Book Reviews

Chemistry. A Life Science Approach. By STUART J. BAUM (State University of New York, College at Plattsburgh) and CHARLES W. J. SCAIFE (Union College, Schenectady). Macmillan Publishing Co., New York, N.Y. 1975. xx + 746 pp. $14.95.

This book presents a basic and complete treatment of general chemistry (11 chapters), organic chemistry (12 chapters), and biochemistry (9 chapters) to be used in a two-semester or three-quarter course. The concepts are presented clearly. No background in chemistry is assumed. The reading level should match that of a beginning college student.

Stoichiometric calculations are presented in the body of the text and with increasing levels of difficulty. This presentation would be a great aid to the beginning student. Problem solutions are presented in the appendix. Pertinent data tables are embedded in the text. The end-of-chapter practice problems are arranged such that concepts necessary to solution of succeeding problems are presented early in the set.

Descriptive inorganic chemistry has been neglected in favor of a thorough treatment of basic chemical principles. Functional group identification of organic molecules is stressed by gray shading of that part of the molecule. The biochemistry treatment is concise but thorough. Good structural formulas of accurate reaction mechanisms are used along with three-dimensional drawings of large biochemical molecules.

The text should prove very useful to a student. It is one that would serve well for later reference to basic principles.

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Synthetic Peptides. Volume 4. By GEORGE R. PETTIT (Arizona State University). Elsevier Scientific Publishing Co., Amsterdam. 1976. xvii + 477 pp. $59.95.

In Volume 4, the author has continued his coverage of the peptide literature, the present work beginning where Volume 3 ended (July 1972) and ending with the first week of January 1974. A fifth volume is now under preparation. The format of the present volume has been changed somewhat. The first six chapters deal with new protecting groups, peptide bond-forming methods, fragment condensation, and solution- and solid-phase repetitive synthesis. This adds a new dimension to this series, and hopefully it will be retained in the future. Chapter Seven contains the usual tables of compound ranging all the way from simple amino acid derivatives to nucleopeptides. Another new feature of Volume 4 is a rather large section on laboratory methods. This appendix was planned for Volume 3 but was not ready in time. This section will no doubt serve some useful purpose. It would have been better if the experiments in German had been translated.

This series is almost a must for the serious peptide chemist who intends to remain knowledgeable in the field.

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Handbook of Atomic Data. By S. FRAGA (University of Alberta), J. KARWOWSKI (Instytut Fizki), and K. M. S. SAXENA (Universidad Autónoma Metropolitana). Elsevier Scientific Publishing Co., New York, N.Y. 1976. 551 pp. $49.75.

This handbook is a tabulation of theoretical atomic parameters for the ground state of neutral atoms and many positive ions for the elements helium through nobelium. The relativistic Hartree-Fock results presented were obtained by calculating relativistic corrections to existing nonrelativistic Hartree-Fock results. Various relativistic corrections to atomic energies such as relativistic mass corrections and Breit corrections are given as well as the total relativistic correction. In addition to energies and ionization potentials, coupling constants (i.e., spin-orbit, spin-spin, Fermi contact, hyperfine structure, electric quadrupole, and magnetic octupole), constants of interest when an atom interacts with an external field (i.e., electric dipole polarizabilities, oscillator strength sums, dispersion coefficients, nuclear magnetic shielding constants, magnetic susceptibilities, Lande factors, and x-ray scattering factors), and various radial integrals and expectation values are presented. This compilation of these parameters serves as a valuable reference for both experimentalists and theoreticians independent of questions concerning the propriety of the theoretical approximations.

The first 46 pages of the book are concerned with a brief theoretical discussion, an indication of how the results should compare with experimental data, and a description of the tabulated quantities. In general, the brevity of this section leaves many questions unanswered. The fact that several different systems of units are used provides a minor drawback. Overall, however, this handbook provides a valuable compilation of atomic parameters for the ground state of neutral atoms and positive ions in a single reference.

Don Madison, *Drake University*

Vibrational Spectra and Structure. A Series of Advances. Volume 5. Edited by JAMES R. DURIG (University of South Carolina). Elsevier Scientific Publishing Co., Amsterdam-Oxford-New York. 1976. xiv + 295 pp. Dfl 100.00 ($38.50).

This volume includes four typescript chapters of rather disparate length, united by emphasis on the versatility and utility of Raman methods. Three chapters emphasize structural interpretation of small molecules and ions, while a fourth emphasizes biological applications of a specific technique (resonance Raman). Literature coverage is through 1974-1975. Extensive author and subject indices are provided.

The chapter by C. Barraclough, I. R. Beattie, and D. Everett (64 pp, 85 references) discusses the relative advantages and disadvantages of high-temperature gas-phase and (cryogenic) matrix isolation techniques for investigating the symmetry of isolated monomers of several simple inorganic molecules. Raman investigations are emphasized, with corroboration by complementary infrared information. The authors briefly but informatively survey the physical basis and potential utility of higher order Raman effects (e.g., stimulated, inverse, and coherent anti-Stokes Raman effects) for structural investigations.

J. F. Scott persuasively demonstrates (34 pp, 42 references) the power of Raman spectroscopy as a complement to x-ray crystallography to refine or correct solid-state structure assignments. Scott discusses examples from five structural classes, including some recent preliminary data. The Raman approach is particularly useful when several structures are possible. Subtle phase transitions can be detected. Raman information on light atoms also complements x-ray information on heavy atoms.

T. G. Spiro concisely outlines applications of resonance-Raman spectroscopy to investigations of biological chromophores (20 pp, 58 references). The extreme sensitivity and selectivity of the resonance phenomenon for probing certain chromophores found at sites of biochemical activity enables the structural study of active sites of biocomponents, frequently under physiologically relevant conditions. Spiro surveys the properties of several chromophores: delocalized π systems, metal ions, and heme proteins. The feasibility of resonance enhancement depends on absorption oscillator strength. Important optical absorption and vibrational modes are outlined for each chromophore class, with comments on prospects for resonance enhancement. Highlights of experimental resonance-Raman results are briefly summarized for several important proteins.

The final chapter, by C. J. Wurrey, J. R. Durig, and L. A. Carreira (157 pp, 150 references), emphasizes the utility of gas-phase Raman spectroscopy for investigation of large amplitude anharmonic vibrations of low energy (generally $\leqslant 500\ \mathrm{cm}^{-1}$).

Both mechanical (force-constant) and electrical (polarizability) anharmonicity are discussed. Numerous experimental systems are reviewed, exhibiting anharmonic torsional, ring-puckering, bending, and pseudorotational vibrations. A brief polemic over apparent bond angle discrepancies between Raman/infrared vibrational and electron diffraction (ED) studies on several "linear" molecules does not make sufficiently clear that ED studies typically provide information on *time-averaged*, as opposed to *equilibrium* geometry. In absence of vibrational data, ED results cannot distinguish between a stiff bent bond at equilibrium or a floppy linear bond subject to large-amplitude bending vibration.

The *apparent* discrepancies between vibrational and ED studies may thus actually confirm a spectroscopic assignment of large-amplitude low-energy vibrations.

This volume will be of greatest interest to vibrational spectroscopists, although the practical information on biological applications, crystal structures, and anharmonic vibrations may prove useful to workers in other fields.

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Alicyclic Chemistry. Volume 4. W. PARKER (University of Stirling), Senior Reporter. The Chemical Society, London. 1976. x + 511 pp. £27.50.

This volume in the continuing annual series covers the literature in the field of "Alicyclic Chemistry" for 1974. The book is divided according to ring size into four main chapters: Three and Four-membered Rings (194 pp, 919 refs, by S. A. Matlin), Five and Six-membered Rings and Related Fused Systems (81 pp, 174 refs, by D. G. Morris), Medium and Large Rings (66 pp, 435 refs, by E. J. Thomas), and Bridged Carbocycles (143 pp, 520 refs, by J. Carnduff). Each chapter is subdivided into a number of general sections dealing with such aspects as syntheses, reactions, mechanistic investigations, and spectroscopic studies. The extensive table of contents and author index provide quick access to specific topics of interest.

The range of topics reviewed is indeed vast and the quality of the coverage is excellent. As with many of the other Specialist Periodical Reports, this series is often the "first place to look" for general information and lead references about an area as well as specific state-of-the-art advances in the field during the period covered.

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Progress in Physical Organic Chemistry. Volume 12. Edited by R. W. TAFT (University of California, Irvine). John Wiley & Sons, New York, N.Y. 1976. xii + 368 pp. $32.95.

This well-known series continues with the present collection of eight articles comprising Volume 12. Five of these papers deal directly with substituent effects in either the aromatic or the aliphatic series. The first paper, "The Nature and Analysis of Substituent Electronic Effects" by R. D. Topsom, describes the function of various substituent constants in a fairly concise presentation. Seven primary electronic effects are defined and the related molecular effects described. The paper is clearly written and quite readable. In the next article, "A Classic Mechanism for Aromatic Nitration", L. M. Stock presents an in-depth review of nitronium ion nitration including extensive kinetic data. Nitration in organic solvents is described and the pros and cons of the encounter theory are presented. The third paper, "The Analysis of the Ortho Effect" by T. Fujita and T. Nishioka, discusses the problems encountered with ortho substituents and the approaches that have been proposed to solve these problems. The authors evaluate these methods and introduce their own approach to the solutions of problems centered around the ortho effect. This article is more a presentation of the authors' theories rather than a review. Equations are developed which are based on linear combination models for proximity effects of ortho substituents. Numerous examples are used to evaluate the proposed equations.

The next article entitled "Quantitative Models of Steric Effects" by S. H. Unger and C. Hansch presents a comprehensive list of steric constants of the Taft E_s and MR type for 161 substituents. The E_s constants listed have been referenced to hydrogen so that they would be on the same basis as other Hammett constants. A procedure is described to correct E_s for electronic effects. The fifth article is entitled "The Alkyl Inductive Effects. Calculation of Inductive Substituent Parameters" by L. S. Levitt and H. F. Widing. This is an excellent review of alkyl inductive effects. The authors have related, linearly, Taft's polar and inductive substituent constants to the molecular gas-phase ionization potentials of the molecules RX, where R is an electron donor and X an electron acceptor. Methods of determining ionization potential are discussed, and methods of calculating parameters relating to substituent effects in alkyl systems are presented. The title of the next paper, "*Ab Initio* Calculations of Charge Distributions in Monosubstituted Benzenes and in Meta- and Para-Substituted Fluorobenzenes. Comparison with ^{1}H, ^{13}C, and ^{19}F Nmr Substituent Shifts", by W. J. Hehre, R. W. Taft, and R. D. Topsom, describes the contents of this paper rather well. Ab initio molecular orbital calculations using the STO-3G minimal base set were used to determine π and σ electron populations at the meta and para positions in monosubstituted benzenes and in meta- and para-substituted fluorobenzenes. For para-substituted fluorobenzenes, the ^{19}F chemical shift correlated best with the fluorine π-charge density, while for the *m*-fluorobenzenes correlation was best with the fluorine total excess charge. The seventh article, "Heats of Hydrogenation:A Brief Summary" by J. L. Jensen, presents a very extensive list of heats of hydrogenation including references. The author discusses the fact that heats of hydrogenation are often in error because of the omission of heats of solution, which in many instances are significant. Various applications of heats of hydrogenation are discussed. The last article, by far the most lengthy (113 pp), is entitled "Electronic Structure and ^{13}C Nmr" by G. L. Nelson and E. A. Williams. This is an extensive review (300 ref) of ^{13}C NMR chemical shift data compared with charge densities at the corresponding carbon atoms. Though, in general, these shifts did not correlate well with calculated charge densities, the review demonstrates the application of ^{13}C NMR to the study of electronic structure of organic molecules, radicals, and ions.

While this volume should be of interest to physical organic chemists, it should be particularly useful for anyone interested in the more theoretical approaches to the solution of problems relating to substituent effects and charge distribution.

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Radiationless Processes in Molecules and Condensed Phases. Edited by F. K. FONG (Purdue University) with contributions by K. F. Freed (University of Chicago), D. J. Diestler (Purdue University), R. Kopelman (University of Michigan), and J. C. Wright (University of Wisconsin). Springer-Verlag, Berlin-Heidelberg-New York. 1976. xi + 360 pp. $39.80.

The purpose of this book is to present a systematic approach to understanding radiationless transitions involving electronic and vibrational relaxation in polyatomic molecules. The general approach is to treat experimental behavior in terms of the theory of adiabatic separation of molecular degrees of freedom. This theory is outlined in the first chapter by F. K. Fong, and the results serve as an introduction to several discussions in the remaining four chapters.

The second chapter by K. F. Freed is a clear exposition with good historical perspective of the problem of radiationless electronic relaxation in polyatomic molecules. The theoretical description is developed and compared with the experimental energy dependence of electronic relaxation, and the need for further experiments is noted.

Chapter 3 by D. J. Diestler complements Chapter 2 by demonstrating the applicability of essentially the same principles of adiabatic separation to the interpretation of experimental studies of vibrational relaxation of molecules in liquid and solid hosts.

Chapters 4 and 5 by J. C. Wright and R. Kopelman, respectively, are concerned with intermolecular energy transfer processes. Chapter 4 deals mainly with resonance energy transfer in rare-earth ions. Typical interactions between ground-state and excited-state ions are described as well as studies, which have become possible as a result of the development of intense, monochromatic lasers, of interactions between excited-state ions. Chapter 5 uses percolation theory to describe the onset of cooperative energy transfer effects in mixed crystals and molecular aggregates. This approach provides a comparison with theoretical descriptions for the multiphonon decay of systems such as exciton interactions in the primary molecular adducts in photosynthesis.

The book achieves its purpose admirably. Although mathematical theory is emphasized, all chapters present a good balance between theoretical and modern experimental aspects. The presentations of theory are generally clear, and sufficient references are listed to allow the interested reader with adequate training in quantum mechanics and statistical mechanics to use this volume as a starting point in understanding radiationless transition theory. Most chapters show a clear distinction between sections discussing experimental work and mathematical derivations. This makes the book convenient for use by researchers and graduate students who are theoreticians or experimentalists.

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