Additions and Corrections

Diffusion-Limited Size-Selective Ion Sensing Based on SAM-Supported Peptide Nanotubes [*J. Am. Chem. Soc.* **1997**, *119*, 11306−11312]. KIANOUSH MOTESHAREI AND M. REZA GHADIRI*

Page 11311, Table 1: The capacitance values for substrate surfaces **3** and **4** should read 2.70 and 1.22, respectively.

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Computer Software Reviews

Database of Palladium Chemistry: Reactions, Catalytic Cycles and Chemical Parameters on CD-ROM Version 1.0. By Jean-Luc Malleron, Alain Juin and Rhone-Poulenc Rorer. Academic Press: Kent. 1997. $545.00. ISBN 0-12-466760-0.

Database of Palladium Chemistry is a searchable database of nearly 3500 entries for various palladium-catalyzed organic reactions. The program is designed to operate on a PC compatible computer with a 486 or higher processor (though pentium processors are highly recommended to minimize waiting). The program is contained on a CD-ROM and requires at least 8 Mbyte of RAM and 20 Mbyte of hard disk space to install the program to the hard disk. The program utilizes the viewer ISIS/BASE for its search tool and ISIS/Draw for viewing and searching chemical structures. Both programs are included with the software package.

The database is a collection of organic synthesis reactions involving palladium that are broken down into 84 different reaction types, such as Intermolecular HECK Reactions or Tandem Acyloxylation-Cyclization of 1,5-Dienes. Each reaction type has a general mechanistic scheme which can be viewed using Word Viewer (also included). These schemes are useful because they often describe the reactions better than title headings. The individual reactions of the schemes can be imported to other programs where they can be utilized.

The database may be searched in a number of ways. Searches may be performed on the whole database or on individual sections of the database. The entries in the database are entered into a generic form that is divided into various fields that may be searched. These fields include graphical pictures of reactions, catalysts, solvents, and reference citations. A search can be narrowed down quite quickly by choosing specific reactions and filling in multiple fields. The search times are less than 15 s even on a slower 486 computer.

A 300 page handbook is include with the program. This handbook is essentially an outline of the database which allows the user to look through the lists of reactions. Unfortunately there is no way to go directly from a handbook entry to the analogous entry in the database. Instead, one can find a given reaction by performing a search on the appropriate substrate involved in the reaction.

The program offers extensive help menus to guide the user through some of the different aspects of the program. With some practice, an average computer user can learn to quickly find references for specific types of palladium reactions. The software publisher did not indicate how often the database will be updated, but users are encouraged to register the software so they can be informed of updates. Overall the program provides a useful tool for both academic and industrial chemists who wish to search for palladium-catalyzed reactions. This database will be a useful addition to any library's collection, particularly if the publishers fulfill their stated intention to publish periodic updates.

The ease with which searchable databases can be updated to include current literature enhances their value. The publishers should be encouraged to allow online access to the database since this would allow more frequent updates.

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Book Reviews

Comprehensive Analytical Chemistry. Volume XXXI. Surfactants in Analytical Chemistry: Applications of Organized Amphiphilic Media. By Edmondo Pramauro and Ezio Pelizzetti (University of Torino, Italy). Elsevier: Amsterdam. 1996. xviii + 521 pp. $265.75. ISBN 0-444-89033-5.

Given the plethora of applications of surfactant-organized media in all aspects of chemical analysis, it is rather surprising that this is only the second monograph (and the first in English) that has been devoted to this general topic. The authors, both of whom are leaders in the areas of colloid and surface science, physical chemistry of surfactant micelles, and their applications in analytical chemistry, have done an excellent job at blending together the pertinent background information, physicochemical properties, and structural features of surfactant media along with the different spectroscopic, electroanalytical, and separation science applications.

This book consists of eight chapters. Chapter 1 (91 pp, 165 refs) provides an overview of micelle-forming surfactants, their aggregation behavior, micellar parameters, and microscopic properties. Chapter 2 (37 pp, 125 refs) discusses solute solubilization and binding in surfactant micelle systems along with the factors that impact solute−micelle interactions. Chapter 3 (71 pp, 133 refs) summarizes the different quantitative theories that have been developed to describe the effect of different charge-type micelles upon the rate as well as equilibrium position of chemical reactions. With this background information in place from these opening three chapters, the authors go on to survey and detail the advantageous utilization of such surfactant media in analytical chemistry. Chapters 4 (63 pp, 138 refs) and 5 (55 pp, 105 refs) describe the different analytical spectroscopic (absorption and luminescence) and electrochemical (potentiometric, conductometric, and voltammetric) measurements that have been successfully conducted in surfactant-organized assemblies. The utilization of surfactant media in separation science is the topic of Chapters 6 (68 pp, 133 refs) and 7 (58 pp, 194 refs), with micellar liquid chromatography, micellar electrokinetic capillary chromatography, and surfactant-mediated extraction−preconcentration (cloud point extraction and micellar-enhanced ultrafiltration) methods being discussed. The concluding chapter, Chapter 8 (50 pp, 154 refs), concerns a description of some other, less traditional, surfactant media (e.g., biosurfactant assemblies, reversed micelles, monolayers and black lipid membranes, vesicles) that mimic biological systems along with their use to date as models and in analytical applications as well.

The stated purpose of this volume "is to provide a comprehensive assessment of the state of surfactants and surfactant aggregates in analytical chemistry ... [particularly] where they can offer significant advantages". The authors have nicely achieved this goal. Overall, this book provides the basic fundamentals on the nature, structure, and

properties of surfactant-organized media as well as summarizes the state of knowledge concerning their utilization in analytical chemistry. By and large, the literature citations are current up through 1995 and provide a good cross-section of the voluminous literature available. The 16-page subject index at the end of this volume is very thorough for a work of this magnitude. The book is also remarkably free from errors, well-produced, and well-illustrated.

The use of different surfactant-organized media has become rather pervasive in analytical chemistry today, and this monograph is a welcome source of valuable information, not only for those considering such applications but also for the more experienced practitioners in the field. Were it not for the price, it could also serve as a useful textbook for a graduate course on this topic. Overall, I find this to be a very timely addition to the series of monographs on comprehensive analytical chemistry. The monograph is highly recommended as a library acquisition as it is probably a bit too expensive for an individual purchase.

Note Added in Proof. Those interested are referred to another recent review of this work: von Wandruszka, R. *Analyst* **1991**, *122*, 101N−102N.

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Organic and Bio-organic Mechanisms. By Michael Page(The University of Huddersfield) and Andrew Williams (The University of Kent). Addison-Wesley-Longman: Essex. 1997. x + 298 pp. £27.99. ISBN 0-582-07484-3.

Page and Williams have succeeded in producing a short text that reports on the intersection of three large fields of inquiry: physical organic chemistry, bio-organic chemistry, and mechanistic enzymology. Their book begins with two chapters that establish the fundamental assumptions for mechanistic investigations, followed by three chapters covering the analysis of specific experimental approaches including free-energy relationships, isotope effects, solvent, temperature and pressure effects, and the use of strongly acidic and basic media. The last third of the book includes two survey chapters covering bio-organic group-transfer reactions and several classes of enzymatic reactions, along with two chapters on various aspects of catalysis.

The style of the early chapters is somewhat disconcerting as the authors often use references to later sections of the text in place of immediate definitions or explanations for unfamiliar concepts and jargon. For example, in the first chapter, Page and Williams use the terms "intrinsic barrier" and "Eigen plot" without definition in an explanation of nonperfect synchronization reactions. The authors direct the reader instead to sections and figures in chapter six. At first reading, this style is bothersome, but in this age of hypertext it does not take much effort to accept the "links" to later chapters, and the style does enhance the book's function as a reference work. There are also a few eccentricities in the book, such as the unconventional use of the term "intrinsic isotope effect" to denote a semiclassical isotope effect maximum, and the presentation of an uncommon notation for isotope effects as convention.

Organic and Bio-organic Mechanisms is at its best when Page and Williams lay out the mechanistic reasoning and assumptions associated with specific problems. The presentation of the use of Brønsted relationships and the chapter entitled Bio-organic Group Transfer Reactions are particularly good in this light. Page and Williams begin their treatment of Brønsted relationships with a discussion of critical assumptions and a prudent description of effective charge as a measure of transition-state character. They next present several literature examples to illustrate the process of crafting mechanistic insights from effective charges. Their Brønsted treatment, as well as their presentations of other mechanistic probes, are further enhanced in an intriguing chapter called Transition-State Structures -- Anomalies. In a similarly appealing approach, Page and Williams organize their group-transfer chapter around the common notion of stepwise vs concerted reaction mechanisms using several introductory sections to outline the issues and pertinent mechanistic reasoning.

The book should be especially useful to enzymologists who want a concise but discerning introduction to the developments of physical organic chemistry over the last 30−40 years as they apply to bio-organic and enzymatic mechanisms. The catalysis chapters are particularly valuable as they showcase the insights and perspectives of Page and Williams on a wide range of mechanistic issues.

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Ligand−Receptor Energetics: A Guide for the Perplexed. By Irving M. Klotz (Northwestern University). Wiley Interscience: New York. 1997. xi + 170 pp. $44.95. ISBN 0-471-17626-5.

To quote part of the preface to this book, "The first step in essentially all biological activities is an interaction between separate molecular constituents, ligand and receptor, to form a macromolecular complex". Certainly, a complete understanding of biology, as well as the ability to mimic biology in man-made systems, requires an in-depth understanding of the energetics of intermolecular interactions. This book focuses upon the mathematics of such interactions, methods to solve for equilibrium constants in complex scenarios, and methods of graphical presentation of the data. To quote the preface again, "The objective of this volume is to present the core principles that provide the foundation for quantitative perspectives".

The first chapter of this book covers the simple mathematics of molecular interactions by following the concentration of free ligand, and the perturbation of properties of the ligand when bound. The second chapter takes on an analysis from the point of view of the receptor binding sites. In this chapter the traditional binding isotherms are covered, along with linearization procedures, and methods to determine the number of binding sites that a receptor possesses. Chapter 3 is quite short, and generalizes the binding equations to multivalent receptors, as does Chapter 4, but from a point of view that the author entitles "ghost-site perspective". These two chapters are quite heavy on the mathematics, and it would have been useful for the author to give a deeper analysis of how to apply these equations to everyday experimental analyses. Chapter 5 is a very useful chapter. It is titled Fact and Fantasies from Graphical Analyses. This chapter covers the pitfalls one may encounter when attempting to measure affinity constants using a wide variety of common experimental and graphical techniques: curve fitting to the typical one-to-one hyperbolic binding algorithm, Scatchard plots, and semilogarithmic plots. This chapter will be an invaluable tool in the hands of our research group, and I would recommend this chapter to anyone working in the field of biochemistry and supramolecular chemistry. Chapter 6 increases one's understanding of the numerical methods for evaluating binding constants, and lists several binding constants for biological entities. The next chapter covers affinity profiles, detailing cooperativity between different binding sites in a single receptor. Chapter 8 covers the mathematics and experimental methods for measuring the thermodynamics of binding, giving several examples of enthalpies and entropies of complexation. Chapter 9 gives a quick overview of the forces that dictate intermolecular association: solvation, dispersion forces, hydrophobic effect, electrostatics, and hydrogen bonding. Further, this chapter includes a quick overview of clathrate compounds. The last chapter is called Molecular Scenarios, and covers the mathematics of regulatory responses to the concentration of effectors, as well as allosteric effects. Finally, the remainder of the book includes four appendices that cover experimental methods in dialysis, more details of graphical analyses, and even more mathematical relationships between different types of binding constants.

In summary, the strengths of the book are the insights into complex multivalent receptors and the experimental methods for accurately determining their individual binding constants. Another strength is the discussion of the limits of different analysis methods for determining the affinity constants. Finally, the book is quite short, does not waste words in explaining its points, and is easy to read. Due to these strengths, I would recommend this book to anyone who routinely measures equilibrium constants for intermolecular complexation events. The weaknesses are minor, but include a lack of insight into how to apply the complex equations to "real-life" scenarios, and a glossary analysis of the forces of intermolecular interactions. Therefore, the book is not appropriate for one that is primarily interested in learning about the microscopic forces that hold molecules together.

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