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NEWS

Book reviews

Molecular semiconductors. Photoelectrical properties and solar cells
J. Simon and J.-J. André, Springer-Verlag, Berlin, Heidelberg, 1985
DM 174, ISBN 3-540-13754-8

This is a useful book. It has appeared at a time when there is a pressing need to take stock of the progress that has been made in the last two or three decades in the physics of the organic solid state. As the authors point out in the preface, 'a survey of the literature on molecular semiconductors leaves one rather confused. It does seem very difficult to correlate the molecular structure of the semiconductors with their experimental electrical properties'. In a sense, this statement (as well as the title of the book itself) begs the question whether the term 'molecular semiconductor' is an appropriate description of many of the organic solids that have been studied; however, a striking feature of this book is that the authors have adopted a critical attitude to the wide range of experimental data on these systems, examining them within the framework of the several different descriptions of molecular solids that have been proposed. This approach has resulted in a detailed and exceptionally well-balanced overview of this interesting area, and for this reason the book will be welcomed by those new to the study of organic molecular solids as well as to those already familiar with the difficulties inherent in the preparation, characterization and description of these important materials. At the same time the authors have managed to keep a practical perspective, and the discussions of junction devices fabricated with organic solids are lucid and wide ranging. The references cover the literature up to the end of 1983.

The book begins with an introduction to the basic notions of solid-state physics and, in this first chapter, emphasis is placed on the limitations of the band theory of solids. The particular importance of localized states and of trapping, tunneling and hopping mechanisms in the case of organic solids is made clear in the second half of this introductory section. The second chapter deals with the photogeneration and transport of charge carriers, and here the classical band description is contrasted with the localized state formulation.

Most of the rest of the book, some 130 pages, is devoted to the metallophthalocyanines and to polyacetylene. These chapters combine a useful literature review with a clear discussion of the importance of impurity doping (accidental and deliberate) on the electrical properties of these systems. The importance of solitons in extended conjugated systems and the different mechanisms of charge carrier generation are described.

The last part of the book surveys a number of other organic solid state systems. Aromatic hydrocarbons and metallorganic derivatives are dealt with rather briefly, whereas charge transfer systems are treated in more depth. Short sections on merocyanine dyes as well as on polymeric materials such as polysulphurnitride, $(SN)_x$, and polypyrrole are also included along with details of the solar cell performances achieved with different materials. Here the results are well ahead of any detailed understanding and it is clear that much remains to be done before confident descriptions of metal/organic solid junctions can be given. The present status of research into organic semiconductors is summarized in the conclusion to this stimulating book which will find a wide audience among physicists as well as physical and organic chemists.

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Standard potentials in aqueous solution

A. J. Bard, R. Parsons and J. Jordan (Eds)
Marcel Dekker, New York, 1985
848 pp., \$29.95, ISBN 0-8247-7291-1

Although sixth in a series of electrochemistry books published by Marcel Dekker under the editorship of A. J. Bard, this book is distinctive in having been commissioned by the International Union of Pure and Applied Chemistry. The work is seen as a successor to the classic, Latimer's 'Oxidation Potentials', extended to include material which has been reported over the last half-century and intended to conform with current IUPAC conventions.

Undoubtedly the publication of such a book is timely and a large amount of data has been compiled. There is a short introductory section in which Professor Parsons discusses methods of determining electrode potentials and points out conventions involved in the use of such, and related, data. He also considers the estimation of single electrode potentials. Most of the book consists of separate chapters devoted to groups of elements, written by more than fifty contributors, as often as not members of the same team who authored Bard's 'Encyclopedia of Electrochemistry of the Elements'. In an attempt to enhance the authority of the book, the editors have had each chapter refereed by a named reviewer.

The inevitable multiplicity of authors has led to a noticeable shortcoming for which the editors must be held responsible. Much of the presented data is of thermodynamic parameters and, particularly in a IUPAC-supported reference book, one expects uniformity of presentation and total absence of ambiguity. Yet, depending on the taste of the individual chapter authors, we find similar thermodynamic data tables variously headed: ΔH^0, ΔH_f^0 or $\Delta H_{f,298}^0$; ΔG^0, ΔG_f^0 or $\Delta G_{f,298}^0$; and ΔS^0, S^0 or S_{298}^0. This inconsistency might confuse the student reader at whom the book is partly aimed, especially as the tables include data for solvated ions as well as gaseous ions and uncharged elements and compounds. Thus the entropy data are a mixture of standard absolute entropies and standard entropies relative to z_+ solvated hydrogen ions. Similarly the ΔH^0 (and ΔG^0) columns contain mixtures of standard enthalpies (and Gibbs' energies) of formation and standard enthalpies (and Gibbs' energies) relative to z_+ solvated hydrogen ions. An attempt is made in the introductory section to make this clear, but the matter is confused by the assertion there that it is conventional that the enthalpy and Gibbs' energy of an element in its standard state are taken as zero; the normal addition of 'of formation' to these terms is eschewed. In an area which often proves troublesome to students it is helpful always to make an explicit distinction between absolute thermodynamic quantities (i.e. relative to the zero-point values), quantities 'of formation' (i.e. relative to those of the constituent elements, each in its standard state) and quantities relative to those of z_+ hydrogen ions. For ions in the gas phase the ΔH^0 and ΔG^0 data are apparently quantities 'of formation at 298 K', and S^0 data are absolute standard entropies at 298 K.

Despite the reference nature of the book the presentation is readable and critical, with calculations of electrode potentials and their temperature coefficients being given in detail. The binding is robust and the price sufficiently low to encourage widespread individual purchase. It is to be welcomed.

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Ion solvation

Y. Marcus, John Wiley, Chichester, 1985
306 pp. + viii, £42.00

The concept of solvation is an important one which pervades either directly or implicitly most aspects of practical and applied chemistry. The qualitative significance of the solvation of ions has been appreciated for many years and the subject has recently attracted considerable attention from the viewpoints of both modern theory and refined experiment. In the latter regard the beautiful, elegant and definitive neutron scattering experiments conducted by Enderby and Neilson and their co-workers have now placed some aspects at least of solvation phenomena in the area of science–fact. This book by one of the leading authorities on solvation is therefore both timely and needed. Professor Marcus has described in some detail the various experimental, quasi-theoretical and theoretical approaches which have been used to study the solvation of ions and, importantly, has attempted to survey and correlate the information obtained from the different methods. His expositions are generally both clear and instructive. The final chapter in which he deals with some illustrative examples on applied aspects of solvation including solvent attraction and phase transfer catalysis was, I thought, particularly well done.

The book contains a large number of tables, some of which are directly relevant to solvation *per se* and others which give information on the properties of both pure and mixed solvents. These latter did strike me as being a useful feature, but I was disappointed to find that there appear to be a large number of errors in the tables and references from the text to the tables are sometimes erroneous. This is a serious deficiency and mars what could have been a very good book. I do not know who is responsible for the errors but suspect that Professor Marcus has been ill-served by the publisher's sub-editing staff.

Notwithstanding the above criticisms this is a book I would recommend to others and particularly to postgraduate students who are working in solution physical chemistry. However, it seems highly unlikely that British postgraduates would go so far as to purchase it since the retail price corresponds to one week's income for them

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Principles of electrochemical reactor analysis
T. Z. Fahidy, Elsevier, Amsterdam, 1985
315 pp., £45.79

Electrochemical engineering has yet to find sufficient favour among most UK academic chemical engineers for it to be a component of their undergraduate courses. In part, this stems from a paucity of suitable textbooks; the availability of this teaching text should do much to improve the status of the subject as an entirely legitimate and desirable component of such courses.

Aimed at chemical engineers and electrochemists, the book fills a gap left by the very few other texts on electrochemical engineering, and complements D. J. Pickett's monograph on Electrochemical Reactor Design published in the same series. The emphasis is on mathematical modelling: there are many worked examples within the text and problems at the end of each chapter, with answers at the end of the book.

There are eleven chapters covering energetics and kinetics of electrolytic processes, with an introduction to convective–diffusion and relevant dimensionless groups, plug flow and continuous stirred-tank reactors, estimation of mass transport coefficients, thermal behaviour of electrochemical reactors, dispersion models, convective diffusion theory, migrational effects, potential and current distributions, process dynamics and optimization. The first of the appendices provides a short bibliography and a few further reading references for each chapter. The other three appendices deal with root finding, Lagranges data interpolation method and an approximate method for computing definite integrals; they are designed to support the use of numerical methods in some of the worked examples and problems throughout the book. A greater emphasis on the modelling of electrochemical reactors coupled to chemical reactors might have been appropriate because of the technological importance of such systems in electroorganic synthesis, electrohydrometallurgy, etc.

Unfortunately, many of the numerical examples incorporate units such as mol/l and cm^2/s. Although electrochemical science has resisted the comprehensive adoption of SI units because of historical reasons, the utility of mA/cm^2, etc., there are no such extenuating circumstances in electrochemical engineering.

The text is in an adequately presentable camera-ready format, though the price for a hardback book of this length is still high for purchase by UK students; a cheaper softcover edition would be welcome. However, the book is highly recommended for its intended readership.

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Instrumental methods in electrochemistry

Southampton Electrochemistry Group,
Ellis Horwood Ltd, Chichester, 1985
443 pp., £49.50, ISBN 0-85312-875-8

This book is rather like a camel.

Everyone knows that a camel is a horse designed by a committee, but I always think that is rather unfair on camels. After all, the camel is able to survive for several days in the most inhospitable of conditions without sustenance by converting the store of fat in its hump into food and water. Its lips are covered with thick coarse hairs to protect them when eating thorny bushes growing in the sand, while its bushy eyebrows and long lashes stop its eyes from getting full of sand. In addition it can provide for its owner milk for refreshment, hair for cloth and droppings for fuel. All of which, it seems to me, makes the camel a particularly well designed beast.

Now I do not want to try and extend the analogy too far, and certainly it should not be thought that any part of this book is suitable only as fuel, but it does put me in mind of a camel. It has, for instance, been put together by a committee. In this case the committee is drawn from the Southampton Electrochemistry Group and the members who have compiled and edited the text are discretely listed: R. Greef, R. Peat, L. M. Peter, D. Pletcher and J. Robinson. From the titles and subjects one can guess which member of the committee has written, or has at least been largely responsible for, each chapter; aficionados of the idiosyncrasies of each of the Southampton team will have fun looking for more subtle indications of the influence of each author. But whether one is an old hand or a tyro in observing the individual traits of the Southampton team, one cannot help wondering, as with a camel, about the rather lumpy and uneven appearance of this text. For example, the book begins with a very gentle introductory chapter giving an overview of electrochemical concepts but then, instead of moving directly on to an expansion of these concepts in consecutive chapters before dealing with the techniques available for studying electrode proceses, chapters on fundamental and practical aspects alternate. Although I could see this would be a useful arrangement if each chapter on fundamentals tied in closely with the following techniques chapter, this is not really the case so one progresses though the text as though one is moving along the backs of a bactrain, or even dromedarian, train.

Having said this about the overall structure though, one nevertheless finds that, like the camel, the individual parts serve very useful purposes. So the chapters on the more theoretical aspects dealing with electron transfer, the electrical double layer, electrocatalysis and electrocrystallization do not have the thoroughbred qualities of, say, Bard and Faulkner's book. They do, however, provide a pragmatic presentation which may allow users of the text to survive without additional sustenance for some period in practical environments away from the oases of specialized research groups. In addition the chapters on techniques covering steady state and potential step methods, convective diffusion systems, potential sweep methods and cyclic voltammetry, a.c. methods and spectroelectrochemistry are also nicely designed to allow the working electrochemist to understand experimental results in terms of physical parameters without having a sandstorm of theory obscuring his vision. In this context the final chapter on the design of electrochemical experiments is especially useful and should allow the beginner to chew over even thorny practical problems without too much pain.

Whether the dedicated and committed electrochemist decides to buy this book will depend on whether he feels he needs to add to his electrochemical menagerie, but if he does decide to spend £50 for this text then we should beware. Any young electrochemist or non-specialist in his group will undoubtedly find that the text will provide as valuable a service as most camels give to their masters. And having lent my review copy to a new research student and seen it disappear into the laboratory, I am reminded of an old Arab proverb: 'If the camel once gets its nose in the tent, its body will soon follow'. Mine is clearly making itself at home!

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