

## Additions and Corrections

**On the Origin of Proximity Effects on Reactivity: A Modified MM2 Model for the Rates of Acid-Catalyzed Lactonizations of Hydroxy Acids** [*J. Am. Chem. Soc.* 1987, 109, 3698]. ANDREA E. DORIGO and K. N. HOUK\*

In the calculation of transition-state energies, some of the dipole moments were read in with the right magnitude but the wrong sign, due to the use of an equivalence statement and the convention in the MM2 code for assigning dipole moments. Specifically the lp (lone pair)-O<sub>2</sub>, H-O<sub>2</sub>, lp-O<sub>3</sub>, and C-O<sub>1</sub> bonds defined in Figure 10 of the paper were assigned values of  $\mu$  equal to +0.9, -1.115, +0.9, and -0.44 D, but they should have the opposite signs. In order to avoid this problem, the dipole moments must be defined, not obtained by equivalence statements. The activation energies derived with these correct dipole moments support the conclusions of the paper and are listed in the following publication: Dorigo, A. E., Houk, K. N. *Advances in Molecular Modeling*; Liotta, D., Ed.; JAI Press: Greenwich, CT, 1988; Vol. I, pp 135-188. We thank Professor Frederic Menger and Michael Sherrod (Emory University) for discussions which caused us to locate this problem.

## Book Reviews\*

**Physical Methods of Chemistry. Second Edition. Volume IIIA. Determination of Chemical Composition and Molecular Structure, Part A.** Edited by Bryant H. Rossiter (ICN Pharmaceuticals, Inc.) and John F. Hamilton (Eastman Kodak Company). John Wiley and Sons: New York. 1987. xi + 624 pp. \$110.00. ISBN 0-471-85041-1.

This volume contains a collection of chapters covering a wide range of techniques and methods for the determination of structure or composition of materials. The intended audience for the book is "intelligent scientists, technically trained but perhaps inexperienced in the topic to be discussed" and the intent is to provide that audience with a resource from which it can be easily determined if the method or technique discussed would be of use in any work that is contemplated. On the whole, this objective seems to have been achieved. Each chapter begins with some introductory material and is followed by a brief discussion of the theoretical background needed for an understanding of the material presented later and some discussion of the instrumentation required along with costs for the equipment in about 1983 dollars. The presentations are readable with only a few typographical errors and do not seem to assume too much about the background of the reader.

The chapters in the book are "Infrared and Raman Spectroscopy" by James R. Durig and Joann F. Sullivan, 131 pages with 234 references; "Rotational Spectroscopy" by Marlin D. Harmony and Alice M. Murray with 60 pages and 72 references and a bibliography of 15 books related to theory and experiment; "Atomic Spectrometry Methods" by James D. Winefordner and Michael S. Epstein with 234 pages and 155 references; "Neutron Activation Analysis" by Vincent P. Guinn with 78 pages and 36 references; "Mass Spectrometry: Principles of Instrumentation and Techniques" by John Roboz with 69 pages and 184 references; "X-Ray Spectrometry" by L. S. Birks and John V. Gilfrich with 37 pages and 16 references; and "Radiotracer Techniques" by Jan Rydberg and Gregory R. Chopin with 85 pages and 36 references.

Norman E. Heimer, *University of Mississippi*

**Heterogeneous Catalysis: Principles and Applications. Second Edition.** By G. C. Bond (Brunel University). The Clarendon Press, Oxford University Press: New York. 1987. x + 176 pp. \$39.95. ISBN 0-19-855526-1.

Basic theoretical principles of heterogeneous catalysis are discussed throughout the thirteen chapters of this elementary textbook. Each chapter is followed by a number of challenging questions directed toward the student reader. A bibliography of selected books and review articles

pertinent to each chapter is included at the end of the book. Chapters 1 through 6 present fundamental aspects of chemisorption and catalysis on metals and oxides. Chapter 5 deals with the kinetics of catalyzed reactions. Chapter 7 discusses the preparation and use of various catalysts, while the remaining six chapters are devoted to major applications of catalyzed reactions in the heavy chemical industry. For example, topics in these chapters include the manufacture of synthesis gas and derived chemicals; catalytic cracking and reforming of petroleum; the manufacture of alkenes and their reactions and isomerizations; the synthesis and oxidation of ammonia; and the role of catalysts in atmospheric pollution control. Less than 1 page is devoted to the use of heterogeneous catalysis in the fine-chemicals industry. Consequently, some catalytic reactions of great utility to synthetic organic chemists, such as reduction of nitro compounds, nitriles, ketones, double bonds, and the techniques involved, are not discussed in any detail. However, the book does contain a wealth of fundamental concepts in heterogeneous catalysis that would be of value particularly to synthetic organic chemists who may have received little training in these concepts. The book is interesting, well organized, and well written and it certainly deserves to be within reach of those persons who often in the course of their work reach for heterogeneous catalysts.

Allan Hydorn, *Warner-Lambert Company*

**The Alkaloids. Volume 27.** Edited by Arnold Brossi (National Institutes of Health, Bethesda, Maryland). Academic Press, Inc.: Orlando, Florida. 1986. ix + 437 pp. \$95.00. ISBN 0-12-469527-2. Also available in softcover: \$69.95. ISBN 0-12-469527-2.

This volume is a valuable addition to the series in that it serves to inform one of recent advances made in various areas of alkaloid chemistry. The book is divided as follows: Chapter 1, Alkaloids from *Tabernaemontana*, by B. Daneli and G. Palmisano; Chapter 2, Corynantheine, Yohimbine and Related Alkaloids, by C. Szántay, G. Blakó, K. Honty, and G. Dörnyei; Chapter 3, Pyrrolidine Alkaloids, by G. Massiot and C. Delaude; and Chapter 4, Metabolic Transformations of alkaloids, by J. P. N. Rosazza and M. W. Duffell.

The first chapter (*Tabernaemontana* Alkaloids) is, in essence, an updated review on this family of alkaloids. Initial discussions focus upon the skeletal variations derivable from tryptophan and secologanin, of which this large family of compounds is comprised. Table I lists over several hundred entries documenting the presence of these alkaloids in plant species. Table II correlates specific compounds with their melting points and species of origin and gives reference to previous volume(s) of *The Alkaloids* series. The rest of the chapter is dedicated to isolation

\*Unsigned book reviews are by the Book Review Editor.

techniques, structural elucidation and chemical transformations of relevant compounds. The biological activity of the Tabernaemontana alkaloids varies greatly as some members of this family possess antimicrobial, cytostatic, antiviral, analgesic, or hallucinogenic properties, and thus the chapter closes with a discussion of the pharmacology of over forty such compounds.

The second chapter (Corynantheine, Yohimbine Alkaloids) nicely summarizes the many synthetic advances made in this area of alkaloids from 1968 to 1984. For example, one can find Wender's synthesis of reserpine (1980) contrasted with the elegant Woodward synthesis (1956). The amount of material presented is great, but it is done so in a clear fashion making reading enjoyable—especially to the synthetic organic chemist. The rest of the chapter includes a section pertaining to the conversion of indole alkaloids to oxindole derivatives and a discussion on the pharmacology of these alkaloids.

Chapter 3 (Pyrrolidine Alkaloids) begins with an introduction to the simplest of these alkaloids (hygrine, hygroline) and progresses to more complex compounds. The following topic, on the occurrence of pyrrolidine alkaloids, is quite extensive. The chapter ends with brief discussions on the synthesis and biosynthesis of these alkaloids.

Chapter 4 (metabolic transformations) is an overview of how one determines transformations of alkaloids in various biological systems. The strategy involved is presented along with a detailed account of the enzymes available and the effectiveness of microbial models often employed. Lastly, the metabolisms of some well-studied alkaloids are described: indole alkaloids—ellipticine, vindoline, lysergic acid; isoquinoline alkaloids—glauanine, laudanosine, morphine; pyridine alkaloids—nicotine, etc.

In summary, Volume 27, as with previous volumes in the series, should be of value to the chemist, the biochemist, and the pharmacologist.

Scott L. Dax, *University of Wisconsin—Madison*

**Thin Layer Chromatography.** By Richard J. Hamilton (Liverpool Polytechnic, U.K.) and Shiela Hamilton. John Wiley & Sons: Chichester. 1987. xix + 129 pp. \$19.95. ISBN 0471-91377-4.

*Thin Layer Chromatography* (TLC) is one of a series of texts in the series *Analytical Chemistry by Open Learning*, a project initiated by the Committee of Heads of Polytechnic Chemistry Departments in the UK. These are self-study texts, although it is strongly recommended that the student undertake supervised, practical laboratory training, 10–15 h worth for the TLC course. Presumably written for laboratory technicians seeking to improve their knowledge, the TLC text would do quite well as a supplement for a sophomore course in organic chemistry. The practical aspects of TLC are firmly emphasized, and the text is replete with self-assessment questions. The answers appear at the end. The coverage is balanced, and given the level aimed at, complete. This series should have wider circulation in the US.

David C. Locke, *Queens College, CUNY*

**Atomic Absorption and Emission Spectroscopy.** By E. Metcalfe (Thames Polytechnic). John Wiley & Sons: New York. 1987. xxi + 289 pp. \$23.95. ISBN 0471-91385-5.

The various methods of analytical atomic spectroscopy are employed in a number of wide-ranging fields by practitioners of equally wide-ranging levels of expertise. This book is part of a series entitled *Analytical Chemistry by Open Learning* which was organized by the Committee of Heads of Polytechnic Chemistry Departments in the United Kingdom as a means of teaching "Distance Learners" about various aspects of analytical chemistry. To date, there are over 25 volumes in the series, covering such aspects as sample preparation, statistics, microprocessor controls, and techniques ranging from atomic absorption to X-ray methods. If this text is any indication, the volumes are written in such a manner as to give technical support personnel the phenomenological background and operating principles of the techniques in question. The material is presented, as the goal suggests, so as to permit a person to teach himself the subject matter. Self-assessment questions (SAQ's) appear throughout each chapter so that the reader can check his understanding of the presented material. The text is very much like a short-course in print.

The first two chapters of the text introduce the basic principles of optical spectroscopy starting with descriptions of the wave-particle duality of light and the fundamental processes of absorption, emission, and fluorescence. The origin of atomic transitions and their elemental specificity, use of the Boltzmann equation to describe energy level populations, and factors affecting spectral line structure are discussed for later reference in terms of the principles behind the optical techniques and their possible spectral interferences. Chapter 3 completes the background material by presenting the basic components of optical spectrometers, their function, and basis of operation.

Chapters 4–6 break the technique of atomic absorption spectroscopy

down into sample preparation and introduction into flames, flameless atom cells, and methods of background correction. Particularly useful is the discussion of how the operating temperature and chemistry occurring in atmospheric pressure flames produce the desired free atoms or cause reduction of ground state atom populations through the formation of ions or molecules. The use of ionization suppressors and protecting and releasing agents is presented very clearly. While the discussion of flame atom cells is quite thorough (at least for this purpose), the coverage of flameless atomizers leaves a little to be desired, especially electrothermal methods. Hydride and cold vapor methods receive an amount of treatment commensurate with their application. Background correction in atomic absorption, treated as something of a black-box in commercial spectrometers, is presented so that the user can at least appreciate the physical basis of the various methods and their respective attributes.

Chapter 7 is a very brief look at the techniques employed for atomic emission spectroscopic analyses. The author describes the basic characteristics and operating principles of flame, direct current plasmas (DCP), microwave induced plasmas (MIP), and inductively coupled plasmas (ICP) with clarity. The advantages, and disadvantages, of the methods are compared, including the preferred sample introduction methods and usefulness for specific groups of elements. Given the role of plasma sources in atomic emission spectroscopy, a total of 23 pages of text seems to be a little deceiving to the reader, if not inappropriate. Under the heading of "Direct Analysis of Solids", the use of d.c. arcs and direct reading spectrometers receives a one-and-a-half page brushing-over, with a token paragraph regarding the glow discharge emission technique. The wealth of research (and recently available commercial instrumentation) devoted to direct solids analysis, particularly in terms of atomization into inductively coupled plasmas, is ignored. It would seem that the total series would have been better served by publishing a separate text on atomic emission spectroscopic methods.

The book ends with a chapter that is quite important for the described readership. The various spectroscopic techniques are compared in real-world terms. Figures of merit including limits of detection, dynamic range, elemental coverage, and the like are discussed. The possibly more important qualities of cost, sample throughput, and methods development time are also presented. A good concluding section presents some of the more recently developed methods of analysis such as continuum source atomic absorption and inductively coupled plasma mass spectrometry, atomic fluorescence, and Fourier transform spectroscopy.

As a whole, the book is quite good at its stated mission of teaching the "distant learner" the fundamental aspects of atomic absorption and emission spectroscopies. The author has presented the information quite clearly and has used the self-assessment questions well in supporting the material. The individual chapters are presented in a logical sequence that gives the reader a sense of continuity and relativity between the methods. The sections of the text dealing specifically with basic spectroscopy and the atomic absorption methods would be an excellent reference for technical short courses. This volume would also be a good reference for instrumental analysis courses and as a general reference in the analytical laboratory.

R. Kenneth Marcus, *Clemson University*

**Topics in Current Chemistry. No. 139. Organic Geo- and Cosmochemistry.** With contributions by H. D. Pflug (Geologisch-Paläontologisches Institut, Justus-Liebig-Universität), T. Nakashima (Institute for Molecular and Cellular Evolution, University of Miami), F. Mullie and J. Reisse (Université Libre de Bruxelles, Laboratoire de Chimie Organique), G. Winnewisser (I. Physikalisches Institut, Universität zu Köln), and E. Herbst (Department of Physics, Duke University). Springer-Verlag: Berlin, Heidelberg and New York. 1987. 178 pp. \$65.40. ISBN 3-540-17010-3; ISBN 0-387-17010-3.

This book is a collection of four review articles on organic molecules in geo- and cosmochemistry. They are respectively Chemical Fossils in Early Minerals, Metabolism of Protoid Microspheres, Organic Matter in Carbonaceous Chondrites, and Organic Molecules in Space.

The chapter on chemical fossils is written by Hans D. Pflug. A section on permineralization of biological matter is followed by a section on analytical techniques and results. In this section principles and procedures are first covered followed by discussions of IR, laser Raman, and UV visible microspectroscopy and, finally, a discussion of laser microprobe mass analysis. Following sections include host sediments, organic metamorphism, contamination, and inorganic chemofossils. In the concluding sections the criteria for proof of fossils in early minerals are defined and four examples are discussed. References number 126.

The chapter on protoid microsphere metabolism is written by Tadayoshi Nakashima. After explaining the scientific interest in this model of primitive abiotic proteins and describing their nature a section discussing catabolic and synthetic enzyme activities of protoids and pro-

tenoid microspheres is presented. Finally, the hormonal and inhibitory activities of protozooids is discussed. The concluding section includes a tabulation of metabolic activities of protozooids. A reference list of 70 citations is given.

Organic matter in carbonaceous chondrites is discussed by Francoise Mullie and Jaques Reisse. The long history of this important area is briefly discussed. Subsequent sections present the nature of carbonaceous chondrites and their origin and age. The last three sections describe organic matter in carbonaceous chondrites, isotope distributions in the organic matter, and the likely origins of the organic matter. The isotope effects are seen to be of special significance. The bibliography presented for this highly interdisciplinary area contains 110 references.

The final review on organic molecules in space is by Gisbert Weinwieser and Eric Herbst. The emphasis here is on the gas phase. Discussions include observations of organic molecules in the gas phase, gas-phase syntheses leading to molecular complexity, and gas-phase model calculations of complex molecule abundance. The last two sections are concerned with grains and formation of complex molecules and the question of how large interstellar organic molecules can be. An unnumbered but lengthy list of references is provided in alphabetical order.

Stan Neely, *University of Oklahoma*

**Pseudopotential Theory of Atoms and Molecules.** By L. Szasz. John Wiley & Sons: New York. 1985. xi + 309 pp. \$54.95. ISBN 0-471-82417-8.

This book presents a comprehensive review of the pseudopotential theory of atoms and molecules. Pseudopotentials qualify here operators that represent the Pauli exclusion principle. The equivalence with the more usual orthogonality conditions leads to an exact pseudopotential formalism for atoms. Such a formalism suffers from the fact that exact pseudopotential hamiltonians are rather complicated operators, but physically plausible approximations are introduced leading to model hamiltonians. This formulation coupled to the frozen core approximation is useful for computation of excited states of atoms. However, the main simplifications appear in molecular calculations. The derivation of an effective molecular hamiltonian leads to a reliable tool for valence only molecular calculations. The emphasis is put on the theoretical justifications of the model, and a characteristic of this book is discussion of problems beyond the usual one-electron approximation.

Michel Pelissier, *Centre D'Orsay*

**Studies in Physical and Theoretical Chemistry. Volume 49. Metallic Superlattices, Artificial Structured Materials.** Edited by T. Shinjo (Kyoto University) and T. Takada (Kyoto University). Elsevier Science Publishers: New York and Amsterdam. 1987. xii + 272 pp. \$117.00. ISBN 0-444-42863-1.

The purpose of this text/textbook is to provide an introduction to the rapidly growing field of metallic superlattices to those interested in the physics, chemistry, and technology of materials. While it is suggested that these materials may be of technological importance in the near future, the emphasis in this text is on basic, fundamental studies of these new synthetic metals. Through controlling structure on the monolayer scale, it is possible to design samples corresponding to specific problems in solid-state physics.

The first chapter of this 7-chapter book provides an overview of the field, from the history of the field to techniques of preparation and characterization. The author makes it clear that, while much in the way of technique has been borrowed from the area of semiconductor superlattices, the metallic materials present a wide variety of potential combinations, offering a very broad range of physical properties to the experimenter. This chapter provides a fine introduction to the specialized chapters which follow.

Two chapters are presented on the topic of diffraction. The various types of chemical and structural order studied in numerous systems are described in Chapter 2 on X-ray diffraction, which also includes an overview of X-ray techniques applicable to these materials. Chapter 3, which discusses Neutron diffraction, is a perfect companion to Chapter 6, which discusses theoretical and experimental results concerning superconductivity in superlattices. In both chapters, the emphasis is on the

interlayer coupling. This is the most important and exciting aspect of metallic superlattice research in that the magnetic properties of a metallic element are modified not by alloying but through interfacial properties.

The techniques and experiments are clearly described in the remaining two experimental chapters, one on Mössbauer and one on NMR. While the Mössbauer chapter is naturally limited to discussion of iron, the NMR chapter provides a window on a variety of unusual magnetic systems.

The last chapter, "Theories on Metallic Superlattices", serves to convince the reader that this superlayering of metals provides new materials displaying a wealth of new magnetic, elastic, and structural possibilities amenable to theoretical as well as experimental study.

The text is well organized. Each chapter is completely self contained, allowing use of any chapter or chapters in a graduate level course. Although much of the information is presented from the perspective of the physicist, this book is basically about the study of materials with multiple interfaces, an area of growing interest in Chemistry. These materials present unusual challenges for chemical and physical characterization. Even experts in these techniques may find this an interesting reference book.

The appearance of this book is quite timely since the number of studies of metallic superlattices is increasing remarkably rapidly. This text is strongly recommended for those considering entering the superlattice field, since it provides an excellent introduction to the literature by presenting a fairly comprehensive listing of studies of binary metal superlattice research from 1967 (virtually the birthdate of the field) to 1986. The entire text is quite readable, providing introductory material at the beginning of each chapter, but proceeding to the most up to date results by the end.

Michael L. Norton, *University of Georgia*

**Methods in Enzymology. Volume 127. Biomembranes. Part O. Protons and Water: Structure and Translocation. Volume 128. Plasma Lipoproteins. Part A. Preparation, Structure, and Molecular Biology. Volume 153. Recombinant DNA. Part D. Volume 155. Recombinant DNA. Part F.** Academic Press, Inc.: San Diego. Volume 127: Edited by L. Packer. 1986. xxvii + 830 pp. \$89.50. ISBN 0-12-182027-0. Volume 128: Edited by J. P. Segrest and J. J. Albers. 1986. xxvii + 992 pp. \$89.50. ISBN 0-12-182028-9. Volume 153: Edited by R. Wu and L. Grossman. 1987. xxx + 622 pp. \$70.00. ISBN 0-12-182054-8. Volume 155: Edited by R. Wu. 1987. xxix + 628 pp. ISBN 0-12-182056-4.

These books are published rapidly enough to be considered as an irregular periodical. They are all hard-bound and set in type, and each has its own index. Volume 127 contains a large number of short contributions, resembling the proceedings of a symposium. They are grouped into two sections: Interactions Between Water, Ions, and Biomolecules; and Protons and Membrane Functions. Volume 128 is similar, but there are five sections: Overview; Preparation of Plasma Lipoproteins; Isolation and Physical-Chemical Characterization of Plasma Apolipoproteins; Structure of Intact and Reconstituted Plasma Lipoproteins; and Molecular Biology of Plasma Lipoproteins. Volume 153 contains 34 contributions in the sections Vectors for Cloning DNA, and Vectors for Expression of Cloned Genes. Volume 155 contains 36 contributions, partitioned into three sections: Restriction Enzymes; Rapid Methods for DNA Sequence Analysis; and Miscellaneous Methods.

**Organic Electronic Spectral Data. Volume XXIII.** Edited by John P. Phillips, Dallas Bates, Henry Feuer, and B. S. Thyagarajan. John Wiley & Sons: New York and Chichester. 1981. xiii + 1051 pp. \$120.00. ISBN 0-471-63557-X.

In its relentlessly efficient way, this series keeps the chemical world abreast (or nearly so) of the published data on UV-vis spectra of organic compounds. The task is large, as can be appreciated from the fact that each page of this book lists the spectroscopic information for more than ten compounds, giving the absorption maxima, intensities, solvent, and reference key. It is no wonder that it required four editors and three additional contributors! The format remains unchanged, with compounds listed in formula-index order; a separate index is therefore not required.