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Water and Solute-Water Interactions

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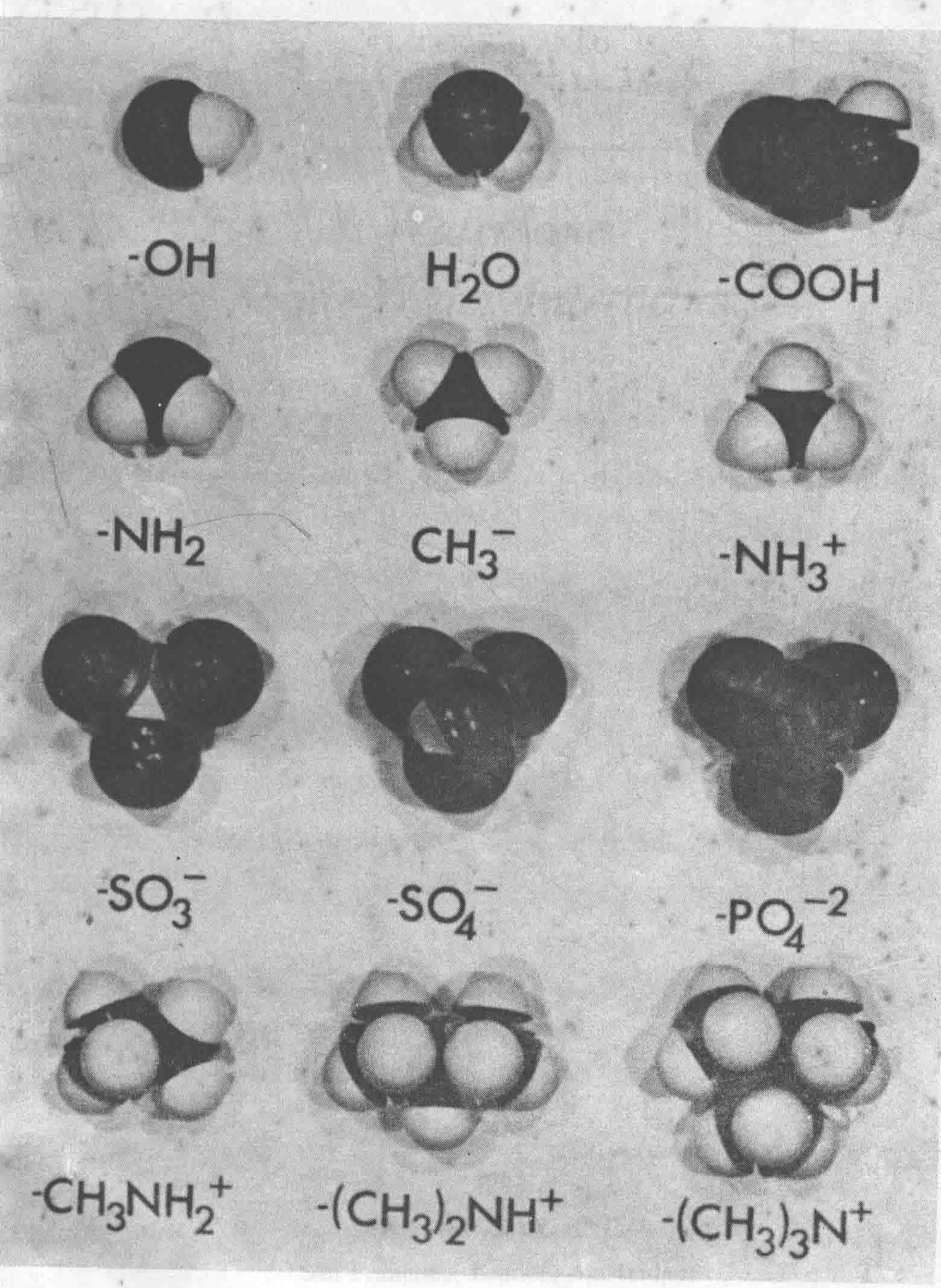
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PREFACE

To lay the groundwork for the development of theories on the structure and functions of biological membranes for a recent monograph (Kavanau, 1964), the author treated extensively many pertinent aspects of molecular and interfacial chemistry. Included in this program was a comprehensive review and discussion of the current theories and status of research in the fields of water structure and water-solute interactions. Because of the general interest of this material for researchers and students in many areas of the physical and chemical sciences, it is reprinted here without modification. References to chapters refer to the complete work, *Structure and Function in Biological Membranes*, Volumes I and II, to be published later this year.

In general, all major viewpoints are presented, with comprehensive literature citations. In many areas several theories leading to more or less similar or to quite dissimilar conclusions are able to coexist, because definitive experimental evidence is not at hand. I have not sought to smooth over the complexities of the problems nor the tangle of the many existing discrepancies. Although this would give a more specious and easily digestible view to the casual reader, it would give a quite misleading one to the researcher and serious student. It is instructive and sobering to be aware of the wide latitude of disagreement that exists over the interpretation of even the most elementary intermolecular phenomena, particularly in aqueous media.

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J. Lee Kavanau

To James L. Van Vliet

CONTENTS

THE STRUCTURE OF ICE

Ordinary ice, ice I (density, 0.924 g/ml; filling factor 0.34), has a highly open centrosymmetric structure (fig. 1) similar to that of the hexagonal form of silica (SiO_2) known as "tridymite" (see Barnes, 1929; Bernal and Fowler, 1933; Pauling, 1935, 1960; Owston, 1958). The oxygen atoms lie in layers, with each layer consisting of a network of open, puckered, hexagonal rings. The oxygen atoms alternately are raised and lowered, each layer being a mirror image of adjacent layers (the structure being in the ABAB···· sequence). Water molecules retain their individuality but participate in four hydrogen bonds. Each oxygen atom is surrounded tetrahedrally at a distance of 2.76A by the four other oxygen atoms to which it is hydrogen-bonded. The hydrogen atoms, however, are distributed asymmetrically, lying on lines connecting adjacent hydrogen-bonded oxygen atoms but closer to one oxygen atom than to the other. Each oxygen atom has two hydrogen atoms near it (the two hydrogen atoms of the molecule) at an estimated distance of about 0.96 to 1.02A (0.958A in the vapor), linked to it by strong bonds, and two farther away (the hydrogen atoms of two neighboring molecules) at an estimated distance of about 1.74 to 1.80A. The unit cell contains four water molecules. This scheme of colinear hydrogen-atom arrangement and hexagonal structure has been confirmed beyond reasonable doubt by neutron diffraction experiments on D_2O ice I (Peterson and Levy, 1957).

Each interstitial region of ice I is bounded by six water molecules at a distance of 2.945A from its center. At the same time each water molecule is the nearest-neighbor of three cavities. The dimensions of the interstitial regions between the coordinated tetrahedra (fig. 1) are greater than the dimensions of the water molecule; Samoilov (1946, 1957b) and Forslind (1952, 1953) propose that each of these regions can accommodate a free, non-associated molecule without greatly disturbing the structural order.

The water molecules in ice I undergo thermal vibrations around their equilibrium positions, the intermolecular movements being both dilational and deformational (Forslind, 1953). The root-mean-square amplitude of vibration of the water molecule (assuming that it vibrates as a single unit) is approximately 0.44A at -10°C (see Owston, 1958). All proton configurations compatible with the conditions mentioned above have nearly the same lattice energy and therefore occur with equal probability, giving a proton-disordered structure (statistically, two "half-hydrogen atoms" lying along each O·····O bond) which does not become ordered on cooling (Pauling, 1935; Wollan, Davidson, and Shull, 1949; Forslind, 1952; Peterson and Levy, 1957). Studies of ice I in an alternating electric field near the melting point show that the proton configurations are highly mobile and vary with time under the influence of thermal fluctuations; the proton configuration "freezes in" at about −183°C (see Bjerrum, 1952; Coulson, 1957).

Apart from the six high-pressure ice polymorphs—ice II and ice III discovered by Tammann (1900) and ices IV, V, VI, and VII discovered by Bridgman (1912, 1935, 1937)—only two other forms of ice are known to exist with certainty: a cubic cristobalite-type structure, ice I*c*, having the same zero-point entropy as ice I (König, 1942, 1944; Honjo, Kitamura, Shimaoka, and Mihama, 1956; Lisgarten and Blackman, 1956; Blackman and Lisgarten, 1957, 1958; Shallcross and Carpenter, 1957; Gränicher, 1958), and an ice of uncertain but probably amorphous structure, "vitreous ice" (Burton and Oliver, 1935; Vegard and Hillesund, 1942).

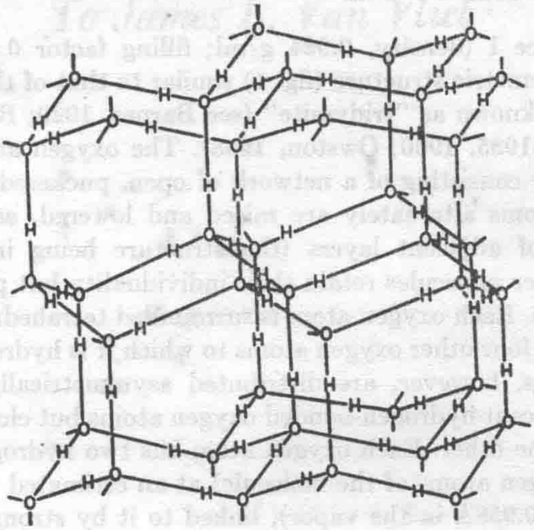

Figure 1. Schematic representation of the crystal structure of ice at low pressure. (After Barnes, 1929.) (Reproduced by courtesy of Drs. G. Némethy and H. A. Scheraga, and the American Institute of Physics from the Journal of Chemical Physics.)

Vitreous ice can be produced only by condensing pure water vapor on a surface maintained below −160°C. It undergoes a partial and irreversible change to ice I*c* at higher temperatures (see Honjo, Kitamura, Shimaoka, and Mihama, 1956; Blackman and Lisgarten, 1958; Dowell and Rinfret, 1960). Although some investigators have assumed that vitreous ice is a glassy form, König (1942) and Vegard and Hillesund (1942) suggest that it is composed of small crystallites. According to Dowell and Rinfret (1960), domains may exist in which there is a tendency toward the same layer structure present in ices I*c* and I, but with random distribution of the molecules within the layers.

Ice I*c* (density, 0.923 g/ml; filling factor, 0.34) also can be formed at low rates of deposition, low pressures, and temperatures of about −140 to −80°C (see Shallcross and Carpenter, 1957; Lonsdale, 1958; Fernández-Morán, 1960) or by heating ices II, III, or V (Bertie, Calvert, and Whalley, 1963). Above −130°C, ice I*c* (and vitreous ice) transforms to ice I at a rate that depends markedly on the thermal history of the sample (König, 1942, 1944; Dowell and Rinfret, 1960; Beaumont, Chihara, and Morrison, 1961; Bertie, Calvert and Whalley, 1963). The latter transition probably was observed first by Dewar (1905). Ice I*c* can be considered to be built up of puckered layers of oxygen atoms identical to those of ice I but with each successive layer shifted half the diameter of a hexagonal ring, leading to the ABCABC····· stacking sequence typical of the diamond cubic system. Another way of viewing the difference is that the three bonds radiating from each of the two oxygen atoms at the ends of a given O·····O axis are "opposed" (eclipsing) in ice I and "staggered" in ice I*c* (as in the eclipsed and staggered conformations of ethane). The unit cell contains eight water molecules (König, 1944); the O·····O distance is 2.75A; the O—H distance is approximately 0.97A; and the protons are disordered as in ice I (Honjo and Shimaoka, 1957). No significant infrared spectroscopic difference can be detected between normal and deuterated ice I, ice I*c*, and vitreous ice (Hornig, White, and Reding, 1958).

A systematic study of the crystal structures of the high-pressure forms of ice has been undertaken in Kamb's laboratory (Kamb and Datta, 1960; Kamb, 1964; see also Lippincott, Weir, and van Valkenburg, 1960; Bertie, Calvert, and Whalley, 1963), the ultimate results of which may advance our understanding of the structure of liquid water and the energetics of the hydrogen bond. The high-pressure polymorphs (ices II to VII) are stable at pressures exceeding about 2,000 atmospheres; they can, however, be studied by X-ray diffraction at atmospheric pressure because they can be maintained metastably at sufficiently low temperatures (Tammann, 1900; McFarlan, 1936).

Ice II (density, 1.17 g/ml) occupies the lowest-temperature portion of the pressure-temperature field investigated by Bridgman and forms only by transformations from other solid phases. It has twelve water molecules in a rhombohedral unit cell with each oxygen atom bound to the four nearest-neighbors at a distance of about 2.80A and having a next-nearest neighbor at 3.24A (Kamb, 1964). It is most remarkable that the protons in ice II appear to be ordered, whereas all other ice polymorphs appear to be proton-disordered (Kamb, 1964).

In ice II a relatively small but significant perturbation of a basic structure (or pseudostructure) in space group R$\bar{3}$c is believed to be caused by long-range ordering of the protons. The pseudostructure contains ice-I-like units built of puckered six-membered rings of water molecules. Apparently there is freedom for the bond angles to deviate markedly from the "ideal" tetrahedral values, so that ice-I-like units can be linked together in a more compact way than in ice I. The hydrogen-bond strain energy, although greater than in ice I, is small enough to be offset by the extra van der Waals-London energy, so that the energy of ice II is only 10 cal/mole greater than that of ice I.

Kamb assumes that the distortion from the pseudostructure occurs in such a way as to bring the O·····O·····O angles presented to the H—O—H groups (donor angles) closer to the angle for which the hydrogen-bond energy is a maximum.[*]

Bridgman's (1912) measurements indicate that the entropy of ice II is 0.77 cal/mole-degree less than that of ice I over the range −75 to −34°C. Kamb's findings suggest (assuming that the difference in lattice-vibrational entropy between ice I and ice II is small) that this measured value is a direct reflection of the entropy of the proton disorder in ice I. One of the potentially most significant findings to emerge from Kamb's analysis is that the strain-energy contribution from the hydrogen-bond acceptor depends primarily upon a deviation from the "accepting plane" that bisects the H—O—H angle of the molecule, rather than upon a deviation from the tetrahedral-bond orientation relative to the accepting water molecule.

Ice III (density, 1.14 g/ml; filling factor 0.44) is dimensionally cubic but symmetrically tetragonal (Kamb and Datta, 1960; Bertie, Calvert, and Whalley, 1963). The arrangement of the oxygen atoms can be interpreted in terms of hydrogen-bonding (Kamb and Datta, 1960), but appreciable deviations from the ideal tetrahedral configuration of the water molecules are present, as in ice II (Kamb, 1963). There are twelve water molecules in the unit cell and each oxygen atom is surrounded by four others at distances of 2.78 to 2.81A. The arrangement of the oxygen atoms is very similar to that of the silicon atoms in keatite, a high-pressure polymorph of SiO_2 discovered by Keat (1954). The latter relationship thus extends the already known structural relationships between the silica and ice polymorphs[†] (ice I-tridymite and ice I*c*-cristobalite).

X-ray powder patterns for ice V have been published by Bertie, Calvert, and Whalley (1963), but the unit cell is not known. Powder data also have been obtained for ice VI but have not been analyzed yet (Kamb and Datta, 1960).

To account for the high dielectric constant of ice I (up to about 100) at low and intermediate frequencies (say at frequencies between 100 and 10,000 cycles / sec at −10 to −2°C), it is necessary to assume that the orientation of the water molecules is changing constantly. Debye (1929) explained the high dielectric constant by the presence of electric dipoles, which frequently turn from one equilibrium position to another under the influence of thermal agitation. Dorsey (1940) calculated the rate of dipole turns per molecule to

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[*] In most hydrates the O·····O·····O angles presented to the water molecules are prevented from adjusting to the angle favored by the water molecules by other steric requirements; thus, the donor O—H bonds deviate by as much as 15 degrees from the O·····O bond. The absence of an ordered arrangement of energetically well-favored angles for H—O—H occupancy may be responsible for the failure of ice I to achieve proton-ordering at low temperatures (Kamb, 1964).

[†] The favorable energetic relationships involving the proton-ordering peculiar to ice II probably are responsible for the fact that ice II has no analogue among the known polymorphs of SiO_2 (Kamb, 1964).

be 8.3×10^5 / sec at 0°C. From the temperature coefficients of dielectric properties, the activation energy for dipole-turning has been calculated to be 13,200 cal / mole (Auty and Cole, 1952).

The mechanism by which the water molecules in ice I become reoriented in an electric field has not been established unequivocally. In an ideal lattice, displacements by proton shifts from one bond to another, no matter how devised, either have improbable energy requirements or lead to no net polarization (see Auty and Cole, 1952). Latimer (1949) suggested that the high dielectric constant of ice might be due to the "atomic polarization" of the proton in the bond. He suggested that dipole reorientation in ice depended upon the jumping of the protons over the potential barrier in the hydrogen bond, rather than upon rotation of the water molecules. However, this method leads to equally serious difficulties with energy requirements and appears to have other shortcomings. Thus, for example, if excitation to the first vibrational level of the stretching mode of an O—H bond is a rate-limiting process (this might logically be a prerequisite to proton-tunneling through and along O—H bonds), the activation energy for D_2O should be only about $\sqrt{2} / 2$ of the value for H_2O (see O'Konski, 1963). Since this is not the case, the dielectric polarization process in ice probably does not involve proton-tunneling. Schellman (1951; see also Schellman and Kautzmann, 1951) proposed that there were missing hydrogen bonds between a few of the oxygen atoms as a result of lattice defects or vacancies and that molecular reorientations through the lattice were made possible by propagation of the missing bonds.

The subsequent model of Bjerrum (1952) accounts for the electrical properties of ice I by postulating the existence of thermal lattice defects of two kinds—ionic and orientational. Ionic lattice defects are formed by the migration of protons from one oxygen atom to another, giving rise to an equal number of H_3O^+ and HO^- ions. Orientational (or valence) lattice defects are formed by the rotation of water molecules through 120° about an $O—H \cdots\cdots O$ axis or, perhaps, by a rotational jump of a proton within the same molecule (Gränicher, 1958). Such a rotation generates one vacant $O \cdots\cdots O$ separation (L-defect) and one doubly occupied $O—H \cdots\cdots H—O$ separation (D-defect) (fig. 2a,b). A subsequent or coupled rotation of the adjacent water molecule into the vacant site separates the D- and L-defects, which migrate in this manner through the crystal.

Two molecules between which there is an L-defect can rotate easily into new positions. Every time one of the molecules rotates, the defect is moved (structural diffusion) and the dipole moment is rotated through 90°. L-defects accordingly might be said to promote dipole-turning (Bjerrum, 1952). The concentration of thermal Bjerrum defects decreases exponentially with decreasing temperature and is calculated to be one per 10^8 hydrogen bonds at 0°C. The concept that the hydrogen configurations are changed only by the diffusion of Bjerrum defects leads to a consistent theory of the electrical, mechanical, and thermal properties of ice.

Dunitz (1963) suggested, however, that the existence of colinear D-defects was unlikely. Thus, the Bjerrum model would imply a separation of only 0.78A between the two hydrogen atoms in the doubly-occupied bond (D-defect). This separation distance would correspond to an enormous (and unrealistic) increase in the mutual repulsion energy (estimated at 60,000 cal / mole) over that for the shortest hydrogen-hydrogen distances known (assuming any reasonable form of the potential energy curve in this region). Moreover, the D-defect must correspond to an energy maximum with respect to the rotation of one or both of the participating water molecules, so that although it might conceivably correspond to a transition state, Dunitz argued that it could not correspond to a stable arrangement of water molecules (see also Cohan, Cotti, Iribarne, and Weissmann, 1962).

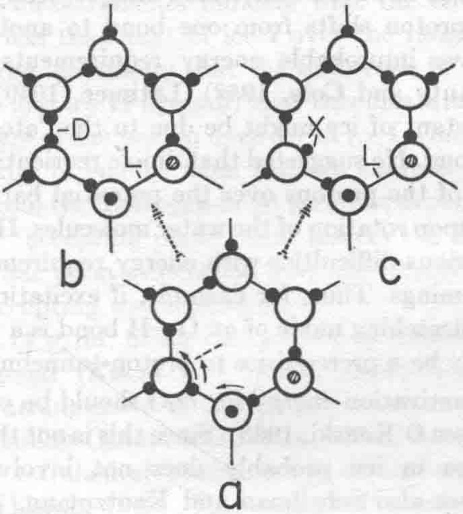

Figure 2. Schematic representation of the formation of a DL (a → b) and an XL (a → c) pair of orientational defects. (After Dunitz, 1963.)

To overcome these shortcomings of the Bjerrum model, Dunitz proposed that a water molecule rotates only 60° about an O—H·····O axis, bringing its second hydrogen atom into a position midway between an O—H·····O and an empty O·····O (L-defect) direction. A subsequent or coupled rotation of the adjacent water molecule through 120° brings its hydrogen atoms into the empty O·····O region (fig. 2a,c). The combination of these two rotations was felt to produce an energetically more reasonable and stable arrangement than a D-defect, one in which the "extra" hydrogen atom is situated symmetrically between two neighboring O·····H—O bonds, being about 1.5A from each of its two nearest-neighbor hydrogen atoms on other molecules. This latter situation, referred to as an "X-defect," is separated from the L-defect, which cannot diffuse back spontaneously.

Once the Dunitz-defect pair has been formed and separated, both kinds of defects can diffuse through the crystal by "jumps" that involve the rotation of water molecules. The X-defects jump by a coupled rotation of two adjacent water molecules through 60°; the L-defects jump by the rotation of one molecule through 120°. A consideration of the activation energies for the diffusion of these defects indicated that the activation energy for the X-defect was three to five times as great as that for the L-defect. Accordingly, Dunitz suggested that the alternating current conductivity of ice arises almost exclusively from molecular rotations associated with the diffusion of the L-defects, the X-defects being present in equal number but being relatively inactive insofar as electrical properties are concerned.

However, Dunitz did not take into account the possibility that relaxational lattice deformations could lower the repulsion and strain energies associated with D-defects. Such relaxation of the lattice might be expected because of the relatively weak bonding in the neighboring H · · · · O bonds (Eisenberg and Coulson, 1963). When the major relaxational changes in bond lengths and bond angles in the neighborhood of a D-defect are taken into account, the total repulsive and strain energy is reduced from about 60,000 cal / mole of the D-defects to only about 5,190 cal / mole. The latter figure includes the repulsive interaction energy of the two hydrogen atoms, the compressional energy of the two O—H bonds, and the bending and compressional energies of the six nearest H—O—H · · · · O bonds (Eisenberg and Coulson, 1963). The energy would be even lower if the six nearest-neighbor oxygen atoms were allowed to relax. It is clear from the analysis of Eisenberg and Coulson that the existence of D-defects cannot be ruled out yet. These workers are preparing a detailed comparison of the total energies of formation of both D- and X-defects.

On the other hand, Bergqvist and Forslind (1962) have revived the view that the reorientations of the over-all molecular dipoles, which are responsible for the high dielectric constant of water and ice, take place almost exclusively by way of simultaneous shifts of the proton positions along the hydrogen bonds without the occurrence of free molecular rotation. The individual shifts are proposed to occur as a sort of chain reaction without the disruption of hydrogen bonds. It is suggested that all orientational processes which depend upon lattice molecules and are associated with the dielectric properties, conductivity, flow, etc., of water or ice depend upon such molecular reorientations (Forslind, 1963). The reduction of the dielectric constant of water by ionic solutes is visualized (Bergqvist and Forslind, 1962) as the result of increased lattice distortion and coupling to solute molecules. It is proposed that these effects reduce the probability of unrestricted simultaneous proton displacements because of the increased number of barriers against the rehybridizations which are necessary for proton exchanges between hydrogen-bonded water molecules. As a result, the dielectric constant becomes reduced with increasing solute concentration.

THE STRUCTURE OF LIQUID WATER

The distinctive structural features of liquid water generally have been ascribed to its partial retention of the tetrahedrally directed hydrogen-bonding involved in the crystalline structure of ice* (see references below)—i.e., as a broken-down form of the ice lattice—but with the length of the O·····H·····O bond increased. Not only are the orientations of the water molecules far from random, but the molecules oscillate torsionally with rather small amplitudes instead of rotating freely. However, free rotation about the axis in the plane of the three nuclei bisecting the H—O—H angle becomes important rather suddenly at about 40°C (see Robinson and Stokes, 1959).

This view of water structure is supported strongly by the results of X-ray scattering experiments and of studies of the infrared and Raman absorption spectra, which indicate that a considerable degree of short-range order and the low coordination characteristic of the tetrahedrally-bonded structure persist in the liquid. Thus, X-ray scattering studies indicate that the average number of nearest-neighbors is 4.4 to 4.6 (probably fluctuating between 4 and 6) and that the average distance between centers is 2.92A. A high concentration of molecules also is found at 4.75 to 4.90A, which is roughly the expected distance (the length of the tetrahedral edge, i.e., $2.92 \times (\frac{8}{3})^{1/2}$) for the next-nearest neighbors if the molecules tend to have a tetrahedral arrangement as in ice (see Morgan and Warren, 1938; Simons, 1939; Finbak and Viervoll, 1943; Gurney, 1953; Brady and Krause, 1957; Brady, 1958; Brady and Romanow, 1960; Danford and Levy, 1962). A distinct maximum at 1.1A is attributed to the closest O—H distance in the water molecule (Danford and Levy, 1962).

Water can be regarded as a particular type of associated liquid in which the association penetrates through the whole volume of the liquid, forming a three-dimensional network, several different configurations of which can coexist simultaneously (see Chadwell, 1927; Bernal and Fowler, 1933; Mikhailov and Syrnikov, 1960). Each of the coexisting configurations corresponds to a characteristic free energy, to characteristic dielectric properties, to a characteristic molecular volume, etc. A change in temperature leads to a change in the relative numbers of molecules associated in each configuration, these shifts accounting for the anomalous properties of water. Most modern theories of water take as a starting point this view that water is a mixture of certain three-dimensional structures.

As useful a guide as these concepts may be to the structure of liquid water, they leave wide latitude in the construction of precise statistical-thermodynamic models.

The "vacant-lattice-point" model. The model of Forslind (1952, 1953) presents the most straightforward departure from the ice I structure and

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* Röntgen (1892) was the first to suggest that there are "ice molecules" in water.

achieves considerable success in accounting for the properties of water on the basis of but few assumptions. The liquid phase is regarded as an essentially crystalline system, closely related to a slightly expanded, idealized ice-I lattice (fig. 3). The structure is very open, with the interstitial spaces between the

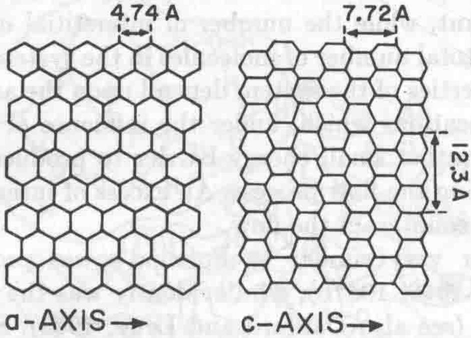

Figure 3. Diagrammatic representation of an ideal water lattice (at 25°C) based upon the ice-I lattice. For a scale molecular model see figure 6. (Reproduced by courtesy of Dr. B. Jacobson.)

groups of molecules in tetrahedral coordination sufficiently large to accommodate free, non-associated molecules without greatly disturbing the structural order. As the temperature of ice is raised, the increasing anharmonicity of the deformational intermolecular vibrations leads to fluctuations in the distribution of the thermal amplitudes, producing localized amplitude peaks that eventually disrupt the weakest bonds. When the thermal amplitudes are sufficient, some of the molecules pass through the faces of the surrounding tetrahedrons and take up interstitial positions.

The resulting lattice defects, each consisting of one vacant lattice point and one interstitial, non-associated molecule (Frenkel defects), increase the anharmonicity of the thermal deformational vibrations of the lattice molecules, greatly enhancing the probabilities of the formation and the propagation of dislocations. Accordingly, the model provides ample opportunities: (1) for molecules to change places; (2) for lone molecules to pass through the faces of the surrounding tetrahedrons to take up interstitial positions (and for their diffusion in lattice interstitial channels); and (3) for lattice defects to diffuse through the lattice, working their way to interfacial boundaries to be annihilated and thus leaving behind lone interstitial molecules (so-called Schottky defects), thereby producing a volume decrease and density increase. The annihilation of the vacant lattice points at the boundaries of the system corresponds to the melting process, the latent heat of fusion of ice being determined by the energy of formation of lone interstitial molecules.

The density increase occurring at the ice-water transition continues until the thermal amplitudes have become sufficiently attenuated by interstitial molecules to prevent the formation of new defects, i.e., until the system has attained thermal equilibrium. The structure of the liquid phase is essentially the same as that of the solid; the chief structural differences are a higher bulk density of the liquid due to the appearance of non-associated interstitial molecules (i.e., new Schottky defects) and an increased number of complete Frenkel defects. In liquid water at 0°C only 9% of the lattice points are computed to be vacant, while the number of interstitial molecules amounts to about 16% of the total number of molecules in the system (Forslind, 1953). The rheological properties of the system depend upon the association of point defects to form dislocations which, under the influence of a shearing stress, will move against a rather small energy barrier to produce the relative displacements constituting the flow process. An excess of interstitial matter will raise the barrier and counteract the flow.

A theory of water very similar to Forslind's was proposed earlier by Samoilov (Samoilov, 1946, 1957b), who evidently was the first to formulate an interstitial model (see also Danford and Levy, 1962). Samoilov also had arrived at the general conclusion that the structure of water (restricted to the short-range order characteristic of liquids) is merely a slightly distorted version of the structure of ice. In his view water molecules which have moved from their equilibrium positions, as a result of the translational movements which become possible on melting, cannot help but pass into neighboring interstitial spaces, which correspond to certain relative potential energy minima. Samoilov proposed that the tetrahedral coordination of ice generally was retained, but that in contrast to ice a definite number of water molecules occupied interstitial sites at any given moment.

The "flickering-cluster" model. The flickering-cluster model of Frank and Wen (1957) and Frank (1958, 1963a) postulates that the formation of hydrogen bonds in liquid water is predominantly a cooperative phenomenon. The existence of a pair of hydrogen-bonded atoms promotes the tendency of each atom to hydrogen-bond to another neighbor, etc. Furthermore, the cooperative element is not limited to linear propagation. Thus, due to a partially covalent character of the hydrogen bond (see Forslind, 1952, 1953; Coulson and Danielsson, 1954; Sokolov, 1956; Coulson, 1957), the remaining lone-pair L-shell electrons of oxygen atoms in a hydrogen-bonded chain of liquid water molecules are more localized, with more nearly tetrahedral sp^3 hybridization, than if the molecules were not members of the chain.* Accordingly, the water molecules are more susceptible to further hydrogen-bonding, which, in turn, imparts additional stability to the existing bond system, giving the process an element of positive feedback.

The net result of the cooperative hydrogen-bonding is that when one bond forms, there is a tendency for several (perhaps many) to form, whereas when

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* That redistribution of charge-clouds takes place when a hydrogen bond is formed is shown by several experimental observations (see Frank, 1963a).