Book Review

# Radioanalytical Chemistry Edited by Bernd Kahn (Georgia Institute of Technology, Atlanta, GA, USA). Springer Science + Business Media, LLC: New York. 2007. viii + 474 pp. $89.95. ISBN 0-387-34122-6.

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BOOK REVIEWS

**Radioanalytical Chemistry**. Edited by Bernd Kahn (Georgia Institute of Technology, Atlanta, GA, USA). Springer Science + Business Media, LLC: New York. 2007. viii + 474 pp. $89.95. ISBN 0-387-34122-6.

At the end of the 19th century, the "hot" topic in science was *radioactivity*, as nanoscience and molecular bioscience are today. The pioneering work of Becquerel and the Curies revealed to the world the existence of high-energy penetrating radiation emitted by naturally occurring elements like uranium and thorium and by their short-lived progeny like radium and radon. The Curies and Becquerel coined the term "radioactivity" to describe the phenomenon. During the 20th century, scores of brilliant scientists built upon their seminal observations to revolutionize both chemistry and physics, developing models and concepts that are at the core of our current understanding of the workings of the universe. In the aftermath of this burst of scientific creativity—and to some degree coincident with or even ahead of these developments—several important nuclear technologies were developed: in particular, nuclear weapons, nuclear electricity, and nuclear medicine, each of which remains a fixture of modern life. Detection and analysis of radioactive materials, i.e., radioanalytical chemistry, were integral to the initial discovery and are essential to ensuring safe operation in these technologies. The need for trained specialists in this field has never been greater. Unfortunately, educational opportunities in nuclear science, radiochemistry, and engineering have declined globally by at least a factor of 3 since achieving their peak in the late 1970s. The appearance of new instructional materials is therefore cause for celebration.

The stated purpose of this text is "to teach radioanalytical chemistry in the classroom and support its application in the laboratory" with emphasis on "the practical aspects of the specialty". It is designed as an upper level or graduate text "to train students to work in, manage, or interact with a laboratory devoted to radionuclide measurement". It is an edited compilation of 17 chapters prepared by 20 contributing authors. The editor is a highly regarded practitioner in the field and is author or coauthor of seven of the chapters. Following the Introduction, Chapters 2−5 address the basic principles of radiometric analysis, sample collection, and analytical chemistry. Chapters 6−10 focus on applications, sample collection/preparation, and data analysis. The information presented in Chapters 11−14 is on the design and operation of a radioanalytical chemistry laboratory, emphasizing issues like quality assurance, safety, and troubleshooting. The final three chapters, in which automated laboratory facilities, chemistry beyond the actinides, and applications of mass spectrometry to the analysis of radioactive samples are discussed, are arguably of the most interest to the practitioner.

Though the subject matter of this book is timely and the chapters are well written, the execution overall is uneven. The introductory chapters (1−5) review fundamental analytical chemistry, emphasizing radiation detection and sample preparation. In the classroom, it would be necessary to amplify considerably the material contained here or to build a course around this book that complements other more thorough courses in analytical and nuclear chemistry as well as radiochemistry. Opportunities to deliver useful lessons on combining conventional analytical methods with radioactive materials are missed. For example, the conduct of a distillation is described without a specific admonition about the hazards associated with distilling radioactive substances. A primary safety rule in a radioanalytical chemistry lab is to *always* be aware of pathways for airborne transport of radioactive materials. A classical distillation would never be conducted on radioactive materials without taking precautions to provide secondary containment.

The bibliographic references in these chapters are considerably out-of-date. The reader might come to the erroneous conclusion that nothing important in analytical separations, for example, was done after about 1970. If the student or the instructor became interested in learning the latest on this subject matter, he or she would be left to conduct an independent review of the prior literature, deriving only minimal guidance from the materials presented here. Of course, the instructor might choose to use a literature search as an educational tool to fill this gap; it is doubtful that this was the intent of the book. The introductory chapters also are devoid of those relevant examples that help make the abstract concrete for students.

The information in Chapters 6−10 suffers some of the same faults with respect to the currency of the bibliography, but overall the basics of conducting radiometric analysis are described in adequate detail. These chapters are arguably more useful as a guide to operations in a working radioanalytical laboratory than they are as a teaching tool. The operational envelope for a commercial radioanalytical chemistry lab is covered in detail in Chapters 11−14. This section could have been shorter without compromising the content and would probably have been more effective if it described the conduct of lab operations using the protocols of a particular laboratory (or several). The generic lab described perhaps offers a chance to discuss design concepts, but the opportunity to say why certain designs might be more efficient than others is not indulged. Chapter 14, dedicated to laboratory safety, is so elementary in its approach that an undergraduate chemistry student might be bored and perhaps offended by its extreme simplicity. A much-condensed chapter that focused specifically on the relationship between radiological safety and general laboratory safety would have been more effective.

As noted above, the final three chapters constitute the most interesting information in the book to experts. Topical and relevant material is described, and their respective bibliographies are current, citing the latest reports from the literature. Remote sample retrieval and detection instrumentation has relevance to nuclear security, power plant operations, and waste management, while creating and detecting transactinide elements a few atoms at a time is a fascinating frontier in chemistry. In Chapter 17,

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"Mass Spectrometric Radionuclide Analysis", the complex mélange of mass spectrometric analytical techniques is described and the differences among the various methods are carefully discussed.

In summary, the excitement that I felt in being given the opportunity to review this book was tempered a bit by its execution. There is good information available in the book, though the coverage in some areas is not deep enough for the book to stand alone as a textbook. It has perhaps greater utility as a guide for the setup and operation of a radioanalytical laboratory. It could have been a much more effective treatise if more attention had been paid to the final details of its publication. A few faults are the uneven status of the bibliography, some redundancy in the information presented in the chapters (which might have been avoided with a careful final edit of the completed book), a number of easily preventable typographical errors (misspelled names of authors in the bibliography and text citations are particularly annoying), and the absence of materials useful for instructional purposes, e.g., worked out examples to describe the use of equations and end-of-chapter study materials. On the positive side, it is generally easy to read, is appropriately organized, and does add a new perspective to the existing instructional materials on radioanalytical chemistry. Overall, this is a useful book that could have been more.

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**Reviews in Computational Chemistry, Volume 23**. Edited by Kenny B. Lipkowitz (Howard University, Washington, D.C.), Thomas R. Cundari (University of North Texas, Denton), and Donald B. Boyd, Editor Emeritus (Indiana University-Purdue University, Indianapolis). J. Wiley & Sons, Inc.: Hoboken, NJ. 2007. xxxii + 484 pp. $160. ISBN 978-0-470-08201-0.

As with previous volumes in the very successful series *Reviews in Compuational Chemistry*, this volume contains a compilation of topics covering computational methods, algorithmic strategies, and applications in the field. The spectrum of topics covered includes chapters on advanced treatments of potential energy surfaces, increasing the efficiency and scaling of computational algorithms, and considerations of data analysis and informatics. The interplay of topics is particularly nice, given that the advanced treatments that are discussed are some of the more challenging computationally, particularly for large molecular systems.

In less than 40 years, the field of computational chemistry has gone from being essentially nonexistent to being an active counterpart in experimental investigations, with high-performance computing, clever algorithmic implementations, and information technology dramatically influencing methods development and performance. A traditional limitation of quantum chemical computations has been the relatively poor scaling of computational effort with the increasing size of the molecular system and/or complexity of the numerical procedure. Great interest exists in finding appropriate algorithms or partitioning schemes to arrive at linear scaling, particularly with the onset of greater power, mode, and availability of computer hardware. Chapter 1, "Linear-Scaling Methods in Quantum Chemistry", presents a thorough and detailed overview of such strategies, as well as a future outlook for computing very large systems with electron correlation, including the ability to capture the collective effects of many hundreds or even thousands of atoms for understanding biochemical or materials phenomenon, for example, where empirical/classical methods fail. The chapter concludes with several significant challenges that still remain for the linear-scaling community, with the ultimate goal of establishing efficient methods that are globally applicable.

Predictions of reactivity and modeling of dynamics take on meaning when accurate transition states and associated reaction paths are considered. Full quantum mechanical treatments of reaction processes become complicated when more extensive computational treatments are required in the analysis. Unlike relatively direct optimization methods for finding minima on the potential energy surface, finding transition states, reaction paths, smf mechanistic and dynamical information requires more complex analytical treatment of the potential energy surface. The surface curvature near the transition state affects factors such as recrossing and tunneling. The purpose of Chapter 3 is to bring into focus modern methods for dealing with such complicated predictions, based on variational transition state theory (VTST). This chapter provides a rich overview of this area, which has expanded from basic VTST for gas-phase reactions covering a wide variation in theories to analysis of partition functions and associated statistical mechanical properties, details of multidimensional tunneling, and direct dynamics computations. VTST was traditionally practical only for reactions of small molecules in the gas phase, but advancements in hardware and algorithms allow extension of the theory in more recent formulations to that based on free-energy sampling and semiclassical tunneling, enabling the study of complex reactions in the condensed phase, particularly when there is an ensemble of reaction paths and strong coupling to the environment.

More subtle quantum effects, arising in reactions where two different electronic states coincide in energy, require understanding of the details of the intersection space. Conical intersections, also called molecular funnels or diabolic points, are ubiquitous in chemical reactions and have attracted much interest due to their important role in fast photochemical processes. Prediction and mechanistic understanding of photochemistry, luminescence, and general photonic properties are highly dependent on the quality of the treatment of these regions of the potential energy surface. In Chapter 2, "Conical Intersections in Molecular Systems", the basics of this field are discussed and how these problems are addressed computationally are explained. The chapter nicely spans from general theory, with exemplary applications in the biological domain, to discussions beyond a double cone intersection and concludes with a perspective for the future.

The complexity of processes involving polymers represents another challenging area from the perspective of molecular size and variable length scales. Even with current computational hardware, the complexity of polymeric processes makes predictive modeling extremely challenging. More recently, it was realized that a connection between the arising length and time scales was necessary, resulting in a number of coarse-graining techniques where simulations on more than one length scale were combined in order to provide a better understanding of the system as a whole. In Chapter 4, "Coarse-Grain Modeling

of Polymers", several of the more recent automatic mapping schemes for coarse-graining in polymer research are presented, ranging from techniques involving Monte Carlo simulations to those involving static or dynamic mappings. Insights on the choice of model are provided, as well as an outlook beyond polymers. There is the general hope that such methods will have applications beyond classical polymer chemistry.

Given that one can carry out computations on an increasingly larger scale with more efficient methods and hardware, questions of storage, efficient data usage, and the consequences of that usage in terms of information content arise. The relationship between information content and energy has become a fashionable topic for systems scientists. It is often stated that such theories regarding information content could be more appropriate for predicting emerging properties. The coverage in Chapter 5 defines the theory of Shannon entropy and explains how it can be used to assess chemical information content in systems chemistry, from organic molecules to chemical ensembles. The applications include chemical structural arrays, like chemical libraries, as well as the population of structure obtained by dynamics methods.

Support vector machines are not physical machines but rather statistical methods used for classification and regression analysis. Knowledge of these methods can direct the chemist to problems of qualitative chemical taxonomy (polar vs nonpolar molecules or groups) or, more quantitatively, to structure−activity relationships (QSAR). Indeed, the authors of Chapter 6 present the topic of "Applications of Support Vector Machines in Chemistry" by looking for patterns and creating classification schemes based on such pattern recognition. Another of the more informatics-oriented chapters, this one orients the reader to the problems of database mining, how to surmount them, and the systems chemistry and chemical engineering where such solutions may have an impact.

The final chapter, "How Computational Chemistry Became Important in the Pharmaceutical Industry", is a historical overview of the importance of computational chemistry in the pharmaceutical industry. It provides a nice perspective that brings the sometime abstract field of computational chemistry into the real-world problems of industrial practitioners, from the use of computational algorithms in popularly available software to the use of informatics tools for treating potential drug candidates on an increasingly large scale.

Overall, Volume 23 is another gem in the *Reviews of Computational Chemistry* series. The volume showcases some of the boundary areas of the field, serves as a resource for chemists looking to expand their view of computational science, and provides an archive of key contributions in these areas. This volume is certainly a must for any library as well as for the leading labs in the world.

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JA076928+

**The Handbook of Homogeneous Hydrogenation, Volumes 1−3**. Edited by Johannes G. de Vries (DSM Pharmaceutical Products, Geleen, The Netherlands) and Cornelis J. Elsevier (Universiteit van Amsterdam, The Netherlands). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2007. 1632 pp. $625.00. ISBN 978-3-527-31161-3.

Hydrogenation, the addition of two hydrogen atoms across multiple bonds, is conceptually one of the simplest, yet most important, chemical reactions. Despite its exothermicity, the reaction must be catalyzed to proceed at a reasonable rate due to the low reactivity of dihydrogen. The heterogeneous hydrogenations of fats, oils, and aromatic compounds are among the most important catalyzed reactions in the chemical industry and are practiced on a huge scale. Homogeneous hydrogenation, the sole topic of this three-volume set of books, is industrially much less important, although numerous such reactions are now practiced commercially. The most notable of these is the enantioselective imine reduction in the synthesis of the agrochemical (*S*)-metolachlor (Syngenta), which is currently the largest enantioselective reaction implemented on an industrial scale.

This handbook contains a Foreword by Brian R. James who, in 1973, authored the last definitive textbook on homogeneous hydrogenation. At that time, homogeneous hydrogenation was still in its infancy and James was justified in devoting a mere two pages to enantioselective hydrogenation. Today, of course, enantioselective hydrogenation is the *raison d'être* for practicing this reaction homogeneously. During the intervening years since the publication of James's book there has been massive growth in the practice of homogeneous hydrogenation, specifically the asymmetric variant of this reaction. A comprehensive treatise dealing with these developments was long overdue, and it is fortunate that de Vries and Elsevier took it upon themselves to edit a handbook that is sure to become an instant classic.

The word "handbook" connotes a concise treatment of a topic with a decided bias toward practical applications. This set of books does not disappoint in having such an applied flavor, although at 1569 pages and with ca. 5000 references, many of which are very recent, it can hardly be considered a concise treatment. To keep the amount of material manageable, hydroformylation and enzymatic hydrogenations (hydrogenases) are not covered. In most reactions discussed, molecular hydrogen (dihydrogen) is the hydrogen source, although transfer hydrogenation is explicitly covered in two chapters, and ionic hydrogenation, using non-platinum group transition metals, is discussed in one. Hydrogenation reactions with main-group metal hydrides, such as $LiAlH_4$, however, are not included.

The list of the 81 contributors from industry and academia is a veritable "Who's Who" in homogeneous hydrogenation and includes the Nobel Prize winner Noyori. In 45 chapters, organized in six parts, these authors have provided a timely coverage of the state-of-the-art in homogeneous hydrogenation. Parts I and II, with their combined 13 chapters, cover the fundamentals of homogeneous hydrogenation, with Part I being aptly named "Introduction, Organometallic Aspects and Mechanisms of Homogeneous Hydrogenation". Here protagonists, like Oro and Carmona (Rhodium), Crabtree (Iridium), Morris (Ruthenium and Osmium), introduce hydrogenation catalysts organized either by metal or by technique. In addition to providing excellent background information for the following chapters, these early chapters give historical perspectives only researchers who were intimately involved with the development of the subject can provide.

Over the years the study of homogeneous hydrogenation reactions has provided insight into many fundamental reaction steps in organometallic chemistry, such as oxidative addition,

reductive elimination, and insertions of unsaturated moieties into metal−hydrogen bonds. The rather short Part II, with its three chapters, covers the most important instrumental tools used in the elucidation of reaction mechanisms, namely NMR methods in general, parahydrogen-labeling in NMR studies, and mass spectrometric studies, the latter technique having become increasingly useful for catalytic studies in recent years. The coverage of these topics is decidedly "hands on" with many examples and spectra and should therefore appeal to practicing organometallic chemists.

Part III, "Homogeneous Hydrogenation by Functional Groups", and Part IV, "Asymmetric Homogeneous Hydrogenation," constitute the central part of this handbook. The chapters of Part III address the hydrogenation of the various functional groups in general. Thus, the hydrogenations of alkenes and alkynes, aldehydes, ketones, imines, and other functional groups are covered in sequence. More specialized topics, such as the hydrogenation of carbon dioxide, dehalogenation reactions, the hydrogenation of polymers, diastereoselective hydrogenation, and hydrogen-mediated carbon−carbon bond formation, round out Part III of the handbook.

To introduce Part IV, Ager wrote a very nice overview chapter, which focuses on the historic development in enantioselective alkene hydrogenation. The early chapters of this part deal with the most important ligands in asymmetric hydrogenations, such as DuPhos and related phosphines, while later chapters are organized by specific functional groups. Chapter 36 is a most welcome introduction to high-throughput experimentation and ligand libraries, and the chapter on industrial applications will appeal to academic and industrial chemists alike.

Part V deals exclusively with phase separation in hydrogenation reactions and covers reactions in two-phase aqueous media, ionic liquids, fluorous phases, and supercritical carbon dioxide, as well as immobilization techniques. Specialized topics, such as catalyst inhibition and deactivation and aspects of chemical reaction engineering, are the subject of Part VI; they nicely round out the very complete coverage of homogeneous hydrogenation in this publication.

This attractively produced three-volume set has the physical qualities readers have come to expect from Wiley-VCH reference books, namely, high-quality paper and crisply printed schemes and figures, some of which are in color. As is the case for many unrefereed books in their first printing, the list of errors is longer than it should be, although most of those that I found were of a typographical nature. The usefulness of multivolume reference books such as this one would be enhanced if publishers were to include the index in each volume.

Despite these minor squabbles, the *Handbook of Homogeneous Hydrogenation* is a major contribution to the literature of chemistry, where it nicely complements many of the other excellent reference works by the same publisher. By their judicious choice of contributors and topics, the editors have managed to create a handbook that will appeal to experts and novices alike and will remain the gold standard in this area of chemistry for years to come. The early chapters, for example, would make excellent supplemental reading in upper-level undergraduate or first-year graduate courses, while the later chapters provide indispensable, cutting-edge information and leading references for all researchers in this important area of catalysis.

This handbook should be on the shelves of every academic and industrial chemistry library, where I suspect it will be in high demand. But at the comparatively low price of $625.00 for the set, any chemist needing continual access to the *Handbook of Homogeneous Hydrogenation* has no excuse not to own his (or her) own personal copy.

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**Organic Syntheses, Volume 83**. Edited by Dennis P. Curran (University of Pittsburgh, PA). John Wiley & Sons, Inc: Hoboken, NJ. 2006. xliv + 254 pp. $59.95. ISBN 0-471-97987-2.

This edition of *Organic Syntheses* contains "an eclectic collection of 28 preparations that reflect many of the most topical research themes in the field" to quote from the Preface and is dedicated to Jeremiah Freeman, who edited the series for 25 years. As with the other volumes in the series, each reaction discussed includes the source of reagents, a discussion of the procedure and its results, waste disposal information, references to the primary literature, and an appendix in which the Chemical Abstracts nomenclature and registry numbers are given.

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**Organic Synthesis: Strategy and Control.** Edited by Paul Wyatt (University of Bristol, U.K.) and Stuart Warren (University of Cambridge, U.K.). John Wiley & Sons, Ltd: Chichester. 2007. viii + 910 pp. $90.00. ISBN 978-0-471-92963-5.

This book is a sequel to Warren's book *Organic Synthesis: The Disconnection Approach*, which focused on retrosynthesis, i.e., planning a synthesis by thinking "backward" starting with the target compound and deconstructing it step-by-step to the starting materials. In this book, strategy and control are the main themes: "we solve problems either by finding an alternative strategy or by controlling any given strategy to make it work." There are five sections: Introduction: Selectivity; Making Carbon−Carbon Bonds; Carbon−Carbon Double Bonds; Stereochemistry; and Functional Group Strategy. A list of general references and a subject index complete the book.

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