high pK_a was determined by use of a novel method, which had been calibrated only with cyclopentadiene, it was important to extend the method to other cases to see that a sensible consistent picture emerges. At the same time it was of interest to learn whether this thermodynamic pK_a was dependent on the exact solvent and electrolyte used. We now wish to report the results of such studies.

Allyl iodide, benzyl iodide, propargyl iodide, *tert*-butyl iodide and triphenylmethyl fluoborate were examined electrochemically using second-harmonic ac voltammetry as previously described.[1,2] All showed two reduction waves, the second being that for reduction of allyl radical, benzyl radical, etc., to the corresponding anion. Good reversible behavior was observed, with a well-defined crossing point. The results are listed in Table I.

The data in Table I show that there are minor but real medium effects on the reduction potentials. Considering only the data at a gold electrode, which we have shown[2] to be the most reliable, we see that the change of solvent from acetonitrile to dimethoxyethane has essentially no effect on the reduction potential of the allyl, benzyl, or triphenylmethyl radicals, but does change that of *tert*-butyl radical by 300 mV (corresponding to 5 pK_a units). Since the radical is reduced to a carbanion in the presence of a high local concentration of the supporting electrolyte cation,[3] one might expect ion-pairing stabilization differences as one goes from the small tetramethylammonium ion to the almost insulated tetraheptylammonium ion. However, significant effects are seen only with the allyl and *tert*-butyl systems, while benzyl and triphenylmethyl are almost unaffected by the change in electrolyte. The small relatively localized *tert*-butyl and allyl anions should be particularly subject to solvation and ion-pairing effects, but pK_a changes of only ~2 units are involved.

Our value for the allyl radical reduction potential agrees well with that of -1.57 V vs. SCE reported by Baizer[4] using polarography in dimethyl sulfoxide with TBAP electrolyte. Furthermore, our data for the benzyl system confirm values from -1.82 to -1.88 V reported from polarography.[5,6] Carbon dioxide trapping[6] has shown that the benzyl anion is the product of this reduction. Thus our data can be used with confidence, together with bond dissociation energies, to derive pK_as for ionization of a methyl hydrogen in toluene, propene, and propyne. The results are listed in Table II.

The pK_as observed are sensible and consistent. With toluene and propene having pK_as in the mid-50s, our value of 71 for isobutane seems reasonable. Methane should have a pK_a higher than that of propyne,[7] and probably less than that of isobutane;[8] so an estimate of 68–70 for methane seems right. Assuming this value, the substitution of one phenyl to produce the benzyl anion is almost as acidifying as is the substitution of the next two to form triphenylmethyl anion. Such a saturation effect of substituents is well precedented.

It is apparent that our thermodynamic pK_a scale is affected somewhat by the exact medium used. For instance, assuming that triphenylmethane always has a pK_a of 31.5, the pK_a of isobutane ranges from 66 to 71 over the extreme of our data on changing solvent from dimethoxyethane to acetonitrile. However, the general consistency of the picture is such that these pK_as should now be considered the most likely thermodynamic values for the otherwise inaccessible high pK_a region.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

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(8) Although this might well reverse in the gas phase when the methyl groups act as an internal solvent. In solution they exclude more polar solvent molecules.

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Book Reviews

Thermodynamics of Nonequilibrium Processes. By S. WISENIEWSKI, B. STANISZEWSKI, and R. SZYMANIK. D. Reidel Publishing Co., Dordrecht-Holland/Boston. 1976. xiii + 274 pp. $36.00.

This book is a translation from Polish of a textbook for technical universities. Thus the symbols and units are those commonly used by engineers and not SI.

The first half of the book presents a development of general nonequilibrium thermodynamics according to a format similar to that in other texts. The second half is devoted to a section on more specialized applied topics: thermoelectric generators and refrigerators, thermionic generators, and magnetohydrodynamic generators. These chapters include discussions of the potentials and problems inherent in practical application of these effects.

There are a number of worked-out examples in the book (31 in all). However, there are no references to specific articles of interest, only a listing of general references to classical and nonequilibrium thermodynamics. It can most probably be used successfully as a guide for study of nonequilibrium thermodynamics in general, but its main contribution is its thorough and application-oriented discussion of heat to electricity conversion devices.

Peeter Kruus, *Carleton University*

Biochemical Analysis of Membranes. Edited by A. H. MADDY (University of Edinburgh). Halsted Press/John Wiley & Sons, New York, N.Y. 1976. ix + 513 pp. $37.50.

The first half of this compilation covers methods for isolation of various types of membranes. These include the cell surface membrane, with special emphasis on the liver plasma membrane, and the membranes of subcellular organelles (separate chapters on mitochondria, endoplasmic reticulum, and nucleus). The first chapter presents a discussion of the cultivation of mycoplasmas and the isolation of their membranes. These microorganisms are particularly useful because their only membrane constituent is the plasma membrane and because its composition is determined by the relative concentrations of lipids in the growth media. These natural membranes are, thus, being used as alternatives to artificial lipid bilayers for studies of the effect of lipid composition on membrane structure and function.

The second section of the book deals with the isolation, purification, and analysis of membrane components. There are separate chapters on solubilization of membrane proteins, analysis of membrane proteins, analysis of lipids, and analysis of carbohydrates. The special problems associated with the handling of membrane proteins are especially well highlighted. A separate chapter describes immunochemistry based techniques for analysis of solubilized membrane proteins. Also included in this section are chapters on enzymatic and specific labeling techniques for mapping the membrane surface.

The most outstanding feature of this work is the wealth of practical experimental detail which fills each of the chapters. Each chapter critically describes the background of the techniques employed, with their scope and limitations, followed by an extensive bibliography; most of the chapters also include a detailed description of the set of experimental procedures utilized in the author's laboratory. The book is thus particularly valuable to the researcher who may wish to utilize some of these methodologies and needs a realistic description of the experimental difficulties.

Leslie M. Loew, *State University of New York at Binghamton*

Principles of Applied Clinical Chemistry Volume I: Maintenance of Fluid and Electrolyte Balance. By S. NATELSON (Michael Reese Hospital and Medical Center) and E. A. NATELSON (Baylor College of Medicine). Plenum Press, New York, N.Y. 1975. xvii + 393 pp. $22.50.

The purpose of this book is to "define the areas of learning encompassed by the science of clinical chemistry." It is the first in a series of volumes on the many topics which are included in modern clinical chemistry. The book presents current information on the chemistry of physiological processes and presents medical applications of this knowledge.

Volume I includes three sections, which are further subdivided into twelve chapters, an appendix, and a subject index. Section I, on body fluids and electrolytes, includes chapters on mechanisms for maintenance of the steady state, acid-base balance, partial pressures of O_2 and CO_2, pH, maintenance of constant ion concentration, maintenance of a steady state between plasma and interstitial fluid, plus chapters on acidosis, alkalosis, and fluid and electrolyte applications. Section II consists of two chapters on the role of the kidney and sweat glands in fluid and electrolyte balance. Section III includes the appendix and subject index. The appendix consists of a short bibliography, six tables, and a derivation of the equation for calculating the amount of alkali needed to bring the blood pH back to the normal level. Each chapter includes a list of selected readings and references and a number of excellent line drawings to illustrate the concepts presented.

The authors have done a fine job in this first volume. The book is designed for use in training clinical chemists and clinical pathologists but could also be quite helpful to the practicing physician who wishes to fully understand and utilize the resources of the clinical chemistry laboratory.

Donald F. Logsdon, Jr., *McClellan Air Force Base*

Block Copolymers. Overview and Critical Survey. By A. NOSHAY (Union Carbide Corp.) and J. E. MCGRATH (Virginia Polytechnic Institute and State University). Academic Press, New York, N.Y. 1977. xvi + 516 pp. $45.00.

There is presently a great deal of interest in the preparation, characterization, and utilization of block copolymers, i.e., chemical copolymers in which there are relatively long sequences of chemically identical units. This interest arises primarily from the fact that many such polymers undergo microscopic phase separation, and the resulting materials frequently have unique properties. Falling into this category are plastics of high impact strength (because of the presence of energy-absorbing elastomeric domains) and thermo-plastic (reprocessible) elastomers which have hard glassy regions serving to crosslink the chains in the continuous matrix into a network structure. Block copolymers can also frequently act as solubilizing agents, making more compatible some physical blends of polymers that would otherwise be essentially immiscible.

The present volume provides a useful and very thorough survey of this relatively new area of polymer science. The first part (79 pp) gives an overview of the subject. It contains comparisons among block copolymers, homopolymers, physical blends of polymers, random copolymers, and graft copolymers, followed by general discussions of synthetic techniques, structural characterization, physical properties, current applications, and prospects for the future. The second part, which makes up the remainder of the book, is a critical survey of block copolymers which have been prepared to date. Its three chapters deal with A-B diblock copolymers, A-B-A triblock copolymers, and $[A-B-]_n$ multiblock copolymers, respectively. The monomeric units A and B include dienes, α-olefins and other vinyl types, ethers, esters, lactones, sulfides, carbonates, amides, urethanes, imines, and siloxanes. The topics typically covered for each system are the synthesis, characterization, morphology, rheology, solution properties, mechanical properties, and thermal properties. (As might be expected from this type of organization, there is quite a bit of duplication of material in various chapters.) The book ends with extensive author and subject indexes.

This is obviously a very comprehensive book, and it will be extremely useful to anyone working on block copolymers.

J. E. Mark, *University of Cincinnati*

Statistical Mechanics. Second Edition. By J. E. MAYER (University of California, San Diego) and the late M. G. MAYER. John Wiley & Sons, Inc., New York, N.Y. 1977. xv + 491 pp. $23.50.

The publication of this book is a particularly happy occasion for the many chemists and physicists who were first exposed to statistical mechanics through the first edition, which was originally published in 1940! This second edition, very extensively revised, is certain to become as much of a classic as was the first.

The first part of the book (43 pp) provides introductory concepts such as probabilities and probability densities, and a relatively elementary treatment of the kinetic theory of gases. Part Two (111 pp) presents the fundamentals of the subject using Gibbs ensemble methods. One chapter of unusual interest deals with the discussion and resolution of a number of seemingly paradoxical issues and should be extremely useful to serious students of the subject. Part Three (304 pp) consists of numerous applications of the methods developed, including quantum statistics. The book concludes with 12 Appendices and a Subject Index.

It was somewhat disappointing to this reader not to find any of the numerous important applications of statistical mechanics to polymeric systems, for example, the helix-coil transition in biopolymers, the elasticity of rubberlike networks, or chain statistics. Also, the complete absence of problems may be a disadvantage with regard to its use as a textbook. These are rather minor criticisms, however. The book represents an extraordinary contribution to the literature on statistical mechanics, and it is a pleasure to recommend it to anyone interested in the subject.

J. E. Mark, *University of Cincinnati*

Methods in Carbohydrate Chemistry. Volume VII. General Methods, Glycosaminoglycans, and Glycoproteins. Edited by ROY L. WHISTLER (Purdue University) and JAMES N. BEMILLER (Southern Illinois University). Academic Press, New York, N.Y. 1976. xix + 293 pp. $29.50.

This volume expands the scope and usefulness of this excellent series. General methods are updated and sections on glycosaminoglycans and glycoproteins are compatible with current technical advances. The articles are written by recognized authorities on the subject with attention given to the details necessary for reproducibility of the methods. The articles are clearly written and well referenced. This volume also contains a very useful cross reference to selected methods found in other collections. The utility of this series is that sufficient information and explanation are provided so that the procedures can be carried out without additional reference to the literature by individuals who are not necessarily experts in the area.

The series is certainly indispensable to technical library collections and of great benefit to both chemists and biochemists interested in carbohydrate methodology and procedures.

Thomas E. Nelson, *Baylor College of Medicine*

The New World of Quantum Chemistry. Edited by BERNARD PULLMAN (Foundation Edmond de Rothschild) and ROBERT PARR (University of North Carolina). D. Reidel Publishing Co., Dordrecht-Holland/Boston. 1976. viii + 349 pp. $29.00.

The New World of Quantum Chemistry or the Proceedings of the Second International Congress of Quantum Chemistry held at New Orleans, April 19-24, 1976, is a follow-up to the Proceedings of the First International Congress of Quantum Chemistry held at Menton (France), July 4-10, 1973. As stated by Pullman in the introduction, one of the primary aims of the Congress is to stimulate interaction between all quantum-molecular scientists of varied interests. Quantum-mechanical concepts are now permeating such areas as biology, pharmacology, and solid-state physics. The program of the meeting at New Orleans testifies to the rapid expansion and progress of quantum chemistry in a relatively short period of time.

In this volume are collected the papers that constitute the Proceedings which are organized into five symposia. Symposium I. Foundations of Quantum Chemistry: R. McWeeny: Present status of the correlation problem. R. Daudel: Quantum mechanical facets of chemical bonds. Y. Ohrn: Methods without wave functions. Symposium II. Molecular Scattering: J. O. Hirschfelder: Introduction. W. Miller: Semiclassical collision theory. R. Levine: Chemical reactivity and chemical specificity. Symposium III. Quantum Organic Chemistry and Beyond: B. Pullman: Introduction. G. G. Hall: Computational methods for large molecules. A. Pullman: The solvent effect. R. Christoffersen: Quantum Pharmacology. Symposium IV. Potential Surfaces, Transition States, and Intermediates in Chemical and Photochemical Processes: S. Peyerimhoff: Potential surfaces for ground and excited states. L. Salem: Transition states and reaction mechanisms in organic chemistry. Symposium V. Surface Quantum Chemistry and Catalysis: K. Fukul: Introduction. J. J. Koutecky: Methods for surface quantum chemistry. J. R. Schrieffer: The chemisorption bond. K. Johnson: Molecular clusters and catalytic activity.

The papers are written in conventional journal style and are generally well written. Other than about a dozen typographical errors, my only criticism is that the line spacing in the paper by Peyerimhoff and Buenker is often inadequate as the subscripts and superscripts occasionally run into the main text. Also the clarity of the figure on p 259 of Salem's paper is poor.

The book certainly belongs in all institutional libraries and the personal libraries of those working in the fields of quantum biology, quantum chemistry, quantum pharmacology, and solid-state physics.

John F. Olsen, *College of Staten Island*

Gmelin. Handbook of Inorganic Chemistry. Eighth Edition. Edited by KARL-CHRISTIAN BUSCHBECK. Published by Gmelin Institute for Inorganic Chemistry of the Max Planck Society for the Advancement of Science. Springer-Verlag, Berlin–Heidelberg–New York. Transuranium Elements, New Supplement Series.

Volume 31. Part B1. The Metals. By RICHARD LESSER and JOSEPH R. PETERSON. 1976. 84 pp. DM 187, $76.70.

Volume 39. Part B3. Binary Alloy Systems. By HUBERT BLANK and CORNELLIUS KELLER. 1977. 275 pp. DM 617, $271.50.

This familiar reference work now incorporates coverage of material on the transuranium elements inclusive of literature appearing up to the close of 1971, and to the end of 1973 in the case of binary plutonium alloys. The general clarity of printing, text, tabular and figure layouts, etc., retain the high standard expected of this series.

While the available material on Fm and Es metals is very limited and fragmentary, substantive material is reported on Bk and Cf, as well as for Am and Cm. Much of the relevant literature thru 1975 has been included for Bk, Es, Cf, and Cm. The data for Np and Pu, of course, are relatively abundant and detailed.

An intervening volume (Part B2, Volume 38) has already appeared and comprises the first part of the treatment of binary alloys. This part has 15 pages on neptunium alloys by C. Keller incorporating literature through 1971, while pages 16–241 embrace the first half of the coverage by H. Blank of the plutonium alloys.

Volume 39 contains a further 266 pages on the binary alloys of plutonium and 5 pages on americium alloys. Only 3 pages are needed to cover the available material on curium and the transcurium elements.

While these particular volumes include a small amount of material regarding the "chemistry" of the elements or alloys (their reactivity with oxygen, moisture, acids, etc.), their primary concern is with the means of preparing the metals, or alloys, their physical properties, and phase diagrams. Much of this material would be of more frequent concern to the metallurgist than to the chemist. The treatments maintain a full to adequate coverage of their topics up to the specified cut-off dates.

To a large extent, the presentation seems to retain the semicritical and authoritative aspects which have characterized this work in past years. The authors avoid making arbitrary comment or exclusions while giving concise summations or tabulations of significant data and integrating or correlating the entirety of the data. Generally, the textual presentation remains crisp and lucid. The "Englished" (?) translations of some (nonessential) prefatory matter are tortuously distorted.

The plastic covering material seems to be reasonably durable in terms of resistance to flexing and abrasion, and it retains gold-stamping well. Its adhesion to the boards leaves something to be desired, however, as does the adhesion to the turn-in of the, rather thin, board papers. By modern standards, the bindings are "adequate".

Charles L. Rulfs, *University of Michigan*

Progress in Inorganic Chemistry. Volume 22. Edited by STEPHEN J. LIPPARD (Columbia University). John Wiley & Sons, Inc., New York, N.Y. 1977. vii + 438 pp. $25.95.

Volume 22 maintains the high standards of this series. The first chapter, by E. I. Stiefel, treating the coordination chemistry of molybdenum pertinent to biochemistry, is extensive and up-to-date through calendar 1975. Necessarily setting aside several classes (iso- and heteropolymolybdates, molybdenum blues, and other poly and polymeric species), the author systematically presents facts and interpretations in the inorganic tradition. Along the way, he persistently points out the implications, direct or tenuous, for molybdenum biochemistry—the enzyme systems: nitrogenase, nitrate reductase, xanthine dehydrogenase, aldehyde oxidase, and sulfite oxidase. This chapter is formidable but stimulating.

The second chapter, "The Derivation and Application of Normalized Spherical Harmonic Hamiltonians", was written by J. C. Donini, B. R. Hollebone, and A. B. P. Lever. It presents a case for greater coherence and uniformity among quantum mechanical calculations on complex ions of low symmetry, nominating their system for the position of "standard". Designed to be readable for those who are comfortable with elementary chemical group theory texts, this chapter lays out an approach in prescription form to be applied to the reader's own project of interest.

It would be handy indeed if such as nephelauxetic ratios could be described and directly compared among situations of both high and low symmetry. Whether this or any other approach can achieve such a goal and, also, complete effectiveness and commanding popularity is problematic.

S. Mitra's chapter on magnetic anisotropy in transition metal complexes is also organized pedagogically and presents several examples from among the d-block elements. The power of this technique to detect even slight splittings of degenerate orbitals, to highlight the orbital contribution to magnetic susceptibility or to evaluate the orbital component in spin-orbit coupling, is illustrated. Two bonuses have been inserted in this chapter: an alternative mathematical treatment of the monoclinic system (only one magnetic susceptibility axis colinear with a crystallographic axis) and an analysis of contact shift and pseudo-contact shift data for proton resonances.

The final chapter, by G. W. Daub, succinctly surveys literature into 1975 pertaining to oxidative cleavage of transition metal-carbon bonds. Citing evidence mostly for d^4, d^6, and d^8 systems, the author supports a type of mechanism involving oxidation of the metal followed by the departure of the metal as a "leaving group" from the organic moiety. The use of "nonelectrophilic oxidizing agents", e.g., $IrCl_6^{2-}$, is extolled. This paper was initially prepared for a chemistry course at Stanford University. Many a chemistry professor will wish that such a paper would appear on his desk.

This volume includes a Cumulative Index for Volumes 1–22.

George D. Sturgeon, *University of Nebraska—Lincoln*

Applied Biochemistry and Bioengineering. Volume 1. Immobilized Enzyme Principles. Edited by L. B. WINGARD, JR. (University of Pittsburgh), E. KATCHALSKI-KATZIR (Weizmann Institute of Science), and L. GOLDSTEIN (Tel Aviv University). Academic Press, New York, San Francisco, and London. 1976. xi + 364 pp. $29.50.

The technology involving immobilized enzymes is rapidly expanding, and this collection of articles by a number of authors will appeal to the specialist as well as to individuals wishing an introduction to the field. A survey of immobilized enzymes introduces this volume. This is followed by highly technical discussions of the chemistry of enzyme immobilization, diffusion and kinetics of immobilized enzymes, design and analysis of immobilized-enzyme flow reactors, and finally a chapter devoted to industrial applications of immobilized enzymes and immobilized microbial cells. Extensive references complete each article.

M. C. W. Smith, *University of Michigan*