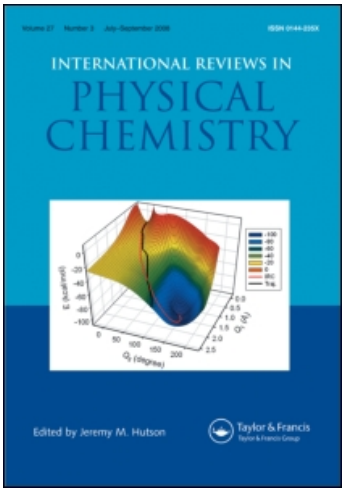

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BOOK REVIEWS

Robert J. Hunter. *Zeta Potential in Colloid Science.* London: Academic Press, 1981, 400 pp. £35.00 ISBN 0 123 61960 2

This is a very solid work which has required much more than sporadic reading on the part of the reviewer. However, for those in the field of colloidal particles (rather than macromolecules) the book will prove valuable, bringing together the theoretical and experimental aspects of ζ potential, as well as dealing with applications to a variety of colloidal problems in systems involving not only simple inorganic ions but also more complex adsorbates. Further, six Appendices are included which provide useful background material on specialized aspects of the subject. The volume thus provides a very complete coverage of the subject within itself. It is worth noting that the electrophoresis of dissolved macromolecules and gel electrophoresis are not considered.

After a short introductory chapter, the foundations are laid in Chapter 2, which contains a thorough theoretical treatment of the charge and potential distribution at an interface, developing first the Gouy–Chapman treatment for flat plates, spheres and cylinders, followed by refinements of this picture for the various models, with mention of double diffuse layers. Chapter 3, on the calculation of ζ potential from the various electrokinetic effects, contains a further body of theory concerning the various experimental approaches. This contains not only the more traditional material occurring in textbooks of 20 years ago but goes on to more recent developments, particularly of Deryaguin and his school. Chapter 4, on the measurement of electrokinetic parameters, deals in detail with the experimental side of electro-osmosis, streaming potentials and micro-electrophoresis. Moving boundary electrophoresis is merely mentioned but a highly condensed section on electrophoretic light scattering provides a starting point (and references) for a developing field. Sedimentation potentials and the use of non-uniform fields are mentioned only briefly. Electroviscous effects, subdivided into primary, secondary and tertiary aspects, and viscoelastic effects are considered in a separate chapter which starts from Smoluchowski's equation and proceeds through to the more recent work. The three further chapters are concerned with the application of the ideas of ζ-potentials to important problems in colloid science, viz. ionic adsorption, colloidal stability, sedimentation volumes and settling times, electrophoretic deposition, and particularly flotation.

This book comes from the pen of one who has worked in and has an intimate knowledge of the field spanning many years. It is clearly and concisely written but cannot be regarded as simple reading. Its usefulness for non-specialists and advanced undergraduates (see Editorial Note) is therefore to be doubted. The book is well produced with few typographical errors. The use of a symbol like $\tilde{\zeta}$ tends to cause eyestrain and the reviewer has strong and obvious objections to the phrase 'parcel of fluid' in hydrodynamic treatments. However, perhaps the biggest fault of the book is its price which will ensure its restricted sale even among libraries.

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K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules. Ionization Energies, Ab initio Assignments, and Valence Electronic Structure for 200 Molecules.* Japan Scientific Societies Press, Tokyo and Halsted Press, New York, 1980 ISBN 0 470 27200 7

For over ten years, the classic 'Molecular Photoelectron Spectroscopy' by D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, lovingly known as 'David and the three Bees', has been *the* source of HeI photoelectron spectra. In the meantime photoelectron spectroscopy has progressed and we are now offered a dignified successor for this well-worn volume in the shape of the present handbook which is an absolute must for all those working in the field of photoelectron spectroscopy or for any theoretically minded chemist. This handsomely produced book contains over 180 photoelectron spectra of simple organic molecules which are needed for the interpretation and rationalization of the spectra of more complicated systems. The selection of reference compounds covers all the fundamental functional groups one usually encounters and the complete He(I) spectra are given, i.e. down to ~20 eV. One of the great advantages of this magnificent collection is, that all spectra have been recorded anew by the same authors and are thus strictly comparable. In addition to their pictorial representation, the vertical ionization energies are listed in tables and, in some 50 cases, the results of theoretical *ab initio* calculations, using a 6-31G or 4-31G basis are presented. In those cases where such calculations are available, the molecular orbitals are graphically displayed in an easily readable form. The ionization energies derived from these calculations are the ones obtained by using Koopmans' theorem and/or by taking the differences of state energies. In the latter case, the relevant linear combinations of configurations are also listed in a shorthand notation.

The book is quite obviously a labour of love and contains an enormous amount of exceedingly useful information, presented as clearly as one could possibly wish. The reviewer hesitates to point out its only weakness, which could have easily been avoided, namely the unfortunate fact that the ionization energy scales of the drawings vary from spectrum to spectrum. This makes it impossible to compare them by using transparent tracing paper.

There is no need to recommend the handbook, because you cannot afford to be without it if you want to be up to date in photoelectron spectroscopy.

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J. W. McGowan (Editor). *The Excited State in Chemical Physics, Part 2.* New York: John Wiley and Sons, 1981. 620 pp. £42.00. ISBN 0 471 05119 5

The last decade has seen a tremendous growth of studies of the formation and properties of excited states. This has arisen not only from the development of new techniques and from interest in plasmas and in new lasers, but also from the extra information that such studies provide as to the detailed mechanism of collisional processes, both reactive and non-reactive. The first volume of 'Advances in Chemical Physics' devoted to the excited state appeared in 1975 and this second part which contains six chapters has a strong emphasis on electronically excited states and on processes involving ionized species.

Unfortunately, the longest chapter continues the popular fallacy that almost any spectroscopic or kinetic data concerned with atmospheric molecules is relevant to atmospheric problems. In this case, readers are treated to 83 figures of potential-energy

curves for N_2, NO and O_2 and their ions on which no energy levels are marked and no indication is given as to which curves are observed and which calculated.

Fortunately the other chapters are much more useful. They begin with a clear account by Brion and Hamnett of the use of electron spectroscopy to calculate oscillator strengths. The other chapters provide authoritative accounts of a series of related topics concerned with collision processes, all of considerable current interest. The chapters by Niehaus on penning ionization and by Tiernan and Lifshitz on the role of excited states in ion-neutral collisions pair together very nicely as do those on molecular beam studies on which Hertel considers quenching of electronically excited atoms and Haberland, Lee and Siska discuss scattering of noble-gas metastables. The accounts are all up to date and clearly presented and make this volume a useful reference work for those interested in collision processes at energies immediately above and below the first ionization threshold.

B. A. Thrush

A. C. Norris. *Computational Chemistry. An Introduction to Numerical Methods.* Chichester: Wiley, 1981, 450 pp. £8.75 (pbk). £19.75 (cloth). ISBN 0 471 27950

This excellent inexpensive text of 450 pages contains eight chapters on the methods appropriate for the solution of numerical problems which are met in chemistry. It is readily understandable by a student who has a sound knowledge of calculus and matrix algebra.

The introductory chapter is entitled 'Problem Formulation and Solution', and the second chapter, entitled 'Computational Errors and their Treatment', discusses the storage of numbers in a computer and the consequent possible round-off errors in computer program calculations. Chapter 3, entitled 'Experimental Errors and Their Statistical Treatment' gives a discussion on random variables, normal distribution and the correlation coefficient. At the end of each of these three chapters there are self-programming exercises on simple physical chemistry problems.

Chapter 4, entitled 'Solution of Non-Linear Equations', discusses the Newton–Raphson and other methods, with a good elucidation of each method's deficiencies. In this and the succeeding chapters, after introducing the theory for each alternative numerical method for the problem, there is a section entitled 'Comparison of Methods', which is so important in this subject. This is followed by both self-programming and non-programming exercises which exemplify the theory, and furthermore by exercises based on complete FORTRAN programs contained in the appendix. For example, for this chapter the program PRONON contains sub-routines for the five methods discussed, and then has further sub-programs related to the exercises, here related in many cases to the Van der Waals equation. Chapter 5, entitled 'Solution of Simultaneous Linear Equations', introduces pivotal and iterative methods for solving these equations, using a simple matrix terminology, which is first explained. Ill-conditioning problems are discussed, and amongst many chemical examples, there is one based on mass spectrometry data. Chapter 6, entitled 'Numerical Integration', introduces the trapezoidal, Simpson and Gauss quadrature methods, although the text is obviously not sufficiently advanced to discuss the full theory of the latter. There are examples based on the integration of Planck's black-body radiation formula, amongst others. Chapter 7, entitled 'Numerical Solution of Ordinary Differential Equations', introduces Runge–Kutta and Predictor–Corrector methods. The associated PROODE has explicit sub-routines for the fourth-order Runge–Kutta and Milne–Simpson methods, which should prove useful. The last chapter, 'Interpolation and Approxi-

mation', gives detailed discussion of cubic splines and least squares polynominal fits. There are many associated chemical problems given as exercises.

The main appendix of computer programs (all in standard FORTRAN, with special emphasis on portability) is 60 pages. All the programs are well commented and are declared by the author to be tested. Answers and comments on the exercises, essential for a book of this nature, are contained in the last 50 pages.

In summary, this text is a simple introduction to numerical analysis, containing a straightforward discussion on all the standard methods available to solve the type of numerical problem which an experimental chemist is liable to meet. (The author deliberately omits eigenproblems, which do not normally fall in this category.) It is very readable, and it does not contain many of the frightening formulae of numerical analysis texts. However, each chapter contains a list of references for further study. Great emphasis is placed on pitfalls of the various methods, and much aid is given on the selection of the appropriate method.

The book is ideal as a text for a course on numerical methods appropriate to chemistry and readily understandable by a student with a knowledge of calculus. The nature of the exercises are such that they give the student an excellent introduction to the problems and successes of this subject. However, I doubt whether many students will have the time available to take such a course—unfortunately many chemistry undergraduates appear reluctant to involve themselves seriously with numerical methods or computation. I consider this also to be an excellent text for chemistry research students. It seems to be written especially for them, and is just the book the enquiring student needs when meeting a problem involving numerical methods and computation.

The book must represent the result of much careful work, and from a first reading, it appears to be error free. It must be recommended.

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O. Popovych and R. P. T. Tomkins. *Nonaqueous Solution Chemistry*. New York: Wiley-Interscience, 1981. 500 pp. £36.75. ISBN 0 471 02673 5

Undergraduate or graduate courses in chemistry often pay little attention to nonaqueous solution chemistry, in spite of the enormous growth of this topic in the past 30 years. The reason for this neglect may be that information on nonaqueous chemistry is largely available only in highly specialized articles scattered throughout the primary literature or in review articles and monographs written for the specialist. The authors of the present book have tried to remedy this situation and aim:

> to provide a single concise and yet comprehensive source of information on nonaqueous chemistry for the advanced student and for the practicing chemist as well. This book is not meant to be a comprehensive review for the specialist. It is an introductory text . . .

The authors define the scope of their book to include mixtures of nonaqueous solvents with water but they exclude studies in fused salts. After an introductory Chapter 1, the various intermolecular forces relevant to non-aqueous solutions are discussed in Chapter 2, with emphasis on the nature of solvation. Chapter 3 deals with the classification of solvents according to various properties. The basic thermodynamics of nonaqueous electrolyte solutions are examined in Chapter 4; Chapter 5

continues the thermodynamic theme with transfer functions and the correlation of properties in different solvents. Chapter 6 deals with acid-base chemistry; transport properties (electrical conductance, diffusion, etc.) are discussed in Chapter 7. The theme of Chapter 8 is the role of spectroscopy in the study of nonaqueous solutions. Electrode processes are discussed in Chapter 9 and solvent effects on the rates and mechanisms both of organic and of inorganic reactions are featured in Chapter 10. Finally, Chapter 11 deals with certain specialized applications of nonaqueous solutions, e.g. in batteries and for electrodeposition. Extensive bibliographies, with citations of primary, review, and monograph literature, are given at the end of each chapter.

The material is presented in an attractive style and is very readable. It seems usually reliable, although the specialist may find occasional over-simplification. Thus in Chapter 2, expressions for energies of interaction involving dipoles are given without stating that they are for the 'point-dipole approximation'. The younger generation, brought up strictly on IUPAC nomenclature and SI units, may be exercised by antiques such as *i*-butanol, kcal, esu, and Coulomb's Law without the 4π. This corresponds, however, to much of chemistry as it really is.

The authors seem prepared for criticism of their choice of material: 'the selections are bound to be somewhat arbitrary, reflecting the interests of the authors.' While the reviewer sympathises with this defence, he cannot help feeling, as a physical organic chemist, that the authors do not show the reader of Chapter 10 a fair picture of present-day understanding of solvent effects on organic reactivity.

However, this book will certainly fulfil a useful role as an introductory text for the broad field of nonaqueous solution chemistry.

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Structure and Bonding. Editors: M. J. Clarke, J. B. Goodenough, P. Hemmerich, J. A. Ibers, C. K. Jørgensen, J. B. Neilands, D. Reinen, R. Weiss and R. J. P. Williams. *Vol. 45*. G. Wendin. *Breakdown of the One-Electron Pictures in Photoelectron Spectra*. Berlin–Heidelberg–New York: Springer-Verlag, 1981. 130 pp. DM66, US $31.50. ISBN 3 540 10584 0

This book is one of a series published by Springer dealing with particular aspects of *Structure and Bonding*. The topic it covers is the study of correlation and configuration interaction effects which have to be taken into account in the interpretation of the various features of photoelectron and absorption spectra involving excitation and ionization of core electrons, e.g. in X-ray photoelectron spectroscopy, in Auger spectroscopy and in soft X-ray or deep vacuum UV absorption spectroscopy. When a core electron is ionized the single hole level is frequently found to interact with configurations with primarily two holes and one excited electron. In systems with empty levels spatially as compact as the occupied ones, the interactions can become extremely strong and result in a breakdown of the one-electron quasi-particle picture. This often leads to the replacement of expected discrete spectral structure by broader features and even a continuum-like distribution. In this volume theoretical treatment is applied to the spectra of a wide variety of elements and it is shown that by comparing the spectra of a sequence of increasing atomic number the energies of coupled states can be systematically shifted in accord with the theory presented. Diagrams representing several aspects of the process are frequently given so that in addition to the relevant

Feynman diagrams correlations are represented in terms of energy level diagrams and often illustrated by real space diagrams. It provides a useful account of the interrelationship between the various Coster-Kronig, Auger, shake-up, shake-off and configuration interaction processes in terms of which the spectra are usually discussed.

Following the interpretation of the XPS spectra of atomic systems given in the first half of the book, the treatment is extended in later chapters to simple molecules and solids including adsorbate systems. It is shown that satellite structure for such systems can be explained in a somewhat similar manner. In view of the present widespread activity in the field of photoelectron and synchrotron UV spectroscopy, this review of related theory has appeared at a most opportune moment.

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OTHER BOOKS RECEIVED

Ilya Prigogine. *From Being to Becoming: Time and Complexity in the Physical Sciences.* London: W. H. Freeman and Company, 1980. 272 pp. £13.50 (hardback), ISBN 0 7167 1107 9. £6.30 (paperback), ISBN 0 7167 1108 7.