, concise, and well-illustrated introduction to chemically induced magnetic polarization provides the background for understanding the mechanisms of intersystem crossing and then the effects of change in solvent viscosity or of using micelles in the context of homolytic reactions effected in a magnetic field (photolysis of dibenzyl ketone and other ketones, of quinoline *N*-oxides in alcohols, of peroxides, pyrene sensitized trans \rightarrow cis isomerization of stilbenes). Four classes of effects are discussed according to the presence or absence of magnetic nuclei and to the mechanism by which intersystem crossing occurs. Cage effects also explain the enrichment of isotopes whose nuclei have a nonzero magnetic moment. Although each abbreviation is explained when it occurs first, a table of all abbreviations would have been useful.

The second review, by O. Hammerich and V. D. Parker, discusses Kinetics and Mechanisms of Organic Cation Radicals in Solution. In more than 130 pages, the authors present developments in mechanistic cation radical chemistry that have taken place since A. J. Bard, A. Ledwith, and H. J. Shine reviewed in 1976 the field for Volume 12 of this series. In line with the current revision of the mechanisms of several well-known organic reactions (at the incentive of J. F. Bunnett and of Russian chemists based on electroanalytical, ESR, and CIDNP evidence), electron pair transfer reactions are viewed nowadays as frequently occurring stepwise. After discussing dimerizations and cyclizations of cation radicals, the authors comment on nucleophilic attack on cation radicals and on electron-transfer reactions initiated by them. Then they present in detail fragmentations according to the bond type undergoing splitting. Finally, they discuss several reactions where evidence for cation radicals as intermediates was obtained: nitramine rearrangements, electrophilic aromatic substitutions with emphasis on nitration, abnormal Wittig reactions, addition of radicals to diazonium ions or protonated

electron-deficient heterocycles, various reactions of aliphatic ammoniumyl radicals.

The last review is entitled The Photochemistry of Aryl Halides and Related Compounds, by R. S. Davidson, J. W. Goodin, and G. Kemp. Several photochemical reactions are possible for aryl halides: homolytic photolysis, electrocyclic reactions, photoisomerizations, photosolvolysis. Which of these reactions does occur depends on the nature of the halogen, on the singlet vs. triplet excited state, and on concentration effects favoring excimer formation. Chloroaromatics are discussed at length according to the nature of the aromatic group (benzene, biphenyl, terphenyls, naphthalene, anthracene), while bromo- and iodoaromatics are treated less extensively. Dehalogenations of haloaromatics assisted by tertiary amines, dialkyl sulfides, or sodium borohydride are described. Finally, several photoinduced nucleophilic substitutions are reviewed: the authors discuss briefly photochemical $S_{RN}1$ reactions and then the formation of vinyl cations and the photoaddition of heterocyclic halo-derivatives to aromatics.

References are collected at the end of each chapter in alphabetical order, and an author index for all chapters is included. A cumulative index of titles and authors for all previous volumes concludes the book.

Electrochemists, photochemists, isotope chemists, and all those interested in the mechanistic organic chemistry will all benefit from this volume. It is sad that Professor V. Gold passed away last fall.

Alexandru T. Balaban, *Polytechnic Institute, 76206 Bucharest, Roumania*

Annual Reports on NMR Spectroscopy. Volume 16. Edited by G. A. Webb (University of Surrey). Academic Press: London and New York, 1985. x + 373 pp. \$100.00.

Reviews of four areas of NMR spectroscopy are contained in this volume. The first, by H. W. E. Rattle, is entitled NMR Studies of Amino Acids, Peptides, and Proteins: A Brief Review, 1980-1982 and includes synthetic peptides, small natural peptides, enzymes, haem proteins, proteins associated with nucleic acids (or membranes), structural proteins, immunoglobulins, and some other proteins such as polycrystalline insulin, barley and wheat thionins, crambin, ovotransferrin, and uteroglobin. Three pages of the 71-page review (which contains 787 references) are devoted to a discussion of advances in NMR techniques as applied to proteins, including various two-dimensional NMR methods and a new way to assign backbone amide proton resonances of small proteins.

The second review, entitled ^{119}Sn -NMR Parameters, by B. Wrackmeyer, contains a compilation of ^{119}Sn chemical shifts on organotin and inorganic tin compounds (to the end of 1983), a review of indirect nuclear spin-spin couplings involving ^{119}Sn , a discussion of relaxation mechanisms for the ^{119}Sn nucleus, and experimental details for ^{119}Sn NMR measurements (all in the liquid state). Either direct observation or heteronuclear double resonance may be used to observe ^{119}Sn . The coupling constants to ^{119}Sn relate to the structure and bonding of this nucleus (113 pages, 30 Tables, 393 references).

Isomerization Processes Involving N-X Bonds, by M. L. Martin, X. Y. Sun, and G. J. Martin, is the third review in this volume. Hindered rotation about N-X bonds, where X is C, S, Se, N, P, Si, B, Pd, As, or O, has been studied extensively by NMR spectroscopy for many years. Accuracy of published results (E_a , ΔH^\ddagger and ΔS^\ddagger) has, however, remained a problem. The authors take care to emphasize experimental methods and data analysis which can yield accurate results. Limitations of each experimental method and sources of error are also discussed. One section deals with the interpretation of dynamic NMR results including solvent effects, theoretical interpretations, correlations with substituent parameters, and correlations with NMR parameters. The 40 Tables are a highlight of this review, covering the literature from 1970 and conveniently separating the vast amount of thermodynamic data according to type of N-X bond (105 pages, 556 references).

The last review in this volume is entitled Multiple Resonance, by W. McFarlane and D. S. Rycroft, and covers the period from mid-1978 to mid-1983. The multiple resonance experiment is broadly defined as "one in which the sample is affected by several radiofrequency fields". Although many pulse techniques are described, the major topics in this review are multiple quantum NMR, two-dimensional NMR, saturation transfer, the nuclear Overhauser effect, and special pulse sequences for "composite pulses" and multiplicity determination for $J(\text{XH})$ coupling. The authors are to be commended for concisely reviewing 1058 references

of mostly complex pulse techniques in only 44 pages of text!

Each of the four reviews holds to the high standards of the "Annual Reports on NMR Spectroscopy" and is a volume to which every NMR spectroscopist will want access.

Laurine A. LaPlanche, Northern Illinois University

Advances in Chemical Physics, Volume 61. Edited by I. Prigogine (University of Brussels and University of Texas) and S. A. Rice (University of Chicago). John Wiley and Sons: New York, 1985. ix + 461 pp. \$75.00. ISBN 0-471-82055-5.

This volume contains five articles. The first, Photodissociation of Diatomic Molecules to Open Shell Atoms, by S. J. Singer, K. F. Freed, and Y. B. Band, addresses the important problem of state-to-state photodissociation cross sections to individual open-shell-fragment electronic states. Here the Born-Oppenheimer approximation is inapplicable and nonadiabatic processes must be invoked. The authors first summarize the extant experimental data and then develop the theoretical methods necessary to describe such results. Molecular and atomic basis functions corresponding to Hund's coupling cases (a), (b), and (c) are developed separately. Methods for calculating photodissociation cross sections are derived from both perturbation and density matrix formalisms. Several numerical examples are presented.

The second article is Reduced Dimensionality Theories of Reactive Scattering, by J. M. Bowman. In this article quantum dynamical approaches to model (i.e., two dimension) reactive scattering are developed and used to derive expressions for rotationally averaged quantum rate constants, transmission coefficients, and integral and differential cross sections from the Schrödinger equation. Observable parameters calculated from the reduced dimensionality theories are compared with each other, with those obtained from full, three-dimensional theories, and with experimental values of these parameters. An unusually honest postscript that reflects of the accuracy of these calculations is appended.

The Theoretical Investigation of the Electron Affinity of Chemical Compounds, by G. L. Gutsev and A. I. Boldyrev, constitutes the third article of this volume. Ab initio and X_α methods of calculating electron affinities (EA) and the related ionization potentials are summarized with emphasis given to understanding the reliability of the different approaches. From the relation between EA and electronic structure of molecules and radicals, rules are developed to qualitatively estimate EAs. These rules are used to identify chemical systems of potentially unusually large electron affinities or unusually small ionization potentials (superhalogens and superalkalis).

The fourth article, Scattering Theory in Superspace, by C. George, F. Mayne and I. Prigogine, presents another aspect of the authors' formulation of the second law of thermodynamics as a fundamental dynamical principle. They show that quantum theory requires an extension to superspace to enable permitted motions to be distinguished from excluded motions. The simple example of potential scattering generates basic questions in the microscopic theory of irreversible processes. The resolutions of some of these questions, such as the use of the second law of thermodynamics as a selector amongst possible states of the system, are shown to enhance our understanding thereof.

Statistical Physics of Polymer Solutions: Conformation-Space Renormalization-Group Approach, by Y. Oono, constitutes the final article in this volume. The two goals of this article are to show that this is the natural approach to solutions of flexible polymers and to popularize the renormalization-group approach among physical chemists and polymer scientists. To the latter goal, both an intuitive background of the theory is explained and numerous simple examples are calculated in great detail.

In summary, this volume contains presentations on five important topics in the area of chemical physics. True to the aim of the series, each article is a comprehensive, individual analysis of the subject of interest. Volume 61 admirably continues this distinguished series.

Ruth McDiarmid, National Institutes of Health

Stoichiometry and Thermodynamics of Metallurgical Processes. By Y. K. Rao (University of Washington). Cambridge University Press: New York and Cambridge, 1985. XV + 957 pp. \$49.50. ISBN 0-521-25856-1.

In his preface, Professor Rao notes that at one time instruction in extractive metallurgy consisted solely of studying process descriptions and operational details. For the most part a much sounder approach has taken root, with emphasis on quantitative analysis. Professor Rao is to be congratulated on aiding this approach with a comprehensive book on physical chemistry and thermodynamics with particular emphasis on applications to metallurgical systems. The chapter headings are the following: Introduction, Stoichiometry, First Law of Thermodynamics, Fuels and Combustion, Energy Balances, Second Law of Thermodynamics, Auxiliary Functions, Theory of Solutions I, The Gibbs Free Energy Change and the Equilibrium Constant, Phase Equilibria, Equi-

libria in Complex Systems, Theory of Solutions II. Each chapter is replete with illustrative calculations and problems of varying complexity.

The task of reading the entire book is impossible in the time available for compiling a review, hence this reviewer has read sections of particular interest to him and offers the following comments for Professor Rao's consideration.

The section (5.6) relating to energy consumption of metallurgical processes is disappointing. The method of analysis is that proposed by Professor Kellogg¹ in which the "process fuel equivalent" and the "material fuel equivalent" are defined. This method takes account of the fuel consumption in the generation of electrical energy, for example, which is subsequently used in the process under consideration. A better method of analysis utilizes the exergy or available energy concept which permits a true thermodynamic assessment of the process.

Apparently, Professor Rao is unaware of the convention regarding electrode potentials recommended by the International Union of Pure and Applied Chemistry.² As a result we have a perpetuation of the unnecessary and confusing "oxidation potentials" and "reduction potentials" (Table 9.11). Adoption of the IUPAC convention would help to overcome that bane of students (and others), the sign of the voltage of an electrochemical cell.

This reviewer also dislikes the term "energy efficiency" (p 431) used in connection with electrolytic processes. A more appropriate phrase would be "specific energy consumption". The word efficiency (e.g., current efficiency) is usually a ratio used to describe the performance of a real process relative to that of a model process and as such is dimensionless.

The index is surprisingly deficient in some respects. Thus, one is alarmed that the word "iron" does not appear despite the many systems involving iron which are discussed.

The above points notwithstanding, this reviewer believes the book will be well received; the detailed discussion of phase equilibria, with application of matrix methods, is outstanding.

(1) "Energy Efficiency in the Age of Scarcity": Kellogg, H. H. *J. Metals* 1974, 26(6), 25-29.

(2) See, e.g.: O'M Bockris, J.; Reddy, A. K. N. *Modern Electrochemistry*; Macdonald and Co.: London 1970; pp 1115-1120.

D. R. Morris, University of New Brunswick

Química General y Biorganica. By J. Castells Guardiola (Universidad de Barcelona). Editorial Alhambra: S. A. 1985. xiv + 543 pp. 3000 ptas.

This is a good General Chemistry book designed to introduce first-year nonchemistry majors to the basic understanding of chemistry. Emphasis is placed on molecular structure and bonding, including organic stereochemistry, chemical thermodynamics, acid-base theories, chemical kinetics, and some representative organic and bio-organic reactions. The general-chemistry treatment given in this book to several topics is excellent. For example, the author discusses extensively the concept of entropy applied to chemical reactions, a treatment not frequently encountered in general-chemistry texts. Also noteworthy is the introduction of the student at this elementary level to advanced concepts in organic stereochemistry such as enantiomeric relationships (Chapter 13); diastereoisomeric relationships in monosaccharides (Chapter 14); alicyclic stereochemistry in monosaccharides, polysaccharides, and nucleic acids (Chapter 15); and conformational analysis in proteins, nucleic acids, and synthetic polymers (Chapter 16). We find adequate the treatment of acid-base concepts (Chapters 26 and 27) and that of nuclear structure (Chapter 1), nuclear reactions (Chapter 3), atomic structure (Chapters 4 and 5), and chemical bonding (Chapters 6-11). However, in our opinion there are several problems with the book.

The thermodynamic coverage is extensive, but the treatment varies in level. The author includes 13 chapters, 188 pages, under chemical thermodynamics (Chapters 17-29), but while, on the one hand, a basic discussion of work and heat is not provided, on the other hand, the general treatment of solutions is at a relatively elementary level. The author makes a valiant effort to present thermodynamics from a molecular point of view. We feel, however, that a more conventional approach might be easier to understand. For instance, Gibbs and Helmholtz energies are dismissed in 2.5 pages because the author considers it "unnecessary or counter-productive to introduce a secondary function (G or A) when the entropy of the universe of a reaction is a direct, clear and fundamental quantity". Yet on Chapter 28 the relationship between maximum useful electric work and the change in the Gibbs energy for processes at constant temperature and pressure is boxed as very important. We believe also that a more conventional symbolism would help the student; for instance, $Q_p(\Delta E)^{T,P,\zeta}$ stands for Q_c at constant temperature (T) and volume (V) and absence of work that is not expansion-compression work ($\zeta = 0$). Q_c is the usual heat transferred for a constant

volume process with no work other than expansion-compression in a closed system, "ter" = thermal, and "air" = surroundings. If the author means ΔE , for a reaction, it would be simpler to say so.

"Química General y Bioorganica" is intended for first-year college students not majoring in chemistry; however, the author extensively elaborates on some advanced subjects in the realm of organic chemistry. This is no problem in itself, but we believe that usually some background material in general organic chemistry is needed before proceeding with more advanced topics. For instance, organic chemistry is introduced in Chapter 12 without reviewing some basic structural considerations, but Chapters 13–16 deal with the application of advanced stereochemical principles to "bioorganic" compounds such as carbohydrates, proteins, and nucleic acids. We feel that the extent and the level with which the author covers this subject is rather unusual for a non-majors general chemistry textbook. Moreover, the virtual lack of descriptive chemistry in general is absurd and unjustifiable. In his extensive and detailed Preface, the author asserts that "... The knowledge of descriptive chemistry is important but ... should be acquired not while studying chemistry but in doing chemistry, i.e. working in the laboratory".

Cosmogonic concepts for the description of the chemical universe as a dichotomy between microcosmos and macrocosmos are abused in our opinion. We felt upon reading this book that certainly our understanding of matter in its different forms can be transmitted to the student more clearly. The lack of other indices but a content index by chapter at the beginning of the book complicates things further. The reader will find it difficult to locate a specific subject, unless he or she is willing, as we have had to do, to perform a search chapter by chapter. For example, we could not find the structure of aspirin in this text and thus assume that it is not given.

In summary, we conclude that there is ample room for improvement and that a good general chemistry book in Spanish is still needed.

Georges G. Siegel, Fernando A. Souto, and Carmen A. Vega,
University of Puerto Rico—Mayaguez

Comprehensive Biotechnology. The Principles, Applications, and Regulations of Biotechnology in Industry, Agriculture, and Medicine. Volumes 1–4. Editor-in-chief, Murray Moo-Young (University of Waterloo, Ontario, Canada). Pergamon Press: New York. 1985. \$995.00. ISBN 0-08-026204-X.

Volume 1. *The Principles of Biotechnology: Scientific Fundamentals.* Edited by Alan T. Bull (University of Kent, Canterbury, UK) and Howard Dalton (University of Warwick, UK). xxv + 688 pp.

This encyclopedic work is aimed at chemists, biochemists, biologists, and engineers. It contains useful information for students, teachers, and administrators; 250 authors, representing 15 countries, have contributed to these four volumes.

The first volume presents the scientific fundamentals of biotechnology, which is defined as the evaluation and use of biological agents and materials in the production of goods and services for industry, trade, and commerce. Section one presents general principles of microbiology. It includes discussions of organisms, various aspects of their cultivation and growth, and DNA technology. A chapter on animal and plant cell cultures provides extensive information on products, culture characteristics, media, and technologies. Among the subjects covered in Section 2, Chemical and Biochemical fundamentals, are aerobic and anaerobic metabolism of glucose, aerobic metabolism of methane and methanol as well as methanogenesis, microbial metabolism of carbon dioxide, hydrogen, and aromatic compounds. Further topics include biosynthesis of fatty acids and lipids, bacterial respiration, microbial photosynthesis, and overproduction and regulation of metabolites. Four chapters are devoted to microbial enzymes.

Volume 2. *The Principles of Biotechnology: Engineering Considerations.* Edited by Charles L. Cooney (MIT, Cambridge, MA, USA) and Arthur E. Humphrey (Lehigh University, Bethlehem, PA, USA). xxv + 632 pp.

Section one presents excellent discussions of bioreactor design, operation, and control. In spite of sophisticated instrumentation for monitoring and controlling fermentation, there will always be significant design problems and uncertainties. Problems with mixing, aeration, and heat transfer continue to plague designers of reactors. Three chapters

are devoted to immobilization techniques. Section two is concerned with processing. Several chapters are devoted to the handling of solids and liquids, sterilization, air filters, heat management, and cell disruption. Cell collection techniques include centrifugation, filtration, and ultrafiltration. Product isolation may be achieved by liquid-liquid extraction, ion exchange, chromatography, distillation, supercritical-fluid extraction, or electro dialysis.

Volume 3. *The Practice of Biotechnology: Current Commodity products.* Edited by Harvey W. Blanch (University of California, Berkeley, CA, USA), Stephen Drew (Merck, Sharp and Dohme, Rahway, NJ, USA), and Daniel I. C. Wang (MIT, Cambridge, MA, USA). xxv + 1136 pp.

Volume three is divided into three sections. The first, Healthcare Products, describes the problems and techniques involved in the production of penicillins, streptomycin and aminoglycoside antibiotics, tylosin, peptide antibiotics, cephalosporins, and cephamycin. The list continues with lincomycin, pharmacologically active marine microbial products, anticancer agents, siderophores, steroids, and products from recombinant DNA. The next section includes food and beverage products. Chapters are devoted to brewing, whisky, fermented soybean foods, baker's yeast, bacterial and fungal biomass, cheese technology, and fermented dairy products. Other chapters include L-glutamic acid fermentation, phenylalanine, lysine, tryptophan, aspartic acid, threonine, and the flavor enhancer, 5'-guanosine monophosphate. Section three is concerned with industrial chemicals, biochemicals, and fuels. Industrial processes, metabolic pathways, and commercial uses of citric, gluconic, itaconic, acetic, propionic, butyric, and lactic acids are discussed. The four chapters on enzymes include starch conversion, protolytic and hydrolytic enzymes, and glucose isomerase. The production of ethanol, acetone, butanol, and 2,3-butanediol is also included. Chapters devoted to microbial insecticides, flavors, fragrances, fats, oils, polysaccharides, and enzymes in food technology complete this volume.

Volume 4. *The Practice of Biotechnology: Speciality Products and Service Activities.* Edited by Campbell W. Robinson (University of Waterloo, Ontario, Canada) and John A. Howell (University College of Swansea, UK). xxix + 1308 pp.

Section one of this volume contains a variety of topics. Liposomes as drug carriers, monoclonal antibodies, transplantation immunology, and artificial cells all have biomedical and chemotherapeutic applications. Uses in agriculture can be found for nitrogen fixation, mycorrhizae, somaclonal variation, virus-free clones, and metabolites from recombinant DNA modified plants. The role of microbes in mineral processing, oil recovery, and the utilization of fungi in the forest-product industry is also discussed. Several chapters are devoted to analytical methods and instruments, including enzyme probes. The section under governmental regulations includes chapters on patenting biotechnological processes and products, hazardous materials, and regulations governing them and problems related to single-cell protein as food. Section three, waste management and pollution control, occupies 393 pages and is equivalent to a text on the subject. The chemistry, microbiology, and ecology of waste treatment are discussed, followed by descriptions of activated sludge processes, fixed film systems, anaerobic reactors, composting, and landfills. Most systems are analyzed with respect to design, operation, efficiency, byproducts, and economics.

Each volume has a glossary and subject index. The subject index in volume four is cumulative. Each volume also has a table of contents and a cumulative table of contents. Unfortunately the latter does not provide page numbers. This set is well illustrated with photographs and diagrams, and extensive bibliographies are included with many chapters. It is perhaps unavoidable that there are few references later than 1981. However, supplementary volumes are planned and on-going progress and trends will be covered in Pergamon's review journal, *Biotechnology Advances*.

Although this set of books is expensive and probably beyond the reach of most individuals, it should be included in the libraries of any academic unit or industry which has workers involved in biotechnology. There is something for everyone. The browsing student will find much to inspire his enthusiasm for the subject, while the comprehensive treatment of many topics and extensive bibliographies will be extremely useful for the professional. There is a lot of information in 7.5 kg.

M. C. W. Smith, *Ann Arbor, Michigan*