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THEORETICA CHIMICA ACTA

Book Reviews

S. Fraga, J. Karwowski, K. M. S. Saxena: Handbook of Atomic Data. Amsterdam and New York: Elsevier Scientific Publishing Company 1976, X + 554 pp., price: US$ 49.75 (Dfl. 129.00)

This book is a sizable compendium containing a big wealth of tabulated data on atoms and ions. When writing about such a book, the reviewer should above all tell the readers what may be found in it.

All the data contained in the book have been produced using a numerical HF-process. Apart from the total energies, the book contains the different relativistic energy contributions, electron affinities, and ionisation potentials; all the magnetic coupling constants, electrical dipolepolarizabilities, oscillator strengths, magnetic susceptibilities, Landé-factors, a number of radial integrals (which may be useful), and different $\langle r^n \rangle$-values; this enumeration describes the largest part of the contents.

The calculation of the data has been performed on a uniform level; therefore they are comparable among themselves, though not absolutely correctly. To give the reader an indication as to the quality of the figures, the reviewer refers to the polarizabilities of a number of atoms on which he can judge well enough at the present time. For Li, Be, N, Ne, Table VI gives (after conversion to a.u.) 107.69, 52.43, 6.748, and 2.632 a.u., whereas the best calculations known so far (by J. Werner and W. Meyer) yield the following HF-values (without relativistic correction): 170.3, 45.63, 7.365, and 2.368[1].

It should be noted that the authors have not included experimental or other theoretical figures in their work. However, this would perhaps have gone beyond the frame of the book.

Seen on the whole, the book is certainly useful to those seeking orientational values of the kind and nature tabulated here.

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[1] These values can be considered as reliable inasmuch as they permit, after inclusion of correlation, a reproduction of the experimental values to about 1% error only.

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A. T. Balaban (Editor): Chemical Applications of Graph Theory. London: Academic Press 1976. 389 pp., price: £14.50

Hardly any mathematical discipline is so close to the ideas of chemistry as graph theory. Its applications were attempted in practically all fields of chemistry, some of which many years ago. Nevertheless, this is the first book providing a fairly complete review of both the "classical" results and contemporary research. Among those few topics which are not included in the monograph, the recent use of graph theory in chemical kinetics should be noted.

The book consists of two introductory chapters followed by nine review articles, written by prominent specialists. The first chapter "Early history of the interplay between graph theory and chemistry" (by A. T. Balaban) may be a stimulating reading-piece to every chemist. The inexperienced readers are likely to become disappointed with a laconic, only five pages long "Exposition of graph theory" (by F. Harary). But almost all graph-theoretical notions necessary for reading the book can be found on these few pages.

The following three chapters (by F. Harary, E. M. Palmer, R. W. Robinson and R. C. Read; R. C. Read; and A. T. Balaban) present techniques for the enumeration of various chemical compounds, based on Pólya's theory. Since the difficult mathematical manipulations of Pólya's theory are jumped over and instead of them numerous chemically oriented examples are given, this part of the book will help chemists to better understand the enumeration of chemical species.

Chapter 6 "Metric spaces and graphs representing the logical structure of chemistry" (by J. Dugundji, P. Gillespie, D. Marquarding, I. Ugi and F. Ramirez) deals with problems which go far beyond the scope of graph theory. This is an excellent and exhaustive review of the investigations on the logical (i.e. mathematical) foundation of the basic concepts of chemistry, especially of stereochemistry.

The remaining five articles cover a surprising variety of fields of application of graph theory – quantum chemistry (D. H. Rouvray), intermolecular interactions (J. Brocas), organometallic chemistry (M. Gielen), polymer science (M. Gordon and W. B. Temple) and computer representation of structures and reactions in chemical documentation (J.-E. Dubois). Especially attractive is the term "graph-like state of matter" (introduced by M. Gordon), by which it is indicated that the behaviour of certain substances is excellently described by means of the mathematical formalism of graph theory.

Finally, the optimistic foreword of V. Prelog is also to be mentioned.

The edition of this comprehensive monograph is certainly an important date in the long history of chemical applications of graph theory.

I. Gutman

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H. Eyring, D. Henderson (Eds.): Theoretical Chemistry, Advances and Perspectives, Volume 2. New York–London: Academic Press 1976. 298 pp., price: US$ 30.00 (£18.30)

This volume contains three contributions which are best reviewed independently.

A. T. Amos and R. J. Crispin: Calculation of Intermolecular Forces, 66 pp.

The authors concentrate mainly on the treatment of intermolecular forces between larger molecules, especially saturated and conjugated hydrocarbons.

Following the first two introductory chapters (introduction, perturbation theory, polarization expansion, exchange contributions) roughly one half of the paper deals with the explanation of the nature of the various contributions to intermolecular forces (Chapter III). Since the authors have in mind especially the application to larger molecules, they can avoid the discussion of complicated and controversial aspects of the theory and concentrate on Coulomb, induction and exchange terms in the lowest order of perturbation theory. The remaining chapters IV and V explain the concept of localized charge distributions and its application in the approximate calculation of intermolecular forces between hydrocarbons.

The presentation is clear and concise throughout. This article will be useful for those interested in a first introduction into the field and those especially interested in hydrocarbons. The bibliography seems to be up to date and includes even topics that are mentioned only briefly. In my opinion the paper could still have been improved by inclusion of a short discussion of recent sophisticated *ab initio* results for intermolecular potential curves (e.g. HF–HF, H_2O–H_2O etc.) and their analysis in terms of perturbation theoretical terms, which demonstrate the usefulness and the serious drawbacks of such simplified treatments.

M. L. Glasser: The Electron Gas in a Magnetic Field: Nonrelativistic Ground State Properties, 65 pp.

Since this article probably is of not too great interest for the reader of this journal, I just give a brief description. The paper is concerned with thermodynamic properties, particularly the Gibbs thermodynamic potential, of a degenerate Fermi gas in magnetic fields. The results are of direct interest in the treatment of white dwarfs, neutron stars or doped semiconductors. The author gives a thorough derivation (roughly 60% of the paper is covered by formulae) of mostly recent results, treating the problem on the Hartree-Fock level and with inclusion of correlation effects within random phase approximation. The special cases of weak, intermediate, and high field strength are discussed on the respective levels.

J. Paldus: Many-Electron Correlation Problem: A Group Theoretical Approach, 168 pp.

The basic problem considered in this article is the construction of pure spin states (eigenfunctions of S^2) from Slater determinants and the evaluation of matrix elements between these functions. It is shown how this may conveniently be done by application of the theory of representations of $U(n)$ (group of unitary $n \times n$ matrices) if the Gelfand-Tsetlin canonical basis (which spans an irreducible representation of $U(n)$) is used for this purpose. The author further achieves a substantial simplification of the general theory, leading to find results which are formulated in terms of a rather simple and appealing pattern calculus.

I have enjoyed reading this article and to share the author's enthusiasm on the subject. Despite this I would like to add some comments. The paper is rather long and many details are discussed in a much broader way than needed. The introduction to Lie groups and their representations covers ~30 pages.

This part is probably of no help for those not already familiar with this field. Since only $U(n)$ is needed, it would have been better to concentrate on these rather simple groups and then discuss some aspects in more detail, e.g. the connection between a Lie group and the corresponding Lie algebra. The text occasionally contains statements like "it can be shown" without explicit references (which are quoted, however, in introductions of respective chapters), which is inconvenient for the interested reader. Similar criticism applies to other chapters.

The pattern calculus is explained after ~ 80 pages, the applications after ~ 110 pages. It is not possible, however, to read only these parts of particular interest for applications since the definitions and results needed are scattered over the whole text.

The author expresses his hope (p. 140) that ". . . (the) formalism presented . . . will become a standard tool in atomic and molecular electronic structure calculations . . .". For this purpose I would have preferred a "streamlined" treatment which concentrates on the essentials.

Concerning the prospects of Paldus' approach I fully agree with the author (p. 211) that "this formalism may in turn be useful for building efficient algorithmus for computer implementation . . . or for a direct handling of small test problems".

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J. F. Clarke, M. McChesney: Dynamics of Relaxing Gases. London and Boston: Butterworths 1976. 576 pages, price: £25.00

The studies of physico-chemical processes in gases called forth the creation of the molecular-kinetic theory even in the past century. However, the interest to various aspects of these problems keeps increasing. This is connected, first of all, with applied problems, such as the differential separation of isotopes, gas behaviour on supersonic streamlining of bodies, upper atmosphere structure, gas lasers. The behaviour of gases is now a subject of quite independent sciences: of gas dynamics, chemical kinetics, physics of atom-molecule collisions. The development of these sciences, both deeper and in scope, has gone so far that specialists concerned with one science are almost unable to be in the know of others and to use the relevant information. This is also true for specialists in gas dynamics. Thus, a book treating systematically the gas dynamics of many-component systems with internal degrees of freedom, in parallel with the physics of atom-molecule collisions and with chemical kinetics, is extremely useful.

The book represents a successful guideline of such a type. It is an essentially improved edition of the "Dynamics of Real Gases" published by the same authors in 1964. It is, in fact, rewritten anew, since it involves the most important results obtained in the ten past years, particularly in the field of atom-molecule collisions and nonequilibrium processes in gases. At the same time a considerable amount of outdated information has been dropped, as well as the educational matter that can be found in routine handbooks. All radiation problems are also left aside.

The first chapter treats the Boltzmann equation for a rarefied multicomponent gas with internal degrees of freedom. Relevant macroscopic transport equations are derived. A great merit of treatment is the detailed discussion of internal degrees of freedom in various transport processes. In particular, the discrepancies connected with determination of the thermal conductivity coefficient of gases with internal degrees of freedom are given an explanation. Finally, a simple model of relaxing gas is proposed on the basis of the general equations derived. The dynamics of a gas with one internal degree of freedom, slowly exchanging energy with the translational degrees, and a mixture of gases are treated in terms of this model.

Gas dynamics problems are the subject of chapter 2. A survey of the analytical theory of the relaxing gas flow model, the propagation of sound in an idealized dissociating and relaxing gas are considered in this chapter. The use of acoustic approximation in describing the relaxing gas flows is treated more extensively than before. The matter concerning nonlinear flows, the theories of characteristics and of simple waves are, in fact, completely rewritten. The theory of shock waves is given on a much wider scale: a traditional description using the Hugoniot curve is followed by detailed analysis of shock wave structures. The effect of relaxation processes in waves with partial and complete dispersion is considered. A description of shock wave structures allowing for transport phenomena is given. The introduction of equivalent bulk viscosity is well-founded, and the restrictions of the continual approach to the theory of shock waves are defined.

In the section on quasi-unidimensional flows of particular interest are the concepts of "sudden freezing" of gas at the nozzle outlet, and the comparison of results obtained in terms of the approximation used with those yielded by more strict analysis.

The methods of calculating cross sections for elementary energy transfer processes are discussed in chapter 3. The rapidly developing theory of such processes has been treated by now in bulky monographs. However, the use of original papers and monographs dealing with relevant problems could appear difficult for specialists in gas dynamics who might be not quite familiar with the quantum theory of

scattering. The authors of the book succeeded in giving a sufficiently simple and clear treatment of the basic concepts concerning the theory of inelastic collisions. The treatment uses colinear collisions of a structureless atom with a diatomic molecule. The model avoids cumbersome complications which would be caused by the anisotropic part of the three-dimensional potential, and at the same time permits describing the basic approximations used in solving the problem of inelastic collisions. The quantum and semi-classical approximations are used in the distorted wave method, and the Massey parameter is introduced. The applicability of various approximations is illustrated by comparison of the results obtained with exact numerical results reported for some problems. Another advantage of the chosen approach is that the model of colinear collision of an atom with a diatomic molecule is taken as basic in all theoretical calculations of elementary vibrational and translational energy exchange processes, which is very helpful in describing the dynamics of relaxing gases.

The chapter on vibrational relaxation of diatomic molecules is also practically new. It had to be rewritten, as within the past ten years basically new results were obtained in this field, the accuracy of measurements greatly increased, the number of subjects investigated became much larger.

Just as in the first book, the treatment deals almost entirely with processes in shock waves and in supersonic flows. A short description of relaxation measurements in shock waves is followed by the kinetics of vibrational relaxation described by a set of kinetic equations for populations of the vibrational levels of harmonic and anharmonic oscillators in a monoatomic inert heat bath and in the parent gas.

The role of V–V exchange in the relaxation of vibrational energy of harmonic and anharmonic oscillators is treated more systematically than in the first book.

The book contains recent results concerning quasi-stationary distributions over vibrational levels of anharmonic oscillators for the case when the stored vibrational energy is considerably in excess over its equilibrium value. This is known at present as the Treanor distribution. The authors give the simple original version of the Treanor distribution without correction for the effect of V–T processes on high vibrational levels. The results of numerical solutions of equations for the anharmonic oscillator populations are used in considering the rate of vibrational relaxation at a fast expansion in the nozzle.

The last chapter 5 deals with kinetics of chemical reactions involving diatomic molecules and atoms: the dissociation of molecules and three-body recombination of atoms, and the bimolecular exchange reactions. The Rice dissociation and recombination theories, and the Wigner-Keck variational theory are discussed. Much attention is given to nonequilibrium effects in the dissociation of diatomic molecules, which is of great importance with high temperatures. From critical analysis of the various approaches to the problem the authors infer that the model of stepwise excitation and deactivation widely used at present is scarcely valid for description of nonequilibrium effects.

The theory of exchange reactions is discussed mostly implying that for thermal reactions with an activation barrier 5 to 10 times higher than the mean energy of thermal motion the nonequilibrium effects can be neglected. In this case a good approximation to the equilibrium rate constant is obtained by means of the transition state method which is used in the discussion of the low steric factor origin.

Unfortunately there is no Author Index. The references to Russian publications are incomplete and given up to 1971 only, whereas several useful monographs, probably not available to the authors, have been issued since then in the U.S.S.R.

The book certainly represents a valuable contribution to the field of nonequilibrium kinetics and may be well recommended to all scientists working in this and related fields of physics and chemistry.

E. E. Nikitin

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