Additions and Corrections

A Theoretical Study of the Allene Effect in [1,*n*] Sigmatropic Hydrogen Shifts [*J. Am. Chem. Soc.* **1995**, *117*, 7487−7492].
FRANK JENSEN

Contrary to the statement in the paper, the activation parameters for the [1,7]-hydrogen shift reaction in (*Z*,*Z*)-1,3,5-heptatriene have been measured experimentally (Gurskii, M. E.; Gridnev, I. D.; Il'ichev, Y. V.; Ignatenko, A. V.; Bubnov, Y. N. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 781), $\Delta H^{\neq} = 20.1 \pm 0.7$ kcal/mol and $\Delta S^{\neq} = -21.4$ eu. These values are very close to those of (*Z*,*Z*)-1,3,5-octatriene references in the paper, and in good agreement with the calculated values.

Reference 14 should include the following: Jiao, H.; Scheyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1763.

Reference 16 should include the following: Jiao, H.; Scheyer, P. v. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1559.

JA955031M

Book Reviews *

Polymers at Interfaces. Edited by G. J. Fleer, M. A. Cohen Stuart, and J. M. H. M. Scheutjens (Wageningen Agricultural University, The Netherlands) and T. Cosgrove and B. Vincent (University of Bristol, United Kingdom). Chapman & Hall: London. 1993. xviii + 502 pp. $112.50. ISBN 0-412-58160-4.

Polymers at Interfaces provides a comprehensive and timely addition to the short list of key references on the topic indicated by this book's title. Before this work, the definitive review of research on polymer interfaces was D. H. Napper's *Polymeric Stabilization of Colloidal Dispersions*, published in 1983. *Polymers at Interfaces* should now find a place on the shelf next to Napper's classic. Chemists, physicists, chemical engineers, and anyone else having an interest in the use of adsorbed or grafted polymers to modify interfacial properties will find this book to be very useful.

The properties of polymer solutions have been studied by physical chemists for many years, leading to better understanding in areas such as solution polymerization and biological macromolecules. Many more technological applications involve polymers that have been adsorbed or grafted from solution at solid−liquid or liquid−liquid interfaces. Examples include adhesion and lubrication, biological membranes, and stabilization and flocculation of many types of colloidal suspensions and emulsions. The technological importance of polymers at interfaces has stimulated continuing research activity devoted to both experimental characterization and theoretical prediction of the structure of interfacial regions containing adsorbed or grafted polymers, not to mention the kinetics of polymer adsorption, dynamics of polymers tethered at interfaces, the energetics of interacting polymer interfaces, and the effects of polymer interfaces on colloidal stability, rheology, and other bulk suspension properties.

The authors of *Polymers at Interfaces* come from two of the foremost schools in the area of surface and colloidal physical chemistry. Gerard Fleer, Martien Cohen Stuart, and the late Jan Scheutjens, all from Wageningen Agricultural University in the Netherlands, are perhaps best known for their theoretical framework for describing polymers at interfaces, known colloquially as "Scheutjens−Fleer" or SF theory. Terry Cosgrove and Brian Vincent, from the University of Bristol, have over two decades of experience in experimental characterization of polymers at interfaces. These stereotypes hide the fact that the Wageningen and Bristol groups have made significant contributions to both the theoretical and experimental sides of this topic.

Considering their past accomplishments, a compendium of reviews of the various authors' research results would have served nicely. Fortunately, the authors have surpassed expectations through a collective effort that integrates the contributions of all into a whole that is more than the sum of its parts. Readers will appreciate the consistent notation, extensive cross-referencing between chapters, and complete literature citations through the book's publication year, 1993. The unified approach enables a critical review that introduces and compares various theoretical approaches to modeling polymers at interfaces. For example, both self-consistent mean field theories and scaling theories receive complete, detailed treatment. In addition, the unified approach leads to parallel reviews of theoretical predictions and corresponding experimental data. The results are highly convincing: in most cases, experimental trends in adsorbed mass per area and polymer layer thickness are mirrored, at least qualitatively, by theoretical predictions.

The volume begins with a comprehensive introduction to the general features of polymers in solution and at interfaces. The specialist in the area may skip these chapters, but the newcomer will find them to be very informative. The third chapter provides an extensive review of experimental techniques that have been used to characterize various features of polymers at interfaces, including adsorption isotherms, bound fraction, polymer layer thickness, and volume fraction profiles. The brevity of the section on kinetic methods reflects the reality that this experimental area has not yet matured. The third chapter also introduces the surface forces apparatus but does not elaborate on its use for measuring force−distance profiles for interacting polymer layers.

Theoretical methods receive extensive coverage in the 130 pages of the fourth chapter. The first section reviews several complementary approaches including enumeration, Monte Carlo, self-consistent field, square gradient, scaling, and stretched brush theories. The second section provides a complete introduction to the lattice-based self-consistent field theory of Scheutjens, Fleer, and co-workers. Several extensions and discussion of analytical approximations follow in the next sections.

The remaining chapters survey experimental and theoretical results for the most important types of polymer interfaces, including homopolymer adsorption, copolymer adsorption, nonionic polymer and polyelectrolyte adsorption at charged surfaces, and terminally-attached polymers. In addition, two chapters review results for polymers at fluid−fluid interfaces and polymer depletion from nonattractive interfaces. The final chapter treats the effect of polymers on the energetics of interacting surfaces. Each of these topics represent an area of scientific as well as technological importance, so practitioners from many diverse fields will find something of interest here.

Considering the importance of polymeric interactions for colloidal stability and bulk properties, the discussion in the last chapter may seem somewhat abbreviated. However, the termination of this volume brings the reader to the current boundary of knowledge. Much further work will be needed to bring our rudimentary understanding of polymeric interactions to the same level of development as we currently have for electrostatic interactions, at least with respect to their effect

*Unsigned book reviews are by the Book Review Editor.

on colloidal suspensions. Through its unified presentation of current experimental and theoretical knowledge on the topic of *Polymers at Interfaces*, this book provides an important resource for both newcomers and experienced researchers in this field.

Harry J. Ploehn, *University of South Carolina*

JA945120J

Chemistry of Non-stoichiometric Compounds. By K. Kosuge (Kyoto University). Oxford Science Publications: Oxford, New York, and Tokyo. 1994. x + 262 pp. $75.00. ISBN 0-19-855555-5.

Chemists have given continuous attention to non-stoichiometric compounds for the last half-century. During this time a substantial research effort on the subject has been advanced and reviewed. Unfortunately, not much of this work has appeared in textbooks. Modern advanced inorganic texts require 1500 or so pages to treat only the most conventional topics of this vast subject. One suspects that authors of these books have a hope that if this awkward subject is ignored it will go away. In fact non-stoichiometry is so pervasive and so important to an understanding of modern materials that it cannot be ignored. A general mechanism for its inclusion in undergraduate education must be devised.

One solution is a small monograph to supplement the regular upper-level inorganic chemistry course, or as the text for a special topics elective in inorganic or solid state chemistry. Professor Kosuge, who has had a distinguished career in the study of non-stoichiometric materials, has written with this need in mind. It would, of course, be valuable to a person beginning materials research who needs a brief overview of non-stoichiometry. This is an English translation of a successful Japanese text written 10 years ago. The occasional disagreement between subject and verb does not seriously impede clarity.

Non-stoichiometry is, of course, inimical to the fundamental concepts on which traditional chemistry is founded—chief among them, the law of constant proportions. The demonstration that this law does not apply to a vast body of solid state compounds is an uncomfortable fact that the majority of chemists who deal only with molecules as vapors, liquids, molecular solids, or solutions can ignore.

Kosuge's text is organized with only three chapters. They are (1) Non-stoichiometric Compounds Derived from Point Defects, (2) Non-stoichiometric Compounds Derived from Extended Defects, and (3) Examples of the Practical Use of Non-Stoichiometric Compounds.

In the first chapter, non-stoichiometry is defined on the basis of the phase rule. The student is helped in understanding this by a brief review of the pertinent thermodynamics. Non-stoichiometric compounds are then considered to possess point defects, and a statistical thermodynamic treatment of compounds having either small or large concentrations of point defects is pursued. In both cases a methodical development of the theory is developed that is spare but adequate. Not only atoms and point defects but also electrons and holes are treated as chemical species.

An attractive characteristic of this book is the integration of discussions of some essential experimental procedures necessary to the field. Further, examples of the types of chemical systems presented are discussed in some detail. This fixes, in the reader's mind, the points developed in concrete and understandable terms. This organization is particularly effective in an introductory text; however, it does not allow for nuances important to more advanced work. For example, in Chapter 1, compounds with either small or large deviations from stoichiometry are treated as having *point defects*. Although interaction energy is taken into account for large deviations from stoichiometry, and some properties of such systems are accounted for in this way, it leaves untreated a more likely state of affairs. Compounds probably do not possess large concentrations of point defects but rather clusters or extended defects, frequently in arrangements that become regular features in the structures of the intermediate compounds of the system.

In Chapter 2, the problem of extended defects is finessed by presenting a major fraction, but not all, of the categories of non-stoichiometric compounds that have been studied. Here the details of the final regular insertion of extended defects (frequently into a "mother structure") to give the intermediate phases are considered and illustrated. These include shear and block structures, and others labeled vernier, micro-twin, intergrowth, and adaptive structures.

Most useful inorganic materials are not pure substances but rather alloys, mixtures, or non-stoichiometric compounds. It is the defects in these materials that frequently give them their useful properties. In the third chapter Professor Kosuge introduces the reader to properties that characteristically result from the essence of non-stoichiometry. These properties include ionic conducting materials, magnetic materials, hydrogen absorbing alloys, and electronic materials. At the outset he explains that he has not included high-temperature superconductors because the field needed to ripen further before its inclusion into such an introductory text on non-stoichiometry.

LeRoy Eyring, *Arizona State University*

JA945020D

Molecular Biology and Biotechnology. Edited by Robert A. Meyers. VCH: New York. 1995. xxxviii + 1034 pp. $59.95. ISBN 1-56081-925-1.

The volume is a convenient, current, and comprehensive one-volume "library" of the theories and the techniques involved in understanding the molecular basis of life and the application of that knowledge ingenetics, medicine, and agriculture. It contains more than 250 articles that are designed as self-contained treatments of the important topics in molecular biology. The articles are presented on a first-principles basis and include appropriate mathematics and references.

JA955367W

Modern Synthetic Methods 1995. Edited by Beat Ernst (Ciba-Geigy, Bern) and Christian Leumann (University of Bern, Switzerland). VCH: New York. 1995. ix + 453 pp. $80.00. ISBN 3-906390-12-8.

This volume covers the conference proceedings of the 7th International Seminar on Modern Synthetic Methods. It gives an overview on the state-of-the-art, trends, and new accomplishments in solvent effects on chemical transformations, in reactions on surfaces, in the synthesis of oligosaccharides and nucleic acid analogues, and in antibody catalysis. The contributions are practice-oriented, combining basic concepts with experimental procedures and up-to-date references.

JA9553664

Phytochemistry of Plants Used in Traditional Medicine. Edited by K. Hostettmann, A. Marston, M. Maillard, and M. Hamburger (Universite de Lausanne, Switzerland). Oxford University Press: North Carolina. 1995. xiii + 408 pp. $130.00. ISBN 0-19-857775-3.

This volume is a compilation of contributions from 16 speakers who presented plenary lectures at the International Symposium of the Phytochemical Society of Europe entitled "Phytochemistry of Plants Used in Traditional Medicine" held in Lausanne, Switzerland, from September 29 to October 1, 1993. The lectures represent reviews of the latest advances and trends in the field of active compounds from tropical and other medicinal plants. The investigation of the pharmacological and phytochemical aspects of different preparations from vegetable sources is becoming commercially significant as the pharmaceutical industry begins to take an interest.

JA955365B

Advances in Electrochemical Science and Engineering, Volume 4. Edited by Heinz Gerischer (Fritz-Haber-Institute, Berlin) and Charles W. Tobias (University of California—Berkeley). VCH: New York. 1995. vi + 430 pp. $145.00. ISBN 3-527-29205-5.

This is Volume 4 of a well-established series covering topics from electrochemical science and its application. There is a strong emphasis on applied science, such as spectroscopy and semiconductor research, and all chapters include numerous references. Recent developments are also explored and critically discussed. Topics covered include scanning tunneling microscopy of semiconductor electrodes, surface chemistry of silicon in fluoride electrolytes, in-situ infrared Fourier transform spectroscopy, electrochemical reactions in nonaqueous and mixed solvents, charge transfer kinetics at water—organic phase boundaries, and electrolytic processes for pollution treatment and pollution prevention.

JA9553617