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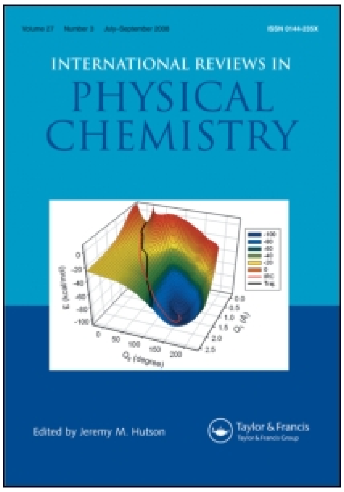

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# Book Reviews

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# BOOK REVIEWS

C. J. Ballhausen. *Molecular Electronic Structures of Transition Metal Complexes.* New York: McGraw-Hill, 1979. 207 pp. ISBN 0-07-003495-8.

To all intellectual disciplines, and in the lifetime of scientific theories, comes a moment of reflection, when the power and limits of the theory can be seen, the assumptions behind its derivations assessed and the body of knowledge correlated by the theory is put into perspective. Professor Ballhausen's book has the object of supplying just such a perspective on the electronic states and optical excitations in transition metal complexes from the vantage point of molecular orbital theory which, he rightly says, is the only model capable of giving a consistent picture of all the phenomena observed in the field. In this, there is an interesting contrast with Professor Ballhausen's earlier book *Introduction to Ligand Field Theory* (1963) which gave greater emphasis to crystal and ligand field theory in covering roughly the same territory of experimental observables. What has happened in the meantime? First of all, the excited states of many more inorganic complexes have been subjected to very close scrutiny by high-resolution absorption spectroscopy using linearly polarized light and low temperatures. Added to this have been new techniques, such as magnetic circular dichroism, which have given much deeper insight into the angular momentum properties of excited states and how they are influenced by vibrational-electronic interactions. Thus we now have data on molecular transition metal complexes going far beyond the physicists' paradigm cases of ruby, $KMnF_3$, etc. The types of excited state which have been studied have also widened greatly. In the early 1960s charge-transfer states were largely 'terra incognita' as far as precise and unambiguous assignments were concerned. Above all, though, our views about the electronic structures of inorganic molecules have been coloured by the advent of photoelectron spectroscopy.

Many of the consequences of these new experimental perspectives are evident in the way Professor Ballhausen approaches his subject in 1980. Considering his own personal interests it is no surprise to see vibrational-electronic interactions playing an important part in the exposition, though inorganic chemists might be startled to find thorough accounts of the Born-Oppenheimer and adiabatic approximations occupying the first half-dozen pages of the book. The reasoning behind it is clear: to open the way for a discussion of electronic states *per se.* As I have already said, this is developed exclusively from a molecular orbital viewpoint, including elegant descriptions of ground-state magnetic behaviour, such as the significance of orbital reduction factors and the origins of the exchange interaction in dimeric molecules. However, it is excited states and electronic transitions that get the largest share of attention. I was sorry not to see a larger number of experimental examples discussed in detail, because clear careful analysis of particular cases is something Professor Ballhausen excels at. Also, given its importance in the wider context of molecular electronic structure, it is a pity that the theory and results of photoelectron spectroscopy get so little space; many of the points made in abstract about vibronic interactions, molecular spin-orbit coupling, etc. find beautiful examples from that field. The style of the book is spare: it is not easily read, but its appeal comes from observing a master in action. Nevertheless, it has an elegiac air and one feels that with it, a chapter of theoretical inorganic chemistry has closed.

P. Day

R. S. Berry, S. A. Rice and J. Ross. *Physical Chemistry.* New York: John Wiley & Sons, 1980. 1320 pp. $41.25. ISBN 0 471 04829 1.

Physical chemistry covers such a wide area that it means different things to different people. The subject is enjoying a period of rejuvenation, following fertilization through its overlap with physics and with biology. It should be challenging and exciting to learn, but frequently we hear complaints from students that it is dull and the least interesting part of chemistry. So the appearance of an important new textbook is to be welcomed. The three authors are very distinguished scientists—each is a person to whom we could look for leadership in science. The preface states 'Our goal is the presentation of the three major areas of physical chemistry: molecular structure, the equilibrium properties of systems, and the kinetics of transformations of systems. The theoretical foundations of these subjects are, respectively, quantum mechanics, thermodynamics and equilibrium statistical mechanics, and chemical kinetics and kinetic theory. These theories, firmly based on experimental findings, constitute the structure required for the understanding of past accomplishments and a basis for recognition and development of significant new areas in physical chemistry. ... Our approach aims toward depth of understanding of fundamentals.' The book is primarily intended for use by undergraduates in North American Universities and Colleges, with the more specialized topics being appropriate for the first year of graduate study.

Part I, entitled 'The Structure of Matter', consists of 11 chapters and 474 pages. It covers quantum mechanics, atomic and molecular structure, intermolecular forces and the structure of solids. Part II, entitled 'Matter in Equilibrium: Statistical Mechanics and Thermodynamics', consists of 15 chapters and 537 pages, covers classical and statistical thermodynamics, the properties of liquids and solutions and critical phenomena. Part III, entitled 'Physical and Chemical Kinetics', consists of 5 chapters and 236 pages. Each chapter is followed by a list of suggestions for further reading and about 20 problems.

The book will make an important contribution to the teaching of physical chemistry. It is scholarly and clear and sets new standards for the presentation of some of the principles of theoretical chemistry in an undergraduate textbook. Students will find the going tough in many parts, but the lead is strong, and there are helpful suggestions for extra reading. The more advanced sections of the book are printed in smaller type on shaded paper; these can be omitted without breaking the flow from chapter to chapter. The accuracy is generally high, but there are three mistakes in equation (4.32), the magnetic field $H$ is wrongly stated on p. 167 to be independent of the presence of matter, calcite is erroneously said to be chiral (p. 387), a molecule is given four—instead of five—independent quadrupole moments on p. 409, the dipole moment of HD is given as $10^{-5}$ D instead of $10^{-4}$ D on p. 411, and torr should be Torr throughout.

It is inevitable that, in a book devoted to such a broad subject, there will be topics that you or I might consider important that are not covered. There is scarcely any discussion of experimental techniques, colloid science, biophysical chemistry, optics, dielectrics, surface chemistry, and group theory. The authors of this excellent book have chosen to emphasize theoretical principles, and this they have done very successfully. The approach will suit mathematically gifted students—and their teachers—but it may not appeal to the large numbers who favour the empirical approach.

The printing, binding and price are reasonable. The mass (2.65 kg) makes it less portable than it might have been but is also available in three separate volumes.

A. D. Buckingham

Ian M. Campbell. *Reaction Kinetics.* London: International Textbook Company, 1980. 163 pp. £13.50 (cased). ISBN 0 700 20275 7 £6.75 (limp).

This treatment of reaction kinetics provides a comprehensive examples course, progressing from a standard appropriate to first year university courses in the early chapters, to more difficult exercises, some suitable for final year students, later in the book. In the main part of the work, each problem is followed by a detailed solution and discussion. Additonal exercises, with answers only, are included in a final chapter. The problems are all taken from the literature and are mostly post 1970; it has required a very considerable effort on the part of the author to discover the material and to organize it into book form.

The examples relate to the gas and liquid phases, and encompass rate laws, reversible and consecutive reactions, complex mechanisms, polymerisation and chain processes, unimolecular reactions, the cage effect and diffusion control, transition state theory and effects of hydrostatic pressure and ionic strength, catalysis, photochemistry, radiolysis, and electrode kinetics. Advanced topics in kinetics, such as application of RRKM theory and molecular beam scattering, are not covered, and essentially it is an undergraduate text.

The exercises should be of considerable value to students, supervisors and lecturers. There is a need for such a set of worked examples, which is not available in other texts. It is clearly printed with an attractive page layout.

A. B. Callear

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F. Wilkinson. *Chemical Kinetics and Reaction Mechanisms.* Wokingham: Van Nostrand Reinhold Co Ltd, 1980, 346 pp. £15.00 (cased). ISBN 0 442 30248 7. £7.50 (pbk). ISBN 0 442 30249 5.

This book is designed as an undergraduate text on chemical kinetics. It is therefore to be expected that much of the material is also to be found in other books on chemical kinetics and on Physical Chemistry in general. Whilst there are the standard treatments of rate equations, physical and chemical analyses leading to kinetic results, order, mechanism and steady-state analyses, the book is wide-ranging and includes consideration of topics such as solution and gas-phase kinetics, chain reactions, photochemistry, oxidation, polymerisation and heterogeneous catalysis. Problems are given at the end of each chapter together with worked solutions. The theory is at a level an undergraduate could cope with, though of varying degrees of sophistication. The discussion of degeneracy in the context of the Boltzmann distribution is, in my view, misleading The book contains the standard diagrams for a model potential-energy surface but the reader is simply given the London equation as an explanation for this. I suggest that it would have been worthwhile to show that, with the Morse parameters for the relevant diatomic molecules and a simple approximation that leads to estimates of the Coulombic and exchange energies, an undergraduate could, in a few hours, construct a crude potential energy diagram for a reaction of the type $A + BC = AB + C$. However, overall, the book is well balanced and achieves its aim as a text for teaching chemical kinetics.

Whilst the choice of material from a subject as large as chemical kinetics must be limited, there remains the question as to whether the undergraduate might have been taken somewhat closer to the frontier of the subject. See, for example, the limited treatment given to modern methods. Some of the space allocated to stationary-state analyses might have been employed for a fuller consideration of the determination of rate data from flow-discharge and time-resolved methods which have made major contributions to the study of fundamental rate processes. Some indication might have been given in the description of the shock tube for the determination of dissociation rates at high temperatures. Whilst I found the treatment of the rotating sector somewhat disappointing from the viewpoint of determining the lifetime of a free radical and translating that into kinetic data, it could have been pointed out that this method is the precursor of the molecular modulation technique, now an important kinetic tool. In describing the pioneering work—in which the author himself shared—on the study of singlet and triplet states of large organic molecules by flash photolysis, there could have been reference to recent developments from the Laboratories of workers such as Rentzepis and Eisenthal to give the undergraduate a glimpse of what can now be achieved by time-resolved studies in solution. Apart from indicating that a sister technique of flash photolysis is pulse radiolysis, the book does not contain any material on the large area of radiation chemistry. Mention could have been given of the work of Dainton and coworkers on the chemistry of the electron, particularly as it is amenable to the primary kinetic salt analysis given in the book. Some description is given of cool flames but the author might have mentioned the general class of oscillating reactions. Too often, the image of chemical kinetics suffers from being simply an undergraduate course requirement; modern chemical kinetics is an exciting, intellectually interesting and developing branch of physical science.

David Husain