Book Reviews

Integrated Chemical Systems: A Chemical Approach to Nanotechnology. By Allen J. Bard (University of Texas at Austin). Wiley: New York. 1994. xv + 324 pp. $49.95. ISBN 0-471-00733-1.

This book represents the author's attempt to provide a systematic approach to the description and study of complex, multiphase and multilayered structures which the author refers to as integrated chemical systems (ICS). It is based on a series of Baker Lectures given by the author at Cornell University in 1987 but includes references to work published as recently as 1993. Chapter 1 (An Introduction to ICS) introduces the concept of ICS by example. Naturally occurring green plant organelles as well as artificial structures such as heterogeneous catalysts, photoelectrochemical systems, microsensors, and instant color film are described briefly in order to introduce several key concepts which the author uses in subsequent chapters. Chapter 2 (Construction of Integrated Chemical Systems) discusses materials for construction of ICS. The materials are categorized by the author into seven categories: supports, catalysts, charge carriers and mediators, linking and coupling agents, photosensitive centers, electroactive centers, and chemically sensitive centers. While specific components of a particular ICS may fall into several of these categories, the author argues convincingly that these functional categories provide the ICS designer with an important framework with which to initiate the design process. Chapter 3 (Characterization of ICS) describes numerous in-situ and ex-situ techniques for characterization of complex samples. The descriptions are brief, with references to monographs on these techniques, and often include descriptive examples which illustrate the utility of the methods. The emphasis is on providing a broad overview of the techniques which are available, with discussion of the comparative advantages of methods and the information which each provides.

The first three chapters of this book provide a general overview of the functional parts of ICS and methods for their construction and characterization. Chapter 4 (Chemically Modified Electrodes) and Chapter 6 (Photoelectrochemistry and Semiconductor Materials) give a more detailed discussion of two important categories of ICS. Chapter 5 (Electrochemical Characterization of Modified Electrodes) provides an abbreviated theoretical background necessary for the interpretation of electrochemical measurements of chemically modified electrodes, along with numerous examples of their use. The author concludes the book with a discussion of several potential applications of ICS (Chapter 7: Future ICS). With the exception of Chapter 5 and the early part of Chapter 6, the book is largely descriptive and the author refers the reader to other manuscripts for more detailed discussion of theory. The examples provided in this book cover a wide range of functional behavior of ICS, and nearly every example is accompanied by a descriptive figure. The figures are often taken from the primary literature and are generally of high quality, both in their reproduction and in their clarity of presentation of the concepts.

Students and researchers new to this area or wishing to develop a broader view of ICS structure and function will find this book an excellent and highly readable introduction to the systematic design and construction of a variety of complex chemical systems. Though the author has not attempted to exhaustively review the vast literature of ICS, researchers in the field will also find this a useful and current reference text, particularly in the area of chemically modified electrodes.

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JA945080J

Fundamentals of Preparative and Nonlinear Chromatography. By Georges Guiochon (University of Tennessee), Sadroddin Golshan Shirazi (Applied Analytical Industries), and Anita M. Katti (Mallinckrodt Chemical Inc.). Academic Press: Boston. 1994. xv + 701 pp. $95.00. ISBN 0-12-305530-X.

This book addresses the fundamental aspects of preparative and nonlinear chromatography with the aim of consolidating this diverse and important field. With an eye for pragmatic outcomes, the authors combine fundamental understandings from chromatography and chemical engineering to create a well-organized and integrated view of this complex field.

In the first several chapters, the authors lay the groundwork with discussion of the mass balance approach to the chromatographic process (Chapter II), the thermodynamics of phase equilibrium for single components (Chapter III) and mixtures (Chapter IV), and the transfer processes required for separation (Chapter V). The various models describing the separation process are addressed in the following chapters. First in this series, linear chromatography is discussed as the limiting case of nonlinear chromatography (Chapter VI). In this case, the equilibrium isotherm is linear and thermodynamics dictate band position but do not affect the band profile. This case allows the isolation and study of the kinetic contributions to the band profile which are incorporated into the nonlinear case in subsequent chapters. At the other extreme, kinetic contributions are considered negligible by assuming infinite efficiency resulting in the ideal model of chromatographic separations. Described for single components (Chapter VII), binary mixtures (Chapter VIII), and displacement separations (Chapter IX), this model provides the means to study the thermodynamic contributions to the separation process. As stressed throughout the text, in practical applications, thermodynamics are central to the understanding and prediction of separation behavior under most conditions encountered in preparative and nonlinear chromatography. However, column efficiencies are finite and the equilibrium-dispersive model is presented as a more accurate model for band profile prediction. As in the ideal case, the equilibrium-dispersive model is described for single components (Chapter X), binary mixtures (Chapter XI), and displacement separations (Chapter XII), with an additional chapter discussing system peaks (Chapter XIII). Using the equilibrium-dispersive model, excellent agreement with experimental measurements is illustrated when accurate isotherm data are available and the adsorption data are correctly modeled. For those cases where the mass transport and/or adsorption—desorption are slow, the equilibrium-dispersive model is inadequate and kinetic models are addressed in the next two chapters (Chapters XIV and XV). Finally, optimization of preparative chromatography and critical comparison of performance are discussed in the last chapter (Chapter XVI).

Fundamental understanding of the separation process is proposed to advance the separation optimization and, therefore, the economic optimization process. It is this synergy between fundamental understanding and practical realization that is the message of this text. As a result, this book would be a worthwhile and welcomed addition to university and industrial libraries alike.

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JA945024I

The Chemistry of Metal CVD. Edited by Toivo T. Kodas and Mark J. Hampden-Smith (University of New Mexico). VCH: Weinheim and New York. 1994. xviii + 530 pp. £91.00. ISBN 3-527-29071-0.

The Chemistry of Metal CVD, edited by Kodas and Hampden-Smith, is a reference book on chemical vapor deposition that should be useful to both students and researchers already in the field as well as those interested in learning more about CVD. The book is composed of nine chapters, each written by a different author or group of authors, and focuses on applications of metal CVD to microelectronics. *The Chemistry of Metal CVD* should be of interest not only to chemists but also to engineers and applied physicists who are familiar with microelectronic device fabrication but not with surface, inorganic, gas-phase, and solid-state chemistry.

Chapter 1, written by the editors of the book, gives an overview of the chemistry of metal CVD. A general discussion of the important issues in fabricating integrated circuits is included. Several terms related to microelectronic device fabrication are defined, and concepts are explained in detail. This chapter summarizes the problems and challenges associated with the application of different metals in device fabrication. For chemists not familiar with microelectronic device fabrication, the information provided in this chapter will be quite beneficial.

Chapters 2–8 describe the chemistry of metal CVD for specific metals that are used or have potential use in the microelectronics industry. The CVD chemistry of Al (Chapter 2), W (Chapter 3), Cu (Chapters 4 and 5), Ag and Au (Chapter 6), Pt, Pd, and Ni (Chapter 7), and other metals (Chapter 8) are discussed. Each of these chapters emphasizes the physical and chemical properties of different precursors currently employed in the CVD of metallic films. Typically, the synthesis of each precursor is described and details such as vapor pressure and structure of the precursor are provided. The quality of the films produced by different precursors is also addressed. Kinetic data are summarized in terms of deposition rates and reaction mechanisms. When possible, ultra high-vacuum surface science studies related to metal CVD are presented and discussed in terms of deposition mechanisms and film quality.

The last chapter, Chapter 9, is a summary by the editors of the previous eight chapters. Topics emphasized in this chapter include precursor choice, precursor delivery, selective deposition, and reactor design. Future directions in metal CVD are also discussed.

Overall, this is a very good reference book on the chemistry of metal CVD that is clearly written and well organized. Each chapter is divided into many sections and subsections; these are all listed in the table of contents. The references and index are fairly complete and up to date. A list of chemical and general abbreviations is given at the beginning of the book, and two appendixes are provided to give examples of chemical nomenclature and definitions of terms used in the microelectronics industry. Because there are a number of contributors to this book, there is some redundancy in the text. This problem is particularly acute in the sections related to precursor nomenclature, abbreviations of precursor nomenclature, and precursor structure in each chapter. However, despite this minor shortcoming, I highly recommend this book to anyone interested in learning more about the chemistry of metal CVD.

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JA945105E

Enzymes in Synthetic Organic Chemistry. Tetrahedron Organic Chemistry Series. Volume 12. By Chi-Huey Wong (The Scripps Research Institute) and George M. Whitesides (Harvard University). Pergamon: Oxford. 1994. xvii + 370 pp. $38.00. IBSN 0-08-035941-8.

This book is thorough, up-to-date, highly readable, and very instructive for both novices and experienced practitioners in this rapidly growing area of chemistry. The authors, noted for their outstanding practical advances in the applications of enzymes in synthetic chemistry, have provided insight and encouraging commentary on harnessing the remarkable power of these natural catalysts in synthetic endeavors. Chapter 1, on general aspects, includes discussions on enzyme kinetics, inhibition, specificity, cofactor regeneration, and reactions in organic media; the chapter concludes with a brief overview of enzyme engineering, site selective modifications, and catalytic antibodies. There follows five chapters on the applications of enzymes to particular types of transformations.

Chapter 2 covers the most commonly used enzymes in organic synthesis, the various hydrolases—amidases, proteases, esterases, lipases, nitrile hydrolases, and epoxide hydrolases. The coverage throughout the book is well organized with clear schemes tables, and diagrams and is remarkably comprehensive. Chapter 2 alone has more than 500 references, with about 10% of them from 1993. Chapter 3 covers the various oxidoreductases with appropriate emphasis on cofactor recycling. Aldolases and other C−C bond-forming enzymes are featured in Chapter 4, with prominence placed on remarkable successes in the synthesis of sugars and related molecules. Chapter 5 continues this theme with excellent coverage of the applications of various enzymes to the syntheses of *N*- and *O*-glycosides and concludes with a prospective on future opportunities. The final chapter examines additions, eliminations, and other group-transfer reactions. There is a subject index.

By groupling together enzymes that carry out related types of synthetic transformations, the authors have greatly reduced the burden of identifying suitable enzymes and conditions to accomplish a particular transformation. Enzymes are clearly important tools for use by synthetic organic chemists and are becoming more so in view of the current interest in the production of enantiopure materials. This book is by far the best effort to date for those interested in using enzymes in the context of organic syntheses. This economical paperback is recommended for personal and library collections and as a text for a special topics course.

Carl R. Johnson, *Wayne State University*

JA945035B

The Origins of Order. Self-Organization and Selection in Evolution. By Stuart A. Kauffman (University of Pennsylvania). Oxford University Press: New York. 1993. xvii + 709 pp. $29.95. ISBN 0-19-507951-5.

Those fundamental laws of Nature discovered since the time of Galileo and Newton have given us little insight into the origin of the most spectacular of nature's creations we call "life". And nature's ability to create order and complexity is not confined to life alone. In this monograph, Stuart Kauffman presents a collection of thought-provoking ideas and theories to answer questions related to *The Origins of Order*.

The aim of this work is not so much to detail the exact chemistry that produced life as we know it but to understand the principles that can create a system that can adapt and evolve. As Manfred Eigen notes in his *Steps Towards Life* (Oxford University Press: New York, 1992; p 4), "We shall come closest to understanding the principle of life if we discover the principles according to which life *could* begin. This is a challenge addressed to the physicist, even if he calls himself a biologist, a biochemist or a molecular biologist." Stuart Kauffman takes up this challenge and, whatever his disguise, sounds like a physicist.

Excluding the first chapter, the monograph consists of three parts: (I) Adaptation at the Edge of Chaos, (II) The Crystallization of Life, and (III) Order and Ontogeny. The first chapter is an excellent outline of the current theories of evolution—a chapter that is very helpful to the readers who are not biologists. The three parts are not interdependent, and they need not be read in the order in which they are presented. Chemists interested in questions of the origins of life may want to start with part II.

In the opening chapter, Kauffman argues that the order we see in life is an order that is founded on and constrained by the spontaneous order that appears in equilibrium and nonequilibrium systems (the latter known among the chemists as self-organizations). In part I, Kauffman addresses a basic question: How does selection create a system that is capable of adapting to its environment? To answer this question, one needs to define precisely terms such as "fitness landscape", on the basis of a protein's capacity to perform a given catalytic function. Here the idea of a "catalytic task space", which specifies in some abstract way all the catalytic tasks, is also discussed. To cover the entire catalytic task space, the number of proteins required is about 10^8, roughly the estimated number of proteins that an immune system is capable of generating. Random mutations cause the proteins to evolve in this fitness landscape. This formalism shows some unexpected results: situations in which there is an evolution that may be described as a spontaneous ordering. The resulting states can be quite frozen and make it difficult for the system to evolve and respond to changes. In other cases, the system goes through states that are unstable and wanders chaotically through various states. Here, Kauffman puts forth the theory that complex systems evolve to a situation in which they are on the border between frozen order and chaos: "Life exists on the edge of chaos." It is at this location that life attains its ability to adapt.

The crystallization of life, the second part, is about the origin of a self-replicating network of polymers. It presents a general theory of evolution of polymers that can catalyze bond formation and bond cleavage. In such a network, as the size of the polymers and the number of possible reactions grow, there comes a point at which the formation of an autocatalytic cycle bcomes so highly probable, it is inevitable. Thus the heretical suggestion that "The origin of life, rather than being vastly improbable, is instead an expected collective property of complex systems of catalytic polymers and the molecules on which they act." Kauffman suggests that it is such a process that created life, not a "primitive genome" based on template replication. Whether one agrees with this view or not, it certainly presents an interesting way of analyzing complex chemical systems. This statistical way of looking at chemical processes may not be related to the chemistry that is being generally practiced in the lab today, but it might well provide the basis for combinatorial approaches to medicinal chemistry (see, *Chem. Eng. News* **1994**, *72* (Feb 20)).

The last part is about cellular differentiation and morphogenesis, the processes through which nature puts cells of the eye, limbs, liver, heart, and all the organs that make up a living creature in the right places. It presents the notion of spatial dissipative structures, or Turing structures, which can carry positional information for cell differentiation. The issues are more specific to the questions in biology, though some general questions relating the number of catalytic cycles in a random catalytic reaction space are discussed. These ideas may have wider implications outside biology.

In all three parts, there are many more interesting ideas, more than one can summarize in a short review such as this. The book does not make easy reading, but the reader who spends the time will be rewarded. It brings together important contributions and contains over 1000 references, and yet one can find omissions—a sign of our times. For the chemist or the physicist who wants to understand the "origins of order" on a simpler level with specific experimental examples, however, works such as *Self-Organization in Nonequilibrium Systems* by G. Nicolis and I. Prigogine (John Wiley: New York, 1977) or *State-of-the-art Symposium: Self-Organization in Chemistry* (*J. Chem. Ed.* **1989**, *66* (3), 186–212) are better suited.

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JA9347402

Advanced Organic Chemistry of Nucleic Acids. By Z. Shabarova and A. Bogdanov (Moscow University). VCH: New York. 1994. xvi + 588 pp. $145.00 ISBN 3-527-29021-4.

This is an excellent book providing an in-depth examination of the chemical and structural properties of nucleic acids. I have found the text to be very well written and organized in a logical manner. The title is slightly misleading, however, since the book covers much more than the organic chemistry of nucleic acids. Included are sections on the in-depth characterizations of the physical and structural aspects of DNA and RNA structures.

Over the past decade, there have been relatively few chemistry texts dedicated to nucleic acids with the depth that these authors undertake. In Chapters 1–4, this book provides the underlying chemical principles of nucleosides and nucleotides. Chapters 5–7 lead the reader through assembly processes of DNA and RNA up to Chapter 8, which then provides an in-depth discussion on the structural properties of DNA and RNA. It was refreshing to see the RNA catalytic studies provided in Chapter 10. The final chapter deals with chemical synthesis of DNA and a well-organized historical view of the developments that have occurred in this field.

The objective of the authors is to provide a fundamental understanding of the chemical and physical properties of nucleic acids. Along with their discussions are invaluable references at the end of each chapter which allow the student or investigator ample opportunity to go to the original data for a more detailed description. This is the best fundamental nucleic acid chemistry text that I have read since the 1984 edition of *Principles of Nucleic Acid Structure* by Saenger. Coupled with the physical chemistry and X-ray crystallographic approach of Saenger's text, the two provide a near complete presentation of nucleic acid chemistry, reactivity, and structure.

This book will be of benefit to nucleic acid biochemists as fundamental information and to graduate students taking advanced nucleic acid chemistry course work. The pertinent information is easy to find and digest, which makes this a desirable text for an advanced nucleic acid chemistry course. I highly recommend the book to nucleic acid biochemists and their students as a standard information text.

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JA945028N

The Chemistry of the Fullerenes. By Andreas Hirsch (University of Tubingen). Georg Thieme Verlag: Stuttgart, Germany. 1994. xi + 203 pp. DM80.00. ISBN 0-86577-560-5.

How can one cope with the recent outpouring of literally thousands of papers on the organic and organometallic chemistry of fullerenes? Andreas Hirsch has now provided the best comprehensive book-length review, covering the literature through early 1994.

Hirsch cogently organizes the material into nine chapters. Following a short history of the field, he outlines production and separation and discusses fundamental properties such as bond lengths, symmetry, and solubility. The summaries of fullerene transformations then begin with anion formation, encompassing MO considerations, reductive electrochemistry, metal reductions, and charge transfer from organic donors. Reactions of fullerenes with diverse nucleophiles are described, together with the polymers, polyadducts, and self-assembled monolayers which have been fabricated via these processes. Hirsch next reviews the extensive published work on [4 + 2], [3 + 2], [2 + 2], and [2 + 1] cycloadditions. Novel materials accessible by these pathways include "pearl necklaces", copolymers, and fullerene dendrites.

The theory and execution of C_{60} and C_{70} hydrogenation reactions are considered, followed by summaries of radical and organometallic additions and polymerizations. A discussion of electrophilic additions includes electrochemical oxidation, oxygenation, osmylation, and halogenation, as well as conversion to fullerols with strong oxidizers and interactions with Lewis acids. The final chapter offers an overview of fullerene reactivity. Practical applications are projected for many areas such as optics, pharmaceuticals, superconductors, catalysis, and lubricants.

Hirsch's volume is timely and well written, thorough, yet concise. The book certainly will prove more useful to chemists than the wider-ranging multiauthor volumes published earlier, and the straightforward presentation should be accessible to nonchemists as well. Strongly recommended.

Amos B. Smith, III, and Robert M. Strongin, *University of Pennsylvania*

JA945100H

Catalyst Characterization Physical Techniques for Solid Materials. Edited by Boris Imelik and Jacques C. Vedrine (CNRS, Villeurbanne, France). Plenum Press: New York. 1994. xxxii + 702 pp. $125.00. ISBN 0-306-43950-6.

This book is a compilation of rather brief descriptions of more than 20 techniques that are currently being used to study catalytic solids. It is a modified English version of a French book published by Technip Editions. The choices of techniques discussed in the book are sound, and it is a useful contribution to the catalyst scientific and technical community.

Although most of the chapters provide an adequate introduction to these techniques, the stated intention of the editors to describe the techniques, to explain their theoretical basis, to define their field of application, and through examples, to objectively assess the validity of their use is not achieved for all the methods. Most of the references in the book are from the 1970s and 1980s, and very few references are from the 1990s. In most cases this does not distract from the basic description of the techniques or the discussion of their theoretical bases. However, it makes the book already outdated for the rapidly evolving techniques and consequently does not give the reader a view of the most recent developments in application of the techniques to catalytic problems. The chapter on SPM (scanning probe methods) is already completely out-of-date and is totally inadequate. The chapters on mass spectrometry and thermal methods are unique and quite useful. The coverage of surface spectroscopies, especially ISS and SIMS, is noteworthy as well as is the coverage of vibrational and optical spectroscopies. The discussions of the resonance techniques, ESR and NMR, also deserve mention as do the chapters on XANES and EXAFS.

In spite of the shortcomings, the book can be recommended to those beginning to characterize catalysts and to those looking for a sound first introduction to the basics of catalyst characterization techniques. It also can be recommended for use as a reference or as supplementary material for classroom activities. Even though the editors have partially achieved their goal of giving readers the elements necessary for identifying the best potential methods for solving their catalytic characterization problems, the readers will still be forced to seek additional literature before picking the best methods and starting such tasks. Unfortunately, the book falls short of one's expectations of work from these renown catalyst characterization specialists.

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JA9450216