traces of unimolecular reactants is irradiated by a pulsed-CO_2 laser. After rapid energy-transfer collisions with the excited SF_6, the mixture is heated to temperatures up to 1600 K. Unimolecular decomposition reactions occur, but are quenched after ~10 μs when expansion cooling occurs. Yields are determined by mass spectrometric sampling of reactants from a slow flow. Here we used *tert*-butyl alcohol with known decomposition parameters,[7] as a temperature standard, monitored at m/e 57. The observed kt of 1.05 per laser shot within the irradiated volume corresponds to a 1600 K temperature. The ferrocene yield was 0.077, or $k = 7.7 \times 10^3\ s^{-1}$. The VLPP Arrhenius parameters of $\log A = 16.34$ and $E_a = 91.4$ kcal/mol give $k_\infty(1600\ K) = 8.6 \times 10^3\ s^{-1}$ and with a pressure falloff calculation predict $k = 7.0 \times 10^3\ s^{-1}$, in good agreement with the experiment. The high Arrhenius parameters, however, predict a significantly higher rate than observed: $1.45 \times 10^4\ s^{-1}$, including falloff. Thus, the laser pyrolysis experiment confirms the 91.4 ± 3.0 kcal/mol VLPP activation energy.

Finally, we must convert E_a to ΔH (and then to $\Delta H(298)$), the BDE. This correction is small for a transition state featuring low vibrational frequencies (~0.5 kcal/mol), giving a BDE value of 91 ± 3 kcal/mol. The use of this kinetic value to derive a thermodynamic one assumes, of course, that there is no additional barrier to decomposition. This analysis also assumes dissociation is a simple one-step process—for example, that $CpFe(\eta^3\text{-}C_5H_5)$ is not an intermediate. The high activation energy and typical A factor support a single-step mechanism.

Given the average bond energy,[1] we can then derive the second BDE, $D_{298}(\text{Fe–Cp}) = 51$ kcal/mol, again assuming the first dissociation does not produce electronically or vibrationally excited product. (In one sense, this is a lower limit). Given this second bond energy, FeCp should be stable and potentially functional as a catalyst below ~550 K.

For comparison purposes, a bond energy for nickelocene can be derived from mass spectrometric ionization and appearance potential measurements.[3] The value of 103 kcal/mol leaves[1] a second bond energy of only 15 kcal/mol, which is highly unlikely since NiCp can be observed at 800 K. While this suggests the first ligand is the more strongly bound in this case also, the probable errors encountered with this method are evident. The 91 kcal/mol bond energy in ferrocene for the η^5-cyclopentadienyl system to iron can also be compared to the η^2-ethylene system in $Fe(CO)_4C_2H_4$, where $D = 37.2$ kcal/mol.[6] This difference of 2.5 times is reasonable when one compares the bonding, although the exact multiplicative factor may be fortuitous. The olefin bond[8] consists of a dative bond between the π electrons and an empty metal d orbital plus the back-bond of the π* orbital with metal d electrons. Ferrocene has three π orbitals per ring for bonding to the metal plus back-bonding through two π* oribtals.

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Registry No. Ferrocene, 102-54-5.

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(6) Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905.

(7) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(8) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 2nd ed.; Wiley: New York, 1966; p 764–777.

Book Reviews

Transport in the Life Sciences. Volume 5. Cell ATP. By William A. Bridger and J. Frank Henderson (University of Alberta). John Wiley and Sons, New York. 1983. x + 170 pp. $59.95.

Considering the diversity and number of reactions in which ATP participates, one would expect a reference monograph dealing with the structure, function, and metabolism of ATP to be large and unwieldy. This monograph has neither of these characteristics. Rather than presenting a comprehensive review of the subject matter, the authors offer a concise, well-written overview, which is divided into two parts. Following a brief historical introduction, Part I, written by Dr. Bridger, is made up of four chapters (65 pages) which deal with ATP as the energy currency of the cell. Part II, written by Dr. Henderson, is comprised of five chapters (97 pages) which are more or less a review of purine nucleotide metabolism with emphasis on the biosynthesis and catabolism of ATP.

The topics presented in Part I include the thermodynamics of ATP hydrolysis, the coordination of metal ions by ATP including the tabulation of ^{31}P NMR parameters, a discussion of the reaction mechanisms of the enzymes involved in the phosphorylation of ADP to form ATP, profiles of the structure–function relationships of selected enzymes which hydrolyze ATP, and the involvement of ATP in metabolic regulation.

The topics covered in Part II are as follows: the pathways of de novo purine biosynthesis; the synthesis of adenine nucleotides directly from adenine and adenosine; the conversion of other purine bases, nucleosides, and nucleotides into adenine nucleotides; the catabolic pathways for ATP, and special pathways for the utilization of the adenosine moiety of ATP in animal cells. Each of the above topics is discussed with due consideration of individual enzymes of the pathways and factors which regulate the pathways. Topics also considered in Part II are as follows: disease states which influence ATP concentrations, most of which are the consequence of inborn errors, and drugs which affect the levels of cellular ATP.

This book is Volume 5 in the series "Transport in the Life Sciences", edited by E. Edward Bittar, and is compatible with the general theme of the series. The two overviews presented on ATP should prove to be valuable supplemental reading for undergraduate, graduate, and medical students taking courses in biochemistry and cell biology. Therefore, it would be appropriate to cite this monograph in chapters on ATP as energy currency of the cell and on purine nucleotide metabolism in introductory texts of biochemistry and cell biology.

William S. Allison, *University of California, San Diego*

Solid Electrolytes. By E. C. Subbarao (Indian Institute of Technology). Plenum Press Publishers, New York and London. 1980. xvi + 298 pp. $35.00.

This book was written for scientists and engineers who are involved in the study of solid electrolytes and their applications. There appears to be a reasonable balance between fundamental studies and practical aspects. A large number of compounds are discussed including zirconia- and thoria-type solid electrolytes and the newer types such as fluorides, β-aluminas, and silver ion conductors.

The initial chapter deals with the principles of defects in ionic solids as well as the structure and properties of important solid electrolytes. Other chapters deal with the experimental problems associated with the use of solid electrolytes for a variety of measurements. There is a considerable emphasis on the thermodynamic studies which have been carried out on binary and ternary alloys and intermetallic compounds with use of oxide and fluoride solid electrolytes. Included also are corresponding results on oxides, silicates, and spinels.

A positive feature of the book is the inclusion of two chapters which deal with the practical and applied applications based on solid electrolytes. This information is of great value to scientists and engineers engaged in the development of devices based on solid electrolytes.

Another feature of the book is its excellent coverage of the literature through 1978. Information in this field is found in a variety of journals so that the extensive references cited and analyzed in a single volume are by themselves a reason which this book should be acquired by all workers in the field.

Aaron Wold, *Brown University*

A Specialist Periodical Report. Photochemistry. Volume 14. Senior Reporter D. Bryce-Smith (University of Reading). The Royal Society of Chemistry, London. 1983. xxii + 571 pp. £88.00.

The first volume in this series of Specialist Periodical Reports was published in 1970, and although the delay between the last date of literature coverage (June 1982) and the publication date (late 1983) of Volume 14 is longer than originally stated in Volume 1, this series continues to be the single most important secondary source of current information on photochemistry. The format is very similar to that of previous years. A short introduction and review of highlights of photochemical research from July 1981 to June 1982 by Bryce-Smith is followed by five parts, entitled Physical Aspects of Photochemistry, Photochemistry of Inorganic and Organometallic Compounds, Organic Aspects of Photochemistry, Polymer Photochemistry, and Photochemical Aspects of Solar Energy Conversion. Within these parts are 14 chapters by 8 authors reviewing most of the literature on such diverse topics as Gas-Phase Photoprocesses, Photochemistry of Transition-Metal Complexes and Main Group Elements, and the whole gamut of Organic and Polymer Photochemistry. This diversity can be considered as both a strength and a weakness of this series. The very broad literature coverage is counterbalanced by the necessarily brief reviews of individual papers, typically one sentence per paper depending on the chapter. There is fuller coverage of those papers presumably considered important by the reviewers. Although there is no subject index, the organization of the topics and the thorough author index make the volume easy to use. It seems quite surprising that coverage of such a broad field as Photochemistry has been continued in a single Specialist Periodical Report. After all, there is no comparable series on Thermal Chemistry. I am personally glad that the basic format of this series has not changed. This volume and its predecessors constitute a wonderful guide to the literature of Photochemistry. The reader can with minimum effort get some feeling for recent activity in any area of Photochemistry. Some minor criticisms can be made. The literature coverage is not always complete. It is unclear, however, whether complete coverage is a goal of this Series. Occasionally papers seem misplaced. Perfection can hardly be expected, however, considering that there are approximately 4000 citations to the work of about 6000 authors in this volume. Such coverage does not come cheaply, but it does not seem to be very well-known that for the modest annual Royal Society of Chemistry membership fee, individual chemists can obtain Specialist Periodical Reports such as this at very substantial discounts off the list prices.

David Creed, *University of Southern Mississippi*

Equilibria, Nonequilibria, & Natural Waters. Volumes I and II. By Ricardo M. Pytkowicz (Oregon State University). John Wiley and Sons, Inc., New York, NY. 1983. Volume I: xv + 351 pp. $49.95. Volume II: xv + 353 pp. $49.95.

These two volumes provide a thorough coverage of a very large subject area. Volume I includes fundamental concepts from chemistry, geology, oceanography, and thermodynamics as applied to aqueous solutions of electrolytes. This volume also provides a good discussion of steady-state vs. equilibrium systems, including several examples of linear models of cycling between reservoirs which can give steady-state conditions. Volume II addresses specific aspects of solution chemistry (acid–base reactions, solubilities of solids and gases, metal complexation, and redox reactions) and concludes with an overview of natural solutions. In both volumes, each chapter begins with a definition of the subject material, and throughout the chapter statements guide the reader as to the intended audience for the discussions that follow. All technical terms are carefully defined, even those that are rather elementary, thus preventing the exclusion of the novice. It is not assumed that the reader will read straight through, so terms are redefined as needed. There are many worked examples to illustrate the principles discussed, and a wealth of data and figures are provided. All of these factors contribute to the value of these books as comprehensive references in solution chemistry and in natural water geochemistry.

The two volumes contain extensive reference and reading lists through 1980, with a few references from 1981. This time frame allows inclusion of work by the author and his colleagues concerning the extent of chloride ion pairing in seawater, work which significantly affects concepts of ionic strength in seawater. Chapter 5 in Volume I (Electrolyte Solutions) provides an excellent discussion of the solution chemistry of electrolytes in water and includes a compilation and comparison of the many equations used to calculate activity coefficients for ions in aqueous solutions.

Very few appropriate subject areas are slighted in these books; there are, however, a few minor omissions. The molecular structure of water and the effects of ions on this structure are covered very briefly. The chemistry of dissolved organic compounds in natural water is also sparsely covered, even though there has been considerable progress recently in identifying structural characteristics of dissolved organic material in natural waters. Solubility phenomena are discussed extensively with respect to carbonates, but these particular compounds are unnecessarily complex for use as examples of solubility principles. These criticisms do not detract significantly from the value of the work.

Only two errors were noticed in the calculations that were checked. Unfortunately they both occur with the same subject material, the fundamental concept of concentration units. The initial discussion of this topic (page 9 of Volume I) makes this material more difficult than necessary, and this discussion is further complicated by an error in an example used for illustration. A similar calculation is presented later in this volume (page 119), and this also contains an error. This combination of errors ensures that yet another generation of students will remain confused about fundamental concentration units. On the whole, however, there are not many errors, considering the complex notation essential for this type of work.

These two volumes are excellent reference books. The scope of the subject material assures relevance to scientists and students in many subject areas. The task was formidable; the author has done an admirable job. He has produced a work which, in my opinion, should meet his stated goals of guiding the beginner, broadening the scope of the specialist, and stimulating the expert.

Joan D. Willey, *University of North Carolina at Wilmington*

Peptide and Protein Reviews. Volume 1. Executive Editor Milton T. W. Hearn (St. Vincent's School of Medical Research, Melbourne, Australia). Marcel Dekker, New York. 1983. vi + 244 pp. $35.00.

This new series of monographs in peptide and protein chemistry was established to help connect such diverse health-science disciplines as immunology and endocrinology with peptide and protein chemistry—the latter area frequently providing scientific leadership for the more medical and biological areas. It is aimed at the professional, at the graduate student, and at the undergraduate—an ambitious range of readership.

The first volume deals with six topics. The microsequencing of proteins is examined basically from the perspective of the need for ever lower limits—now picomoles—for sequencing the ever smaller amounts of biochemically important peptides and proteins. Aspects of the structure and function of the isocitrate dehydrogenases, especially as studied in Colman's laboratory, are summarized; it provides a valuable contrast between the NAD^+ (DPN^+) and $NADP^+$ (TPN) dependent enzymes in considerable detail. An analysis of the conformation of functionally and structurally homologous proteins with a very strong emphasis based on circular dichroic spectra is presented. A review of studies on the incorporation of acetylcholine receptors into model membranes was made possible by the recent delineation of the conditions required for the isolation of functionally intact receptors from *Torpedo* electric organ membranes. The exciting area of neuronal peptide–protein complexes is reviewed with emphasis on developments toward describing the functions of these polypeptides in neuronal pathways and in non-neuronal sites. The functions of enzymes, cell membranes, and subcellular components of thyroid glands are reviewed all the way from examination of general aspects through descriptions of protein structure modification in regulation of nuclear events up to aspects of thyroid dysfunction.

Most of the reviews are written very much from the perspective of and about the work of the authors; for some of the authors with extensive published work, this was useful and needed. The contents vary from virtually explicit experimental protocols to the more customary summations of findings and the attendant generalizations that are typically useful. Some of the articles had an irritating number of typographical errors and questionable literature citations—the insulin sequence was announced in 1955 not 1945. I believe it is a valuable addition to the genre of shorter and more quickly published reviews and may fill a useful niche in the structure-to-function relationships of proteins and peptides.

Richard A. Day, *University of Cincinnati*