15 and 16 (Groups V and VI) resemble those with N or S, respectively, in the participation of the lone pair in an aromatic sextet. This statement, without qualification, is in fact incorrect for P and As.

This book can be strongly recommended for use as a text in a course on heterocyclic chemistry; it is also a convenient source of general information on this field, and the references are well chosen to guide the reader to more complete coverage.

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JA9756376

S0002-7863(97)05637-0

Thermodynamics of Molecular Species. By Ernest Grunwald (Brandeis University, Massachusetts). John Wiley: New York. 1997. xx + 323 pp. $64.95. ISBN 0-471-01254-B.

It is difficult to do justice to this book in a short review, because every chapter is packed with chemical observations, calculations, and conjectures, each of which could itself be the legitimate subject of a separate review. Despite a wide scope, which includes topics from thermodynamics as well as kinetics, Grunwald's book has a simple purpose, and that is to explore the consequences of adding chemical species to the set of thermodynamic variables, which in the case of solutions, consists ordinarily of temperature, pressure, and the mole fractions of chemical components. In quantum mechanical terms, a *species* can be described by the configuration coordinates of a local minimum of the potential energy surface. By contrast, a *component*, as defined by Gibbs, is a substance that can be independently isolated and purified. This definition leaves out, for example, H_3O^+ and OH^-, produced by the spontaneous ionization of water. Nonetheless, many such ionization products, oligomers, isomers, etc., can be detected in liquid solutions by modern spectroscopic methods. Rigorously, the effects of species on reactions should be taken into account by statistical thermodynamics. There are formidable mathematical difficulties in such a program, however, and Grunwald's book explores to what extent these can be circumvented by applying thermodynamics.

On the face of it, the extension of thermodynamics to cover species should lead to an uncontrollable increase in the number of thermodynamic variables. However, because of the existence of chemical equilibria linking the concentrations of components and their descendent species, the consideration of species introduces no new *independent* variables and consequently does not come into conflict with the Gibbs phase rule. Moreover, selection of species need not proceed ad hoc, but as shown by Grunwald, their practical existence is limited by an energy-concentration criterion, which he calls the *stability theorem*.

In the case of two-component solutions, the production of species is logically restricted to solvent−solvent interactions, solvent−solute interactions, and solute−solute interactions. As concrete examples of these three cases, the book analyzes the isosbestic point in the Raman spectrum of liquid water, the effect of aprotic solutes on the dielectric constant of liquid carboxylic acid solvents, and the dimerization of acetic acid in liquid benzene, respectively.

In addition to the *stability theorem*, the basic concepts and results of the book are codified in more than a dozen other simply stated and clearly derived theorems. Some of these are obviously general and profound. One is called the *tolerance theorem*. This theorem depends on the concept of molar strain, which refers to the extent of reaction, and the concept of molar stress, which refers to the derivative of the total free energy with respect to the strain. Inter alia, one is reminded that in chemical kinetics the law of mass action is an expression relating the strain rate to the stress (Castellan, G. W. *Ber. Bunsen-Ges.* **1963**, *67*, 898. Haase, R. *Z. Phys. Chem. (NF)* **1987**, *153*, 217). Since the free energy has a minimum at equilibrium, the energy effects of strain errors associated with any given model show up only in second order. After reminding us that one of the connections between kinetics and thermodynamics is transition state theory, Grunwald suggests that the tolerance theorem is behind the surprising effectiveness of empirical reactivity correlations such as Hammett plots and the Brønsted catalysis law.

Although not a textbook (there are no homework problems, for example), Grunwald's monograph can be easily read by anyone having a firm foundation in undergraduate physical chemistry. Certain terminology is particularly efficacious in this regard. For example, elementary textbooks often refer to partial derivatives such as $(\partial f/\partial x)_y$ as the "partial derivative of f with respect to x with y constant". Taken literally, this implies that when $(\partial f/\partial x)_y$ is subsequently differentiated with respect to y, the resulting second partial derivative $(\partial^2 f/\partial y \partial x)$ should be zero. Grunwald neatly avoids this confusion by declaring that, in $(\partial f/\partial x)_y$, x is the "active" variable, while y is the "inactive" variable. The implications of such thermodynamic derivatives are investigated rather thoroughly in the book. Indeed, several chapters consider the difference between thermodynamic derivatives calculated with molar strain inactive as opposed to molar stress inactive. The difference terms, called "molar shifts" are often small, but can be important in special cases.

Although not comprehensive of all of chemical thermodynamics, this book is a *must* for chemists interested in solution phase molecular interactions. The latter chapters concentrate on analyzing, for example, hard sphere and potential energy solvent cages, environmental isomers, solvation in dilute solutions, and the thermodynamics of ions in aqueous solutions. Beyond its emphasis on the solution phase, however, Grunwald's book describes a general system of thermodynamics, which should make it of interest to all chemists. If the book goes through subsequent editions, it may well become a classic of the chemical literature.

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JA9755018

S0002-7863(97)05501-7

Ion Properties. By Yizhak Marcus (Hebrew University of Jerusalem). Marcel Dekker: New York, Basel, Hong Kong. 1997. iv + 259 pp. $135.00. ISBN 0-8247-0011-2.

The book *Ion Properties* by Yizhak Marcus is a thorough compilation of numerical data on ion properties. The breadth of the data assures that this book will be of significant interest to biologists, chemists, and physicists alike. This reviewer found the book much more complete and easier to use than, for example, the *CRC Handbook of Chemistry*. A particular strong point of the book is that it comes with a computer disk for even easier access to the researcher's data of interest (the database is created by Microsoft Access Version 2.0 for Windows). Furthermore, the data in the book is timely, the result of a "systematic" literature search through the end of 1994, but there are many references with later dates also. The author also clearly summarizes the methods and equations utilized to obtain the particular quantities of interest in each subject area before he begins to tabulate data. Finally, the author thoughtfully includes the CAS number, the Chemical Abstract name, a general name (if different from the Chemical Abstract name), and the formula for each ion.

The data is grouped by a general subject heading into eighteen chapters. Just a few of the subject areas that are covered include ionization potentials, electron affinities, ion radii, magnetic susceptibility, polarizability, electrode potentials, ion transport, hydration numbers, coordination properties, and ion−solvent properties. A particularly complete subject area that is covered is the thermodynamic properties of both isolated and hydrated ions, with data tabulated for heat capacities, enthalpies, Gibbs free energies, and entropies.

A word of warning to specialists is that the book is focused primarily on solution chemistry. Therefore, although there is still an impressive amount of data on ions in gas and solid phases, experts in these areas will find that coverage is less complete. Also, the book is more complete for aqueous data than for nonaqueous solvents. Most researchers, however, will find this book a very useful place to begin a literature search for ion properties.

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JA975635L

S0002-7863(97)05635-7