range could, providing the resolution problem is minimized, outline the potential energy surface of PF_5. Another, possibly better, approach to an analysis of the energy surface is through molecular beam studies. In the solution state, asymmetric solvation may favor the C_{4v} state for PF_5; the stable adducts derived from PF_5 and strong donor molecules[24] represent the extreme case (actually octahedral structures). In the crystalline state, packing forces or intermolecular P–F–P interactions may lower the C_{4v} state relative to D_{3h}. A single crystal X-ray study of PF_5 should be made.

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(24) E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1962).

Book Review

Fused Salts. Edited by BENSON ROSS SUNDHEIM, Department of Chemistry, New York University. McGraw-Hill Book Co., Inc., 330 West 42 St., New York, N. Y. 1964. ix + 435 pp. 14.5 × 22.5 cm. $18.50.

The proliferation of research with and on fused salts in recent years has made the appearance of a second book on the subject welcome. Before the publication of this volume (and "Molten Salt Chemistry," edited by M. Blander, Interscience Publishers, New York, N. Y., 1964) the only compilations of research in the field were a few scattered review articles and published proceedings of symposia. Since fused salt research has many aspects ranging from the most highly theoretical to the almost entirely technological, an exhaustive treatise on the subject would have been a formidable task and the editor has wisely avoided the attempt. Instead, the book consists of seven independent essays on seven aspects of fused salt research. Each chapter is intended to be a critical review, rather than a compilation of references, by authors who have made original contributions in the fields on which they write.

The first chapter, "Structural Aspects of Ionic Liquids," is by H. Bloom and J. O'M. Bockris. The authors discuss the various conceptual models of ionic liquids—the quasi-lattice, hole, crystallite, polyhedral hole, liquid free-volume, and significant structure models. Attempts to evaluate the distribution function from intermolecular force laws are dismissed as having given little indication of the nature of a liquid. Transport properties are discussed briefly and a qualitative comparison is given of predictions from various models of the volume change on fusion, entropy of expansion, and diffusion parameters. The remainder of the chapter deals largely with the evidence for the existence of complex species in ionic melts from Raman spectra, conductance, viscosity, surface tension, thermodynamic activity, ultraviolet spectra, and potential–time transients at electrodes.

The longest chapter of the book is by T. Førland on "Thermodynamic Properties of Fused Salt Systems." Following a discussion of the fusion process, in relation to disorder in solids, and a brief discussion of theories of the liquid state, the author presents derivations of classical and statistical thermodynamic equations for binary fused salt mixtures and reciprocal salt mixtures, including mixtures of ions with different numbers of charges. Brief mention is made of the formation of complex species in fused salt mixtures. A section on experimental methods for the determination of thermodynamic properties, and thermodynamic calculations associated with the methods, follows. Phase diagrams are treated here, but no attempt is made to present a systematic compilation of the multitude of types of phase diagrams found for multicomponent salt systems. This section contains diagrams of apparatus used for filtration, cryoscopic measurements, electromotive force measurements, calorimetry, and measurements of surface tension and density. The final section is a discussion of thermodynamic data for one- and two-component systems, reciprocal mixtures, metal–slag equilibria, complex formation, and polyanionic systems, such as silicates, borates, and beryllium fluoride.

B. R. Sundheim has contributed a chapter entitled "Transport Properties of Liquid Electrolytes." In the first section, he develops the phenomenological equations of irreversible thermodynamics for the description of conductance, transference, diffusion, thermoelectricity, and thermal diffusion in fused salts. Experimental methods are described for determining the above transport properties and extensive tables of results are included. The transference numbers reported for pure fused salts are attributed to the properties of the salt alone with little discussion of admonitions to the contrary.[1] Transport results are discussed in terms of statistical mechanical and phenomenological theories of transport.

H. A. Laitinen and R. A. Osteryoung have written "Electrochemistry in Molten Salts." They deal with dynamic rather than static measurements. The equations and some experimental details of chronopotentiometry are outlined, with particular reference to molten salts. The application of chronopotentiometry to the measurement of diffusion coefficients and complex association constants is reviewed. The need for rapid transient techniques in the determination of electrode overpotentials is pointed out. The evaluation of parameters of electrode kinetics is described from impedance measurements, the voltage-step method, the double-pulse method, and the Faradaic-rectification method. Polarography of a number of cations in molten salt solvents with a variety of stationary, rotating, and dipping solid microelectrodes is described, as well as the results obtained at low temperatures (in nitrate mixtures) with dropping electrodes. A good representation of the Russian literature is included.

D. M. Gruen has contributed "Spectroscopy of Transition Metal Ions in Fused Salts," which deals with the electronic spectra of these ions. Following an introductory section on the effect of melting and temperature changes on the ultraviolet absorption spectra of pure salts, Gruen reviews the results of electronic absorption spectra of dilute solutions of 3d, 4f, and 5f ions in fused salt solvents, to which he and his co-workers have contributed significantly. The results are interpreted in terms of the coordination numbers of the ions and the associated crystal field splitting. Experimental methods are not discussed, nor are vibrational spectra reviewed.

J. D. Corbett has contributed "The Solution of Metals in Their Molten Salts." The section on experimental methods is particularly desirable in a chapter on these unusual systems. The most extensive studies have been of the alkali metals and

(1) G. Scatchard, *Ann. Rev. Phys. Chem.*, **14** (1963).

their halides and of cadmium and its halides. As the title of the chapter indicates, there is little information on the metal-rich end of the phase diagram, and the solubilities of metals appear to be confined almost entirely to their own rather than foreign salts. Evidence from various systems is reviewed for the basic models of the solution process—the formation of subhalides or the solution as metal ions and electrons (the electrons being either "free," transferred to energy bands of the salt as a whole, or distributed over a number of neighboring cations). The author does not make the distinction here which other authors have made between "metallic" and "nonmetallic" solutions, based on the effect of dissolution of metal on the electrical conductivity of the solution.

Very little work has been done in the field of "Reaction Kinetics in Fused Salts" (*i.e.*, reaction kinetics in solution as distinct from electrode kinetics), aside from that of F. R. Duke (and his co-workers), who has contributed the final chapter. The author discusses the acid–base properties of the nitryl ion relative to pyrosulfate and dichromate ion, the decomposition of bromate, catalysis by heavy-metal ions, and the chlorate–iodide—iodate–chloride reaction, all in molten alkali nitrates.

The book as a whole succeeds in its aim of giving a good idea of the level of understanding in the field. However, although the editor's preface states that the authors were encouraged to evaluate and comment on the pertinent literature, there are few definitive critical analyses in the book. Since chapters for a book such as this must have been completed at different times, the literature surveys do not all cover the same period. Although many references to 1962 and 1963 work are given, much of the literature beyond 1961 is not covered. For the beginner in the field, a more uniform treatment of experimental methods, perhaps as a separate additional chapter, and a single chapter on theories of fused salts, to reduce the duplication in several chapters, might have been useful. This is a book which beginners in the field can read with profit and which old-timers will need to refer to.

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BOOKS RECEIVED

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