J. CHEM. SOC. FARADAY TRANS., 1993, 89(9), 1397–1400

BOOK REVIEWS

Diffusion in Zeolites and other Microporous Solids. By J. Kärger and D. Ruthven. John Wiley and Sons, Inc., New York. 1992. Pp. xxxiv + 605. Price £117.

An understanding of the mechanism of diffusion in microporous materials is vital for the industrial utilisation of these materials in areas such as catalysis and separation processes. Once the basic phenomenology had been established at the turn of the century attention began to focus on the molecular mechanisms underlying diffusion and the importance of well defined pore systems became realised. The zeolites being both crystalline and microporous seemed at first sight to be a godsend in this venture, but the path of true scientific investigation rarely does run smooth and this one proved to be no exception. A major difficulty arose because it was impossible to prepare crystals of large enough size for measurements by "classical" methods to be unambiguous. Furthermore, many applications employ quantities which are huge by laboratory standards and consequently compacts, in which the microporous space is incorporated with larger voids of undefined geometry, are the norm for these applications. Perhaps for these reasons physical scientists (with one or two notable exceptions) have tended to steer clear of the subject and it was largely left to chemical engineers, harder pressed perhaps by everyday industrial necessities, to make most of the progress. The advent of microscopic methods, particularly NMR techniques, in the seventies promised to change all this; at last a probe was available which could operate at the molecular level and for which crystal size would no longer be a problem. However the first results from these measurements were devastating: the diffusion coefficients differed by orders of magnitude from those previously obtained classically; was it possible that we either did not understand or could not measure diffusion at all? As the authors say in their Preface their interest in the subject was in part stimulated by these puzzling discrepancies. In the last 20 years or so much light has been thrown on the subject and as a result of a huge effort, the worst of the scandal has been resolved; much of the credit for this achievement must go to groups led by the authors of this book. As expected therefore they bring immense expertise and authority to the subject. These qualities are, of course, not in themselves enough to guarantee a worthwhile text, but no reader will be disappointed by the result in the present case. The book is both thorough and accessible without straying into obfuscating detail. Both the theory and the practice are covered in sufficient depth to carry a reader from a general postgraduate level to one where the current literature can be followed with enjoyment and confidence. The text travels from the basic phenomenology, through the development of molecular mechanistic theories, the principles and practice of measurements by both macroscopic and microscopic methods and finally into a comprehensive survey of results and data. The latter section, as the title suggests, concentrates largely on zeolitic materials, but most of the earlier sections are of quite general application. In the end one is left with an impression of the vast scope of this subject; there can be few basic areas in chemistry or chemical engineering which are untouched during the journey from theory to practice covered in this book. Anyone entering this field can find themselves challenged as much by its demands on mathematical as experimental skills; as much by the need to understand processes at their deepest molecular level as by the need to improve them in response to pressing industrial need. This book would certainly be essential reading for anyone who takes up these challenges. The text is everywhere readable and informative and no laboratory with an interest in the field would wish to be without a copy.

D. Nicholson

Received 11th December, 1992

Theoretical Atomic Physics. By Harald Friedrich. Springer–Verlag, Berlin, 1991. Pp ix + 316. Price DM 58.00.

This book provides an enabling resource, covering the necessary quantum theoretical techniques that are required for understanding and interpreting the results obtained from the application of new high precision experimental techniques in atomic physics; indeed, the text is very timely in view of the resurgence of atomic physics in recent years. The emergence of new techniques, for example, the use of electromagnetic traps to provide the possibility of performing experiments on individual atomic species, have provided fertile ground for the parallel development of largely non-relativistic quantum mechanics, but texts describing such developments are rare. Professor Friedrich's book, which is aimed at students who have a knowledge appropriate to a first introductory course in quantum mechanics, aims to fill this gap with bound states and continuum states treated in a unified way. However, readers with a traditional chemical background may have to prepare themselves by reading parts of one or more of the basic texts cited in the first paragraph of the introduction to Chapter 1, unless, of course, they have attended special option courses where, for example, the solution of the Schrödinger equation for the bound states of the usual range of model systems as well as the treatment of scattering processes, have formed an integral part of the course.

The text has five chapters, each one concluding with a list of references and a good sample of problems, and an Appendix describing the properties of relevant special mathematical functions. Building on a basic quantum mechanics backgound, which is revised in the opening chapter, the author then develops a relatively conventional description of the bound states of atoms and ions and of the selection rules determining the transitions between them. Chapter 3 contains an economical account of atomic spectra, which emphasises the power of both single-channel and multi-channel defect theory, after a timely reminder, in the introductory paragraph, that the problem of dealing with highly excited states of many-electron systems is still largely unresolved. Elastic scattering of an electron by a real atom (neon) is then investigated in some detail (Chapter 4), while the inelastic formalism is applied in depth to excitations and e–2e reactions on hydrogen. The final chapter emphasises new topics that have emerged in the last decade, multiphoton absorption, coherent states and chaos.

The book has no pretension to be an exhaustive study, but tries to teach some important general ideas spiced by simple examples that exemplify them. This is largely successful (with the proviso noted above relating to prerequisites!), and the book will provide a good staging post to specialist texts. Some students may find some of the mathematical arguments a little terse, but the significance of the results is usually put into a clear physical context. The book is well produced, and forms a welcome addition to the atomic physics literature.

G. Doggett and J. A. D. Matthew

Received 18th December 1992

A Computational Approach to Chemistry. By D. M. Hirst. Blackwell Publications, 1990 £24.95 (paperback).

Nowadays, computer calculations are having an enormous influence on every aspect of chemistry. This relatively new development has come about through the efforts of many theoretical chemists who have invented the theories, algorithms and computer programs that are needed to simulate chemical problems. This useful book by David Hirst presents a broad overview of this field. The computational methods for providing fundamental chemical information on molecular structures, potential-energy surfaces, energy levels and reaction rate constants are clearly presented. Futhermore, the book describes the computational techniques that are used to model complex chemical reaction systems in combustion, atmospheric and interstellar chemistry and also to simulate liquids, proteins and macromolecules.

One aspect of the field of computational chemistry is that new developments have been very rapid recently. This book was written in 1989 and published in 1990. Since that time several new computational techniques have become fashionable that are not described in the book but would be essential topics in a book written in 1993. These techniques include coupled-cluster theory in quantum chemistry, density functional methods for molecules and solids, hyperspherical coordinates for chemical reactions, wavepacket techniques applied to molecular photoprocesses and the Car-Parrinello method for the structure and dynamics of solid surfaces and condensed phases.

The book is easy to read despite the fact that it has been essential to include many of the basic equations, and some derivations, that are central to the computational algorithms. A judicious choice of examples and applications of the computational techniques makes the book relevant particularly for non-specialists. This inexpensive, paperback book is appropriate for final-year undergraduates, first-year graduates and scientists from areas outside of chemistry, such as biochemistry, physics and materials science, who need to learn more about this field. Those who need to use the methods and computer programs in their own research will probably need to make use of more detailed books and papers and the well chosen set of references will enable interested readers to obtain the computer programs they require from the original authors.

D. C. Clary *Received* 23*rd December*, 1992

Modelling of Structure and Reactivity in Zeolites. Ed. by C. R. A. Catlow. Academic Press, London, 1992. Pp. x + 260. Price £45, $97.

As early as the mid-eighteenth century attention was drawn to some strange porous materials, called zeolites and considered as a curiosity. A hundred years later a first analysis of the crystal structure was proposed, and this was the beginning of a constantly increasing interest of the scientific community for these minerals. Meanwhile, the zeolites proved to be good solid catalysts and were frequently used in the oil industry. A large amount of information resulting from various experimental investigations (X-ray diffusion, spectroscopies, ...) is now available in books or in widely published reports. The situation is rather different concerning the efforts made by the theoreticians to interpret, understand or even predict the structural or electronic properties of zeolites, their work is dispersed in reviews and only accessible to restricted communities. The present book has the great merit of presenting in one volume, accessible to a wide public of scientists, the main methodologies used to explore this area and describe some relevant results recently obtained.

The book gathers ten articles (here designated as chapters) representing the work of twenty three contributors. Participation of different specialists permits the covering of almost all the aspects of theoretical research in the area of zeolites, without too many redundancies or inconsistencies.

The work is organized so as to progress from simple methods towards more sophisticated techniques. Chapters 2 and 3 review sample approaches based on topological arguments or on methods adapted from solid-state physics (lattice dynamics) and aiming at the prediction of structural properties.

Molecular dynamics and the closely related subject of molecular graphics are developed in Chapter 5 and 6. The application of quantum chemistry methods is described in Chapter 8 and 9. Finally, methods to predict zeolite crystallization are given in Chapter 10. Not included in this progression are Chapters 4 and 7. Chapter 4 focuses attention on the key problem of adsorbed molecules and the contributions of various theoretical methods (molecular mechanics, Monte Carlo, ...). The important question concerning the determination of electrical properties of zeolite is considered from the point of view of the density functional theory in its empirical version leading to the electronegativity equalization method (Chapter 7).

Among all the subjects considered, some merit special attention. This is the case with molecular dynamics. A clear and concise description of the method is given with mention of some specific aspects such as the intermixing of two distinct subsystems (framework and sorbate). Related to this subject is the review of computer graphics. It is not only the source of very attractive pictures, some of which illustrate the book, but is also an indispensable tool for people working in the field of zeolites, since these complicated structures are very difficult to visualize. The authors give a general overview of the possibilities offered by recent software with emphasis on the facilities offered to the users. Despite their qualities, these reviews are sometimes missing critical discussions: even a short presentation of molecular dynamics should not avoid clearly indicating the limitations and pitfalls of methods whose possibilities are often overestimated. In particular, the dependency of the results on the nature of the intermolecular potential implemented in molecular dynamics methods deserves more careful attention.

Another aspect of interest is the growing importance of quantum chemistry methods in the analysis of electronic properties of zeolites. Recent applications of *ab initio* and semi-empirical methods are reviewed. They demonstrate that local properties, like the mobility of acidic proton, can be investigated, and bring some information at the microscopic level on the sorbate molecule and crystal framework. The coupling of these methods with molecular dynamics, in particular for the construction of intermolecular potentials, has not been sufficiently developed, though it is a key problem for further developments.

The book will probably be useful for people working in the field as a landmark of the state-of-the-art, but it will also constitute a very good introduction for all scientists who would like to enter the extremely rich and fascinating area of zeolites.

M. Allavena *Received* 24*th December*, 1992

Catalysis Science and Technology. Volume 9. Ed. by J. R. Anderson and M. Boudart. Springer–Verlag, Berlin, 1991. Pp. xii + 190. Price DM 128.00.

This volume is the latest in a splendid series on catalysis and is devoted to the mechanisms and dynamics of heterogeneous catalysis. The volume comprises three substantial contributions from distinguished workers in the respective areas: the determination of mechanism in heterogeneous catalysis (86 Pp., R. L. Burwell, Northwestern University), dynamic relaxation methods in heterogeneous catalysis (43 Pp., K. Tamaru, Science University of Tokyo), and the dynamics of heterogeneously catalysed reactions (54 Pp., G. L. Haller and G. W. Coulston, Yale University). Each chapter, although long, is arranged neatly into subsections making for very easy and enjoyable reading.

The first chapter on mechanisms starts at a very basic level before proceding to cover the kinetics of adsorption processes, the use of isotopes, the kinetic isotope effect, stereochemical effects, catalyst alteration, selective feeding and selective scavenging, poisoning, indirect mechanistic probes, and chemisorption by chemical techniques. Finally, the chapter describes briefly the application of a number of spectroscopic techniques including infrared, Raman, EPR, visible-ultraviolet, NMR and Mossbauer.

Chapters 2 and 3 are arranged in a similar fashion. The former covering dynamic relaxation encorporates sections on the theory and experimental procedures before describing in detail the decomposition of ammonia over tungsten and molybdenum, the NO/H_2 reaction on transition metals, the hydrogenation of CO to form hydrocarbons, and adsorption-assisted desorption and decomposition.

The final chapter describes the dynamics of a number of systems including the associative chemisorption and diffusion of CO on metals, dissociative chemisorption of H_2, N_2 and methane on metals, and the dynamics of ethane, propane and butane dissociative adsorption and CO oxidation.

Each chapter is well referenced (a total of 355 numbered references), although it is disappointing that Chapter 1 contains only two references later than 1986. The subject index is adequate. Overall, this volume is a very useful contribution to workers in the field, and at 128DM (*ca.* £53 or 28p per page) should be within the means of most individuals.

P. G. Harrison *Received 7th January*, 1993

Advances in Spectroscopy Volume 19. Spectroscopy of Advanced Materials. Ed. by R. J. H. Clark and R. E. Hester. Wiley, Chichester, 1991. Pp. xix + 405.

Previous volumes in the series Advances in Spectroscopy have covered a wide range of spectroscopic techniques and their use to study an equally broad spectrum of materials. Volume 19 has been given the sub-title 'Spectroscopy of Advanced Materials', indicative of the emphasis on the materials being studied rather than the spectroscopic techniques utilised to study them. The editors do not, however, indicate what they mean by the term 'Advanced Materials'. If one construes it to mean materials with potential for technological application at some time in the future the term is appropriate. Readers expecting to find materials poised to move from a research and development phase into applications will be disappointed. The strong bias to polymeric and organic conductors will surprise others. Only 34 of the nearly 400 pages are devoted to semiconductors. This is surprising in view of the major advances made in elemental and compound semiconductors and structures which are now having an important impact on device technology. Magnetic materials are covered in 20 pages of the chapter on neutron spectroscopy, again not at a level commensurate with their technical importance. In their preface the authors state 'This book is devoted to materials science'. This is a more apt description of the contents and 'Spectroscopy of Materials' a more accurate sub-title.

Research workers in materials, particularly in the areas of conjugated polymers and organic charge transfer salts will find this volume of value as a reference work. The opening chapter by R. Bozio and C. Pecile covers the optical, IR and Raman spectroscopy of charge transfer crystals and organic conductors. There is an extensive introduction to the spectroscopic properties of materials with charge transfer interactions. Theoretical models connecting spectra with crystal structure and electronic properties are presented. The well known experimental methods are discussed very briefly before recent work deriving information on crystal and electronic structure from spectra is described. Overall this is a very useful introduction to this topic. In contrast the second chapter on non-linear optical properties of conjugated polymers by S. Etemed and Z. G. Soos has a very brief introduction and presupposes some contact with non-linear optics. There are then reviews of recent theoretical and experimental work which will be useful to those working in the area.

Chapter 3 on pulsed neutron studies has an appropriate introduction covering experimental methods, necessary for a general audience. Since the theme is spectroscopic, rather than structural, uses of neutrons the discussion of magnetic materials covers the splittings of the energy levels of rare earths and actinides in magnetic materials, with a brief discussion of spin waves in cobalt. Other topics covered are vibrational modes of hydrogenous materials and tunnelling spectroscopy in molecular solids.

Chapter 4 is an account of photoluminescence spectroscopy in thin film semiconductors by J. O. Williams. II–VI and III–V materials are considered and a concise resume of the origins of photoluminescence presented. ZnSe is used as an example of a bulk material and AlAs–GaAs layered structures as an example of quantum wells. This is an all too brief exposé of an important topic.

The final two chapters return to the theme of conjugated polymers. There is an extremely detailed and thorough review of the vibrational spectroscopy of polyacetylene and related polymers by M. Gussani, C. Castighani and G. Zerbi. This review should be read by anyone interested in this topic and is highly recommended for starting graduate students. The final chapter by A. J. Epstein, R. P. McCall, J. M. Ginder and A. G. MacDiarmid deals with polyaniline. The central theme is that polyaniline is structurally and physically more complex than other conjugated polymers and displays new effects. The recent rapid increase in research on polyaniline would suggest that this message has already been effectively promulgated.

D. Bloor *Received 7th January*, 1993

Thermoreversible Gelation of Polymers and Biopolymers. By J-M. Guenet. Academic Press, London, 1992. Pp. xi + 280. Price £40.

The book brings together published work on synthetic and biological networks. It treats the two types of network in parallel, in terms of Gel Formation: Thermal Behaviour and Phase Diagrams (Chapter 1), Gel Morphology and Molecu-

lar Structure: Gelation Mechanisms (Chapter 2) and Mechanical Properties and Rheology (Chapter 3). Further, synthetic polymer networks are divided into two classes, namely, solvent-induced gels and crystallization-induced gels. The subject matter is treated in fundamental terms, in the quest for molecular explanations for physical gelation phenomena and for gel properties.

The material is presented essentially as a review of experimental work on model gelling materials which has been carried out over the last two decades or so. For this reason only a limited number of systems is considered. Amongst the solvent-induced synthetic polymer gels discussed are polystyrene, poly(methyl methacrylate), poly(4-methyl pent-1-ene) and poly(γ-benzyl-L-glutamate). The crystallization-induced gels considered are polyethylene, poly(vinyl chloride), poly(vinyl alcohol) and copolymers (briefly). Results on gelatin, carragenan, agarose, amylose and amylopectin, gellan and cellulose derivatives are used to represent biopolymer gels.

The book concludes with appendices on the theoretical approaches used to interpret various types of experimental measurements important to the understanding of the formation and properties of thermoreversible gels. The topics treated are phase diagrams and transitions, diffraction by helical structures, scattering by semi-rigid molecules and the elasticity of rigid networks. Surprisingly, viscous behaviour and viscoelastic behaviour are not treated.

The book is recommended as a useful review of fundamental studies in the developing field of the formation, structure and properties of thermoreversible or physical gels. Perhaps more effort should have been made at comparisons between biological and synthetic systems and more use made within the main text of the theoretical material in the appendices.

R. F. T. Stepto

Received 20th January, 1993