



Solid Forms of Water

Physics and Chemistry of Ice. Papers from a symposium, Ottawa, Canada, Aug. 1972 by E. Whalley; S. J. Jones; L. W. Gold

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the nature of molecular collisions that lead to chemical reactions. However, the difficulties of producing and detecting beams of either neutral or ionized molecules at energies in the range of chemical interest, roughly 0.005 to 5 electron volts, were serious enough to delay the growth of the field until after the successful experiments of Taylor and Datz in 1956 on the reaction $K + HBr \rightarrow KBr + H$. Subsequent work pursued actively in many laboratories showed that the high hopes for the results of molecular scattering experiments could be realized to a considerable extent. Molecular beam studies now provide information of significance in many fields, for example, about transport properties, energy transfer, and chemical kinetics. Now that reliable results are available in quantity from studies using molecular scattering, many people are likely to want to learn how to interpret and use these results, and others will want to start similar studies of their own. This is therefore a suitable time for a comprehensive account of the subject to appear.

Fluendy and Lawley have written the first book devoted to explaining what molecular scattering is, how apparatus is built to study it, how the results are interpreted, and what significance the results may have for related problems in chemistry and physics. It was an ambitious undertaking, and they have carried it out well. The book is for those who care to learn about the details as well as to understand the principles. It has several particularly attractive features. In the sections on scattering theory, the authors emphasize the physical interpretation of the quantities appearing in the equations and lead the reader gently into what is for some a difficult subject. They offer a useful guide for those who may hesitate to go directly to the original literature. Kinematic diagrams, useful to those working with scattering problems but often a source of confusion to those listening to discussions of molecular beam work, are clearly described. There are good discussions of the criteria for the design of apparatus as well as of the sources of noise in experiments. Because greater advances have been made in the study of elastic and reactive scattering, the sections on these subjects are much more extensive than the one on inelastic, but nonreactive, scattering.

Unfortunately, many errors and misprints were overlooked in the proof-

reading. Users of the book will have to be on their guard if they are not to be misled. There are many references throughout the book, but a few more might have been helpful in directing readers interested in extended treatments of some of the topics to the original sources.

The book will be appreciated by chemists working with molecular beams or interested in the results of scattering experiments. It is a significant contribution to physical chemistry.

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Dielectric Systems

Aqueous Dielectrics. J. B. HASTED. Chapman and Hall, London, 1973 (U.S. distributor, Halsted [Wiley], New York). xiv, 302 pp., illus. \$18.50. Studies in Chemical Physics.

The author of this book contributed to the first research in this field using the technology made available by the development of radar, and his laboratory has continued to play a leading role in research on aqueous dielectrics. This account covers a wide field: the dielectric behavior of pure water in the liquid and solid states, of ionic and nonionic aqueous solutions, of biological tissues, of water in the absorbed state, and of fallen snow and other wet materials important in earth science.

Three of the ten chapters are mainly theoretical, and there are extensive theoretical passages in some of the others. The accounts of the numerous theories that have been developed for the molecular interpretation of the dielectric constant and its frequency dependence in the various systems listed above are at a level such that the whole comprises an annotated bibliography covering the period from about 1920 to 1971, with a few references to more recent work. Especially useful is the chapter on the theory of heterogeneous dielectrics.

The dielectric relaxation process well known in water and aqueous solutions has a correlation time τ of about 8 picoseconds in pure water at 25°C. In this book the evidence for a "second relaxation" process in these systems, with a correlation time $\tau' \approx 0.05$ picosecond in pure water at 25°C, is carefully presented. For solutions, how-

ever, the main experimental coefficients are the molal changes in the static dielectric constant and in τ ; for these coefficients there is little critical comparison of data from various sources, and in some cases the newer data seem to be neglected altogether. Most of the tabulations of the molal coefficients that are given are organized for the comparison of the data with various theoretical calculations.

The remaining chapters give the reader a good idea of what dielectric measurements have been made on the various more complicated aqueous systems and the interpretations that have been inspired by the data.

The text reads well, but the book suffers from slipshod editing. Some literature citations are missing, and others are given in duplicate in the same list. There is little correspondence between the order of references in the lists and the order in which they are cited in the text. There are undefined symbols. It also must be remarked that there is substantial duplication of the material in the chapters on dielectric phenomena in Felix Franks's treatise on water, two of which were written by Hasted.

The book is aimed at those in the "sciences where water is important"; the members of this audience can be sure they will find some useful information in it.

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Solid Forms of Water

Physics and Chemistry of Ice. Papers from a symposium, Ottawa, Canada, Aug. 1972. E. WHALLEY, S. J. JONES, and L. W. GOLD, Eds. Royal Society of Canada, Ottawa, 1973. xiv, 404 pp., illus. \$30.

Owing to the shape of its molecules and their capacity to form directed hydrogen bonds, water displays a rich variety of crystal structures. Of course the most familiar is hexagonal ice, but at least ten other solid polymorphs can be formed under suitable experimental conditions. These are joined by a topologically fascinating family of water-molecule networks that appear in hydrate crystals. Properties of all of these forms of solid water were relevant to the international symposium reported in this volume.

The basic principles of molecule arrangements in ordinary ice were stated over 40 years ago by Bernal and Fowler. Most important was the formation at each molecule of a tetrahedral pattern of hydrogen bonds to four nearest neighbors; furthermore, the separate nonlinear molecules remain intact. Pauling amplified this idea in 1935 by pointing out that these "ice rules" still permitted substantial freedom in the orientation of molecules within the tetrahedral network. With suitable modifications, these structural manifestations of water-molecule interactions persist through all the various ice polymorphs and hydrate crystals. That is hardly surprising, since precisely the same intermolecular forces operate in all thermodynamically distinct phases containing water. For the same reason, study of the ices will also inevitably aid in the important task of understanding liquid water and aqueous solutions.

Occasional violations of the Bernal-Fowler-Pauling ice rules give rise to point defects, including vacancies and interstitials, Bjerrum orientational defects, and ionized molecules. These control most kinetic properties for single crystals, such as electrical conduction, dielectric and nuclear magnetic relaxation, sound absorption, and self-diffusion. Distinguishing the separate contributions made by the motion of the various defect types has become clearly desirable, and several papers in this symposium illustrate the effort that is being devoted to that task. General optimism that the contributions will eventually be separated has sprung from the view of ice as a "protonic semiconductor" subject to controlled doping; however, one of the papers in this collection pointedly questions the validity of proton semiconduction. In any event, from reading this book it is clear that precise and controlled experiments with clean interpretations are difficult and that the few available procedures that approach those ideals can be improved.

While the problems of point defects in perfect crystals are themselves challenging, a far broader technical scope is forced on researchers in this field by the demands of meteorology, oceanography, glaciology, and even astronomy. This has led to inclusion in this book of papers devoted to dislocations and plastic flow, properties of nucleation clusters, crystal surface topography, and growth mechanisms. The general impression conveyed is that consider-

able expansion of fundamental knowledge bearing on each of these topics should be encouraged.

Over 60 technical articles appear in this volume. Together with the recorded discussion remarks, they seem to convey a comprehensive view of the status of the field in 1972. The collection offers an implicit invitation and provides a means for qualified outsiders to consider making their own contributions to this interesting subject. Such a prospect is made all the more alluring by tight editing (which has all but eliminated typographical errors) and the attractive appearance of the text. In addition, the editors offer extra deft and graceful touches, including an opening essay on ice as an evocative image in literature and a closing poem entitled "The Ices."

An earlier international symposium on ice was held in Munich in 1968. Surely others will follow. We shall be fortunate if their proceedings are as comprehensive and are reported as effectively as those in Ottawa.

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