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THE PHYSICS OF ICE - A UNIQUE HYDROGEN-BONDED SOLID

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The world is spun between two giant hands of ice
(Douglas Stewart: The Fire on the Snow)

INTRODUCTION

Water, in its various phases, is one of the most abundant and important substances in the universe. It contributes substantially to the mass of the giant planets Neptune, Saturn and Uranus, it is the principal component of many comets, and here on earth it has played an essential role in the shaping of the landscape, the development of weather and climate, and the evolution of life. It is small wonder that there is an immense scientific literature about the physical, chemical and geophysical behaviour of water, and what I shall deal with represents only a tiny fraction of present knowledge.

In particular I shall be concerned with the solid phases of water - known collectively as ice - and, within that area, mostly with those properties that are best understood at the microphysical level. Before I begin, however, I should point out several of the unusual macroscopic properties of the ice-water system which give it its unique importance.

Much of the geophysical importance of water arises from the fact that the temperature of the earth's surface is close to the melting point of ordinary ice at ordinary atmospheric pressure, so that the melting-freezing phase transition is common. Add to this the relatively high vapour density in equilibrium over water at ordinary atmospheric temperatures (around 10 g m^{-3}), and we find that water vapour is also geophysically important. The properties of water are unusual among the small molecules, as has been emphasised by Pauling (1960), and derive from the particular geometry and electronic structure of the water molecule, as we discuss in more detail below.

Water is one of a small group of materials for which the solid phase is less dense than the liquid at the low-pressure melting point. Others include silicon and germanium. If it were not for this circumstance, lakes and oceans would freeze from the bottom rather than the top; they would be virtually completely solid, and marine life - perhaps all life as we know it - would have failed to develop.

Finally, water is far from inert electrically, as is clear from the spectacular phenomenon of lightning. On a more modest but more significant scale, the electrical conductivity of aqueous electrolytes and the mobility of protons within even pure water are ultimately responsible for the development of animal nervous systems, without which life would be dull indeed!

Within this goldmine of material for discussion, I have chosen to concentrate on the solid phases of water. This is dictated partly by personal interest, but also by the fact that the scope is then reasonable. Even within that field the literature is immense, but we are well served by a number of substantial books and reviews, including those by Fletcher (1970,1971) and

Hobbs (1974), as well as by articles on more specific aspects of the subject. One of these sources should be consulted for a detailed bibliography up to about 1970, as well as for a more detailed discussion of the topics mentioned here. The general literature on water as a substance is larger by an order of magnitude, but the basic properties have been summarised in a compendium by Dorsey (1940). Liquid water and its properties are dealt with in discussions at the molecular level by Eisenberg and Kauzmann (1969) and by Ben-Naim (1974), and a broader view is given in the 5-volume treatise edited by Franks (1972).

THE WATER MOLECULE

Most of the characteristic properties of water derive from the particular geometry and electronic structure of the water molecule, H_2O . As a simple molecule with only three nuclei and 10 electrons, it has been the subject of detailed study by quantum chemists, and our basic theoretical understanding is now good. We do not require much sophistication for our present purposes, but it is comforting to know that a relatively simple analysis leads to conclusions which are borne out by careful calculation.

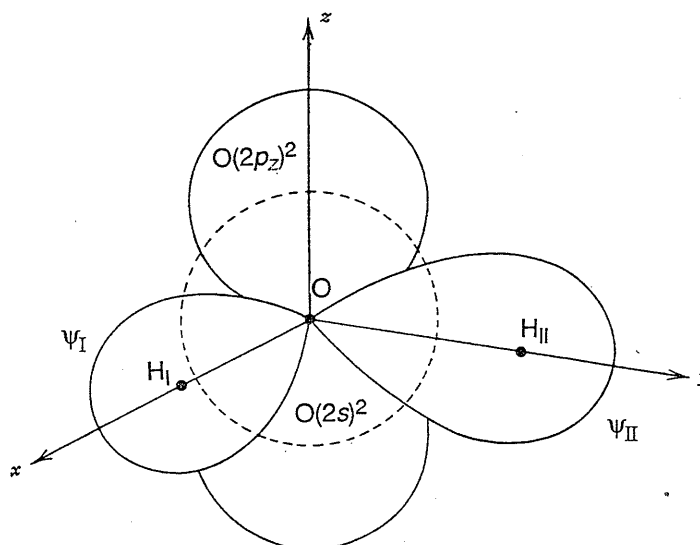


Figure 1. Simple approximation to the bonding orbitals of a water molecule gives a triangular shape with a bond angle of 90° .

In its ground state an isolated oxygen atom has an electronic configuration $(1s)^2(2s)^2(2p)^4$, while each hydrogen atom is in the state $(1s)$. As a preparation for modeling the formation of bonds in the molecule, we can rewrite the oxygen configuration as $(1s)^2(2s)^22p_x2p_y(2p_z)^2$, and maximum overlap between orbitals on adjacent atoms can be achieved by placing the hydrogen atoms I and II on the x and y axes respectively. The bonding orbitals then have the form

$$\psi_1 = a_1O(2p_x) + b_1H_I(1s)$$

$$\psi_2 = a_2O(2p_y) + b_2H_{II}(1s)$$

where a_1, b_1, a_2 and b_2 are constants constrained by normalisation requirements and determined by minimising the total energy. Each of the orbitals ψ_1 and ψ_2 can accommodate two electrons of opposite spin and, since these orbitals have a concentration of negative charge between the two positive nuclei, they form chemical bonds. The shape of the H_2O molecule is thus, to a first approximation, triangular, as shown in Fig. 1, with a bond angle of 90° . The constants b_1 and b_2 are equal, from symmetry, and turn out to be less than $1/\sqrt{2}$, so that the O-H bonds are partially ionic.

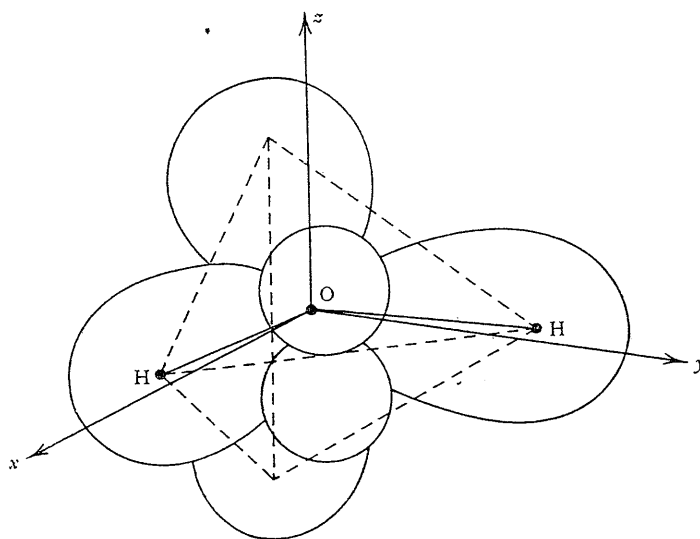


Figure 2 Idealized tetrahedral shape of the water molecule. The proton vertices have net positive charge and the lone-pair vertices negative charge. The lone-pair charge is diffuse.

The second approximation (Ellison & Shull 1955, McWeeny & Ohno 1960, Bishop & Randic 1966) recognises that, because of their charge distribution, the two bonds will repel each other and tend to open out the H-O-H angle. This necessarily affects the electronic configuration of the remainder of the oxygen atom, which is reflected by the necessity to include contributions from the $2s$ and $2p_z$ orbitals in ψ_1 and ψ_2 . The result of minimising the total energy with respect to all the parameters involved, including the positions of the hydrogen nuclei, gives a bond angle of about 104.5° , which is very close to the ideal tetrahedral angle of 107° . The hybridization of the bonds in this way gives a concentration of electron density, associated with hybridization of the $O(2s)^2$ and $O(2p_z)^2$ electrons in the simple model, in two "lone-pairs" localised more-or-less in the direction of the other two vertices of the tetrahedron. This nearly-tetrahedral hybridization of the oxygen orbitals is closely similar to the tetrahedral sp^3 hybridization of carbon-atom orbitals in methane (CH_4), though there is no longer exact tetrahedral symmetry.

Our final simple model, therefore, is that of a nearly tetrahedral water molecule with two positive vertices near the protons, and two negative vertices associated with the lone pairs, as shown in Fig. 2. In reality the molecule is less symmetrical than this model would suggest, the negative charge of the lone pairs being distributed more broadly than the partly screened positive charge associated with the protons, and this shows up in the measured (or calculated) electric multipole moments of the molecule (Glaeser & Coulson 1965). The dipole moment, about 6×10^{-30} C m, is large and particularly important for many of the properties of ice.

BONDING BETWEEN WATER MOLECULES

The simple tetrahedral model of the water molecule gives a remarkably effective model for the bonding together of water molecules if we add the restriction that the bonds O-H...O between molecules tend to be straight, so that the tetrahedra join vertex-to-vertex rather than edge-to-edge. This feature can be made to emerge from simple charge-distribution models of the water molecule, but is in reality more complex than this and involves a further distortion of the electron orbitals of the interacting molecules, which is equivalent to an electrostatic polarisation of one molecule by the multipole moments of the other. Clearly this polarisation will be rather different depending upon the number of bonds being made by each molecule, and this nonlinearity in the polarisation gives rise to cooperative effects in the bonding - the energy advantage of making 4 bonds to a molecule is more than four times the energy advantage of making a single bond.

The single bond, and indeed the multiple bonds, formed between water molecules are examples of hydrogen bonds, the proton with its attendant electron cloud forming a bridge between the two molecules. These bonds are of great importance and have been the subject of intense study. Both molecules are, of course, active partners in the bond, one through its proton and the other through a lone-pair electron distribution. The proton is by no means close to the centre of the bond but belongs unambiguously to its parent molecule, the O-H...O distance being about 2.76 Å and the O-H distance about 0.96 Å. There are possibly two energy minima for proton positions along the bond, but the energy of one is very much higher than that of the other because it represents the formation of an ion pair $[\text{OH}]^- [\text{H}_3\text{O}]^+$. This is illustrated in the simplified calculation of Lippincott & Schroeder (1955) shown in Fig. 3. The shape of the lower energy minimum gives the O-H vibration frequency, the shift of which away from its free-molecule value gives an indication of the strength of the bond.

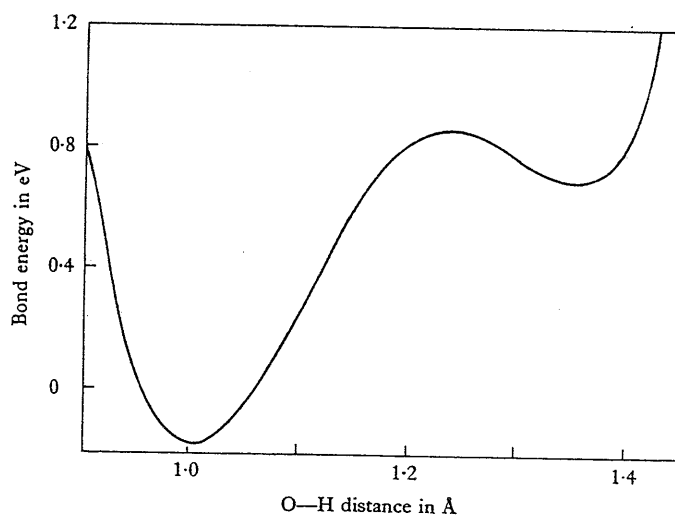


Figure 3 Calculated form of the energy curve for displacement of a proton along the bond between two water molecules (after Lippincott & Schroeder 1955). It is not clear whether or not the subsidiary higher minimum is real.

To put some rough figures on the energies involved, the binding energy of the water molecule - the difference between its ground-state energy and that of its three constituent atoms - is about 10 eV, or 5 eV for each O-H bond if we take a simple view. The energy associated with a single hydrogen bond

between two isolated water molecules is uncertain, but is comparable with, though smaller than, that of a hydrogen bond in ice, about 0.3 eV. Hydrogen bonding between water molecules thus represents a relatively small perturbation to their total energy.

The whole behaviour of water in its various phases is, however, dominated by this tendency to form cooperative tetrahedral hydrogen bonds. As we see below, all the solid phases of water have exact 4-fold coordination, though not always with regular tetrahedral bonding. Even in liquid water, no more than about 10 percent of the bonds can be considered to be "broken" (as we can estimate from the ratio of the latent heat of fusion to the latent heat of sublimation), and it may be more realistic to regard this fraction as being much smaller, with a greater assortment of distorted bonds. The partial collapse of the structure under the influence of non-directional Van der Waals forces between the molecules accounts for the fact that the density of water is greater than that of ice, a topic to which we return below. Various models take, for simplicity, the extreme views that liquid water has either a uniform 4-bonded but distorted structure (for example Pople 1951) or, conversely, a structure consisting of "flickering clusters" of 4-bonded molecules lubricated by a sea of unbonded monomer (for example Némethy & Scheraga 1962). A realistic model certainly lies somewhere between these extremes. Unfortunately a discussion of the liquid state would take us too far from our central subject.

THE STRUCTURE OF ORDINARY ICE

Ordinary ice exists in immense quantities on the surface of the earth, its abundance being measured in cubic kilometres and its purity in parts per million. The flow of glaciers suggests that it is, to some extent, plastic but its typical mode of failure is brittle. Single crystals over a kilogram in weight can be recovered from temperate glaciers, but more familiar are the tiny and often perfectly symmetrical forms of snowflakes (Nakaya 1954). These beautiful hexagonal crystals suggest an underlying hexagonal crystal structure, but their varied and intricate forms pose puzzling problems about their growth mechanism. The phase transition between ice and liquid water at 0 °C occurs commonly on the earth's surface, and is important in the formation of rain, both in nature and as a possible mechanism for enhancing precipitation (Fletcher 1962a).

X-ray studies of ice crystals (Lonsdale 1958, Owston 1958) show that the oxygens are arranged in a hexagonal structure with the space-group symmetry $P6_3/mmc$ or D_{6h}^4 . This structure is shown in Fig. 4. Each molecule has exact tetrahedral coordination, and the structure can be thought of as consisting of

crinkled layers, normal to the c -axis and arranged in a sequence ABAB... as in the close-packed hexagonal structure. The structure is closely related to the diamond cubic (diamond, silicon, germanium), which also has tetrahedral coordination and consists of similar crinkled layers lying normal to the $[111]$ direction with a stacking sequence ABCABC... as in the close-packed cubic structure.

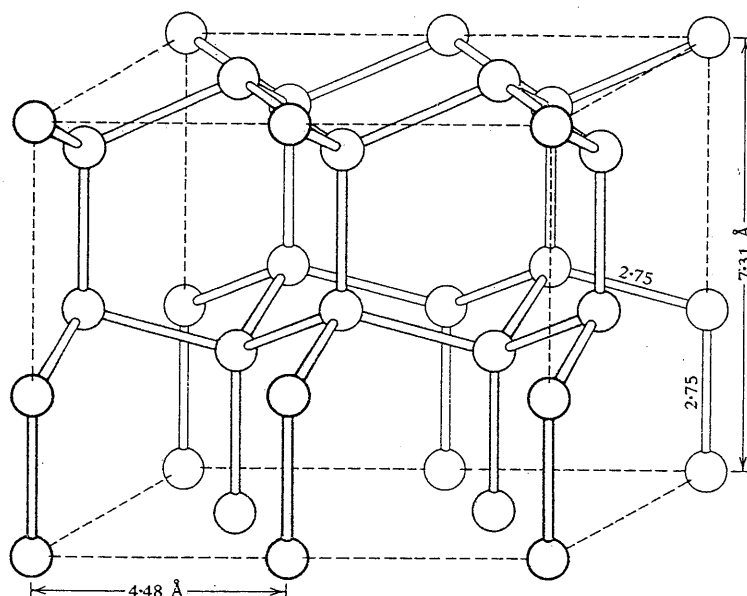


Figure 4 Positions of oxygen atoms in the ice structure (after Kamb 1968). Note the tetrahedral bonding, the 6-fold rings, and the crinkled sheets normal to the hexagonal axis.

The tetrahedral coordination of the ice structure contrasts with the 10 or 12-fold coordination common in metallic crystals and accounts for the low density (0.916 to 0.918 g cm⁻³) of ice. The slightly collapsed structure of liquid water has a first-coordination-shell occupancy of nearly 5, which accounts for the fact that the density of the liquid is greater than that of the solid. This feature is shared with silicon, germanium and other 4-coordinated solids.

Another unusual property common to ice and these other tetrahedrally bonded solids is that their thermal expansion coefficient is negative at very low temperatures (below about 70 K in the case of ice). It goes to zero, of course, at 0 K. The explanation (Collins & White 1964) appears to involve the

behaviour of transverse vibrational modes of relatively low frequency which have a negative Gruneisen parameter γ (relating change in mode frequency to change in volume, with a negative sign in the definition) and tend to dominate the behaviour in this temperature region.

The scattering of X-rays depends upon electron density, so that X-ray diffraction methods are able to determine only the positions of the oxygen atoms in ice. The protons have only a small associated electron density and are therefore nearly invisible. This immediately raises the question of proton positions in the ice structure. All simple tests suggest that the crystal is non-polar and has the same symmetry as that of the oxygen framework. This could be achieved if the protons were all midway along their respective bonds, but this seems unlikely, given the small energy of the hydrogen bond between pairs of water molecules compared with that of the O-H bonds within the molecules. This clearly favours the continued existence of intact water molecules within the ice structure.

It is possible to devise an arrangement of protons so as to maintain intact water molecules and give a nonpolar structure, but the resulting unit cell contains 96 molecules. No superlattice lines associated with such a structure have been detected. The true structure, as put forward by Bernal and Fowler (1933), is fascinatingly different. They proposed that the proton positions are disordered, but constrained by the following rules:

- there are two possible proton sites on each bond;
- there is only one proton on each bond;
- there are just two protons close to each oxygen.

These constraints, known as the Bernal-Fowler rules, allow a very large number of proton configurations in a macroscopic crystal, most of which are nearly nonpolar. The configurational freedom does, however, allow polar configurations and can thus account for the very high dielectric constant of ice (about 100). Fig. 5 illustrates a possible proton configuration consistent with the Bernal-Fowler rules.

Fortunately this disordered structure can be confirmed by neutron diffraction, since neutrons are scattered by nuclei, rather than by electrons, and the scattering cross-section of hydrogen is comparable with that of oxygen. The experiments usually use heavy ice, D_2O , instead of H_2O in order to reduce diffuse scattering, but this has very little effect on the properties of the ice. The diffraction results show a structure with a half-hydrogen at each of the sites on each bond. This, together with the absence of any superlattice lines, confirms the disordered structure, and the detailed results show that the intramolecular O-H distances are very little changed from their magnitude

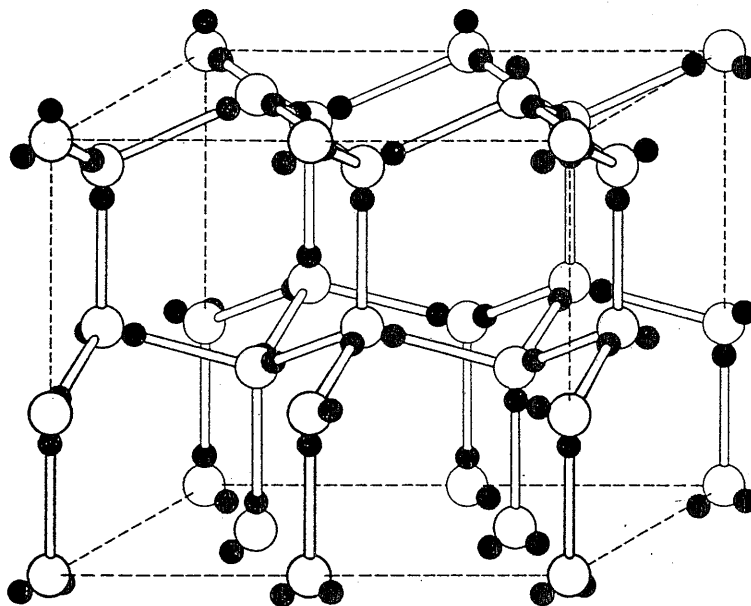


Figure 5 One possible configuration of protons in the ice structure of Fig. 4 (after Fletcher 1970). The proton positions must obey the Bernal-Fowler rules.

in the isolated molecule. Ice is truly a molecular solid, with the molecules bound together by cooperative hydrogen bonds.

The proton disorder in ice has an interesting thermodynamic consequence. Indeed there is a configurational entropy associated with the disorder which is quite easily calculated to first order (Pauling 1935). In a crystal of N molecules, there are just $2N$ bonds, on each of which is a proton with two choices of position. This gives a total of 2^{2N} configurations. However many of these violate the third rule above. Indeed, of the 16 possible arrangements of 4 protons around a given oxygen site, only 6 satisfy the rule by having just 2 protons near the oxygen site. The number of allowable proton configurations is thus $(6/16)^N 2^{2N}$ or $(3/2)^N$. The configurational entropy associated with the proton disorder is therefore $Nk\ln(3/2)$ or $k\ln(3/2)$ per molecule.

This calculation is actually oversimplified, since it neglects the detailed connectivity of the ice structure. The existence of many closed 6-fold rings in the structure complicates the calculation greatly, but reduces the final configurational entropy by only about 1 percent (Nagle 1966).

We expect, of course, that the configurational entropy of an ice crystal in equilibrium at 0 K will be identically zero, but in fact the proton disorder becomes quenched into the structure at about 100 K and persists at all lower temperatures, so that the metastable crystal has a residual entropy at 0 K equal to the configurational entropy of the protons. This quantity has been evaluated experimentally by Giaque & Stout (1936), who compared the measured increase in entropy in taking ice from a temperature near 0 K to the vapour state near room temperature with the true entropy of water vapour at this temperature, which is known from statistical mechanics. The discrepancy of $3.4 \pm 0.2 \text{ J mole}^{-1} \text{ deg}^{-1}$ is within 2 percent of the value calculated above.

In a later section of this review we see that the role played by proton disorder in the physics of ice is crucial. Before looking at this in detail, however, there are some other structural matters that we should discuss.

OTHER PHASES OF ICE

Because the ice structure is very open, with a coordination number of only 4 compared with the value 12 achieved in close-packed metals, it is not surprising that it tends to collapse when a large static pressure is applied. There are, indeed, 7 stable high-pressure polymorphs of ice, our knowledge of which is due in the first place to Bridgman (1912, 1937) and more recently to Kamb (1968), Whalley and their co-workers (see Fletcher 1970 for a detailed bibliography). A phase diagram, detailing all the known stable phases, is given in Fig. 6. The phase Ice IV, originally reported by Bridgman, is now known to be metastable and is therefore not included. The melting-curve boundary between liquid and Ice VII has been followed up to at least 200 kbar, where the melting point is about 440 °C. Details of the triple-point relations associated with this phase diagram are given by Fletcher (1970, p. 54)

The first thing to be noted is the way in which the liquidus, or melting curve, between ordinary ice and water drops in temperature with increasing pressure at a slope of about 10 degrees per kilobar. This is a necessary consequence of the fact that water is more dense than ice, so that the pV term in the Gibbs free energy

$$G = U - TS + pV$$

favours a shift in equilibrium, at a given temperature, towards the phase occupying the smaller volume. The fact that the liquidus curve against all the higher ices rises with increasing pressure shows that they are more dense than water at the same pressure.

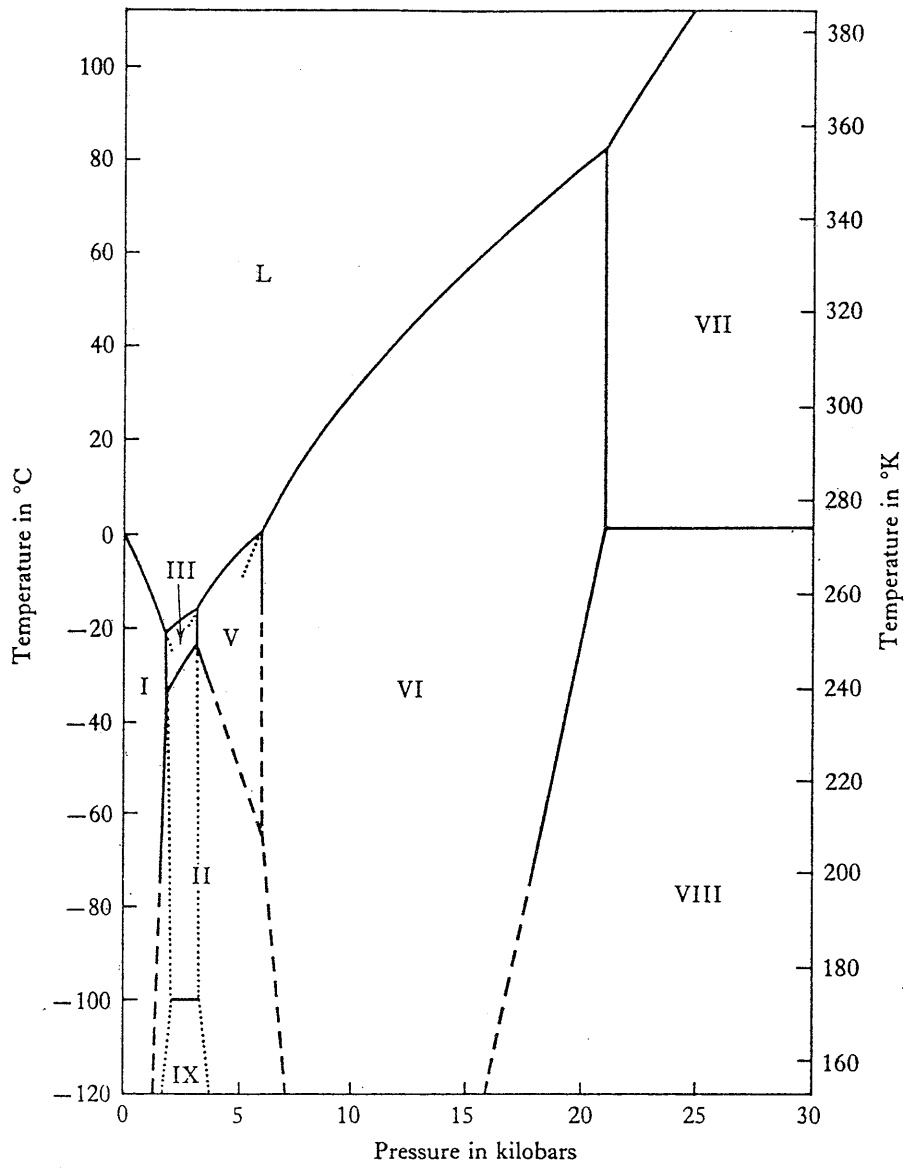


Figure 6 The phase diagram of water (after Fletcher 1970 from data of Bridgman, Whalley and others).

Ordinary ice, shown as Ice I in Fig. 6, is more properly known as Ice I_h , with the subscript denoting that it is hexagonal. This is because there is also a cubic form of ice, with oxygen atoms arranged in the closely related diamond cubic structure, which we should call Ice I_c . It is possible, though by no means certain, that Ice I_c is marginally stable against Ice I_h at temperatures below about 150 K. Ice I_c has not been grown directly, but is recovered as a recrystallisation product when pressure is removed from one of the high-pressure ices at liquid nitrogen temperature and the crystals are allowed to warm gradually. The protons in Ice I_c are disordered, as they are in Ice I_h , and other properties of the two forms are very similar.

Elucidation of the structures of the high-pressure ices has relied largely upon X-ray analysis, with information on the proton positions being obtained more indirectly. Thus it is known that, without exception, the water molecules in all the structures retain their 4-fold hydrogen bonding up to the very highest pressures studied. The bonds are, however, generally quite distorted in angle and, instead of the exclusively 6-membered rings found in Ices I_h and I_c , the structures of Ices II, III and V contain rings with 5 or even 4 members. This gives a closer packing, since the large cavities characteristic of the Ice I structures are avoided, and hence a greater density and enhanced stability at high pressure. The free energy gained by collapse of the structure more than compensates for the increased energy caused by bond strain.

The dielectric constant of Ice II is only 3.7 at -30°C , indicating that the protons have assumed an ordered arrangement on the distorted bonds. Perhaps rather surprisingly, the dielectric constants of Ices III and V are respectively 117 and 144, compared with 99 for Ice I, showing unequivocally that the protons in these structures remain disordered. If Ice III is cooled metastably below -100°C however, the protons suddenly become ordered and the dielectric constant falls to a low value. This order-disorder transition has a small latent heat associated with the configurational entropy change, and the ordered form is designated Ice IX.

The Structure of Ice VI, which has a large stability domain, is particularly interesting (Kamb 1965). It consists of two completely independent, identical 4-bonded frameworks, which interpenetrate so that the molecules of one occupy the cavities of the other. This structure can be termed a self-clathrate, after the clathrate structures in which cages of 4-bonded water molecules surround inert gas atoms to form stable structures, often a nuisance in gas pipelines at low temperatures. The Ice VI structure achieves a density of 1.3 g cm^{-3} at 1 bar and -175°C , compared with 0.92 g cm^{-3} for Ice I. Its dielectric constant is 193, nearly twice that of Ice I.

This pattern is repeated in the structure of Ice VII, in which the two interpenetrating frameworks each have the diamond cubic structure (Kamb & Davis 1964). The molecules of alternative frameworks are very close together and the Van der Waals forces between them are strong, giving a very stable structure. The density is 1.66 g cm^{-3} at 25 kbar. In fact the oxygen atoms of the combined structure occupy a body centred cubic structure with a coordination number of 8. Only the close-packed face-centred cubic structure has a higher possible density, and to achieve this would involve forsaking 4-fold bonding. For all reasonably attainable pressures, Ice VII is thus the ultimate high-pressure ice.

The dielectric constant of Ice VII is also high - about 150 - indicating proton disorder. This phase, like Ice III, shows an order-disorder transition and becomes ordered below 0°C . The low-temperature ordered phase is designated Ice VIII.

Finally we should mention that, when ice is formed from the vapour by deposition onto a substrate at a temperature below about -160°C , the deposit is vitreous, as determined from X-ray diffraction. Between this temperature and -130°C the deposit crystallises to the cubic Ice I_c, with heat evolution of about 100 J g^{-1} , about one third of the entropy change in the crystallisation of liquid water. There is still some uncertainty about the precise nature of this vitreous state.

SURFACES, NUCLEATION AND CRYSTAL GROWTH

Because phase changes are so important in the ice-water system, they have been studied in considerable detail. The homogeneous nucleation of droplets in supersaturated water vapour provides a stringent test of the statistical and kinetic theories describing the process, as also does the nucleation of water droplets on positive or negative ions, as in the Wilson cloud chamber. The nucleation of droplets on tiny solid particles or on hygroscopic nuclei is similarly important in the formation of clouds in the atmosphere, since the droplet concentration and size distribution are both important for the initiation of precipitation. An outline of these processes is given by Fletcher (1962a).

Turning to ice crystals, it is clear that the processes of nucleation and growth depend in detail upon the nature of the interface between an ice crystal and its parent phase, be it vapour or liquid. The ice/vapour interface is certainly complicated, as is clear from the extreme habit variations, from needles to dendritic plates over a range of a degree or two, observed in tiny ice crystals grown from the vapour (Nakaya 1954, Hallett & Mason 1958). The beautiful

dendritic forms exhibited by snow crystals can generally be accounted for by simpler kinetic effects.

It has been suggested that this behaviour is caused by a surface phase change which occurs at slightly different temperatures on different crystallographic planes. Such a phase change would cause large changes in the surface mobility of water molecules, and hence in the kinetics of crystal growth (Mason *et al* 1963), without implying a large change in the surface free energy. The driving force for the phase change could derive from the proton disorder, or equivalently from the disorder in molecular orientation, within an ice crystal. Calculations (Fletcher 1962b, 1973) suggest that, because of the difference between the polarisability of the protonic and lone-pair vertices of a water molecule, the energy of an ice surface can be lowered by orienting the surface molecules so as to expose one type of vertex preferentially. There is an entropy penalty associated with this orientation which would be severe if it were allowed to penetrate the bulk crystal, and a state of lower free energy can be achieved through the agency of a thin liquid-like disordered layer on the surface. This layer, of course, has its own associated free-energy penalty, and the liquid-like film is stable only within a few degrees of the melting point, where its thickness ranges from a few molecular layers to a few tens of layers. A similar effect may occur in certain other hydrogen-bonded crystals (Fletcher 1973). While this theory is attractive and seems to explain many peculiar observed results, the existence of such a transition layer is not yet proven.

The ice/water interface is somewhat less controversial, but is still not well understood. The surface free energy of liquid water near 0 °C is about 80 mJ m⁻², that of an ice/vapour interface about 100 mJ m⁻², and that of the ice/water interface probably about 20 mJ m⁻² but decreasing with decreasing temperature. Theory suggests that the interface is broad and has considerable structure because of the bonding coherence-length in the liquid (Fletcher 1975), but the growth of ice crystals from water does not clearly indicate a preferred growth mode, both continuous and dislocation growth being suggested for different crystal planes under different conditions.

MECHANICAL PROPERTIES OF ICE

Ice is an ideal material in which to study mechanical phenomena, once an environment below its melting point has been established. This is particularly because it is transparent and, being hexagonal in structure, optically anisotropic. Its crystal structure can thus be easily observed between crossed polarisers. All the standard methods of X-ray topography can also be used to study dislocations and their motion (Higashi 1988).

Ice exhibits ordinary elastic behaviour, together with plastic deformation, creep or brittle failure under appropriate conditions. Most of these phenomena can be understood on the basis of elastic theory and dislocation motion, but some, such as elastic damping, require the notions we develop in the next section. Details may be found in Fletcher (1970) or Hobbs (1974). It must suffice here to note that, from the structure shown in Fig. 3,

it is reasonable to expect that the crinkled molecular layers of ice should slide fairly readily over each other, with the help of appropriate dislocations, to give glide in the (0001) basal planes normal to the *c*-axis. This type of glide is relatively rapid in common experience, since large masses of ice, such as found in glaciers, are within a few degrees of their melting point. The flow of glaciers is also aided by pressure melting when an obstacle is encountered on the glacier bed. A review of glacier motion has been given by Nye (1951, 1967).

OPTICAL AND THERMAL PROPERTIES OF ICE

The optical and thermal properties of ice are both associated with lattice vibrations, so that it is convenient to treat them together. Once again we begin with the water molecule. Setting aside the electrons (which contribute an ultraviolet absorption with peaks near 1700 Å and 1200 Å), it has a total of 9 degrees of freedom, corresponding to the coordinates of its three constituent atoms. More usefully we can think of these as three translational coordinates for the centre of mass, three rotational coordinates, and three internal coordinates specifying the two O–H bond lengths and the H–O–H bond angle. The infra-red spectra with which we are concerned here derive from these internal coordinates, broadened by contributions from the rotational modes.

More properly, then, we consider three normal modes as shown in Fig. 7. These represent respectively symmetrical and antisymmetrical combinations of the O–H stretching modes ($\tilde{\nu}_1$ and $\tilde{\nu}_3$) and the bond-bending mode $\tilde{\nu}_2$. The optical wave numbers associated with the stretching modes are both close to 3700 cm^{-1} (a wavelength near 3 microns) and that of the bending mode is near 1600 cm^{-1} (6 microns). From detailed study of these modes in the absorption spectrum of water vapour, the bond lengths, bond angle, and elastic coefficients of the molecule can all be determined.

These same modes can also be identified in the absorption spectrum of ice and are shifted only a little from the frequencies found for the vapour, reflecting the relatively minor effect of hydrogen bonding upon the structure of the molecule itself. The translational and rotational modes however, which were free in the isolated molecule, are constrained in the solid and become lattice vibration modes and molecular libration modes respectively. The

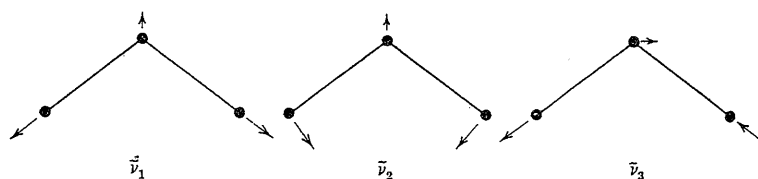


Figure 7 The three normal modes for vibration of a water molecule.

libration - rotation of the molecule against the elastic restoring torques of its neighbours - occurs at a relatively high frequency and gives a band over the range 500 to 1050 cm^{-1} . The translational modes, both longitudinal and transverse, have frequencies in the range 0 to 300 cm^{-1} . Because of the disordered orientations of the molecules in the ice crystal, all these modes are optically active, and it is possible to derive the density of vibrational states directly from the optical absorption spectrum (Bertie & Whalley 1967). The resulting density-of-states curve is shown in Fig. 8.

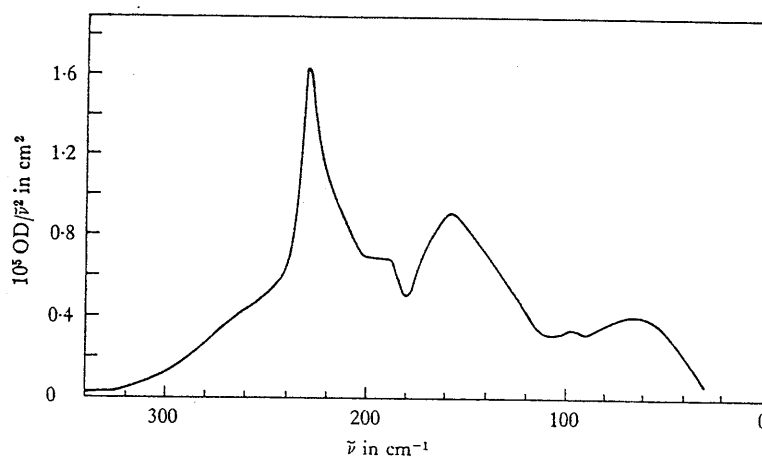


Figure 8 A semiquantitative representation of the spectrum of vibrational states of ice, as derived from the function (optical density)/(frequency)² (after Bertie & Whalley 1967).

The spectrum of lattice vibrations is, of course, closely related to the specific heat and thermal conductivity of the crystal. To a first approximation

the specific heat of ice below its melting point can be represented by contributions from a Debye continuum with a characteristic temperature Θ_D of about 315 K ($\tilde{\nu} = 220 \text{ cm}^{-1}$), contributed by the lattice modes, and an Einstein peak with characteristic temperature Θ_E 1040 K ($\tilde{\nu} = 723 \text{ cm}^{-1}$), contributed by the libration modes. The intramolecular modes do not contribute significantly at these temperatures. The thermal conductivity, as we might expect, varies as T^3 at very low temperatures, goes through a maximum of about $500 \text{ W m}^{-1} \text{ deg}^{-1}$ near 40 K, and falls at higher temperatures as T^{-1} . Its value near 0°C is about $2 \text{ W m}^{-1} \text{ deg}^{-1}$.

POINT DEFECTS IN ICE

In addition to the plane defects (surfaces, grain boundaries and twin planes), line defects (dislocations) and point defects (vacancies and interstitials) that can occur in any pure crystal, ice possesses an additional set of defects specifically related to its bonding structure. These are the ion states and the so-called Bjerrum defects or valence defects (Bjerrum 1952), and are associated with violations of the Bernal-Fowler rules. As illustrated in Fig. 9, there are four of these defects - a positive ion state H_3O^+ (\oplus), a negative ion state OH^- (\ominus), a doubly occupied bond (D) and an empty bond (L). The ionic defects result from the transfer of a proton from one end of a bond to the other, creating a pair of complementary ion states which can then separate by further proton jumps as shown. The valence defects are similarly induced by the oblique jump of a proton from one bond to an unoccupied position on another bond of the same molecule, or equivalently by the rotation of the molecule through an angle of 120° about one of its bonds. Again, a complementary defect pair is produced and these can separate by further similar proton jumps. In a pure crystal without surfaces or grain boundaries, the concentrations of \oplus and \ominus ion states clearly must balance, as must the concentrations of D and L valence defects.

In principle one might calculate the formation energy of ion states and valence defects from first principles and from this derive their equilibrium concentrations. It is difficult to get reliable answers in this way, however, since allowance must be made for the elastic relaxation of the structure in the vicinity of the defect and this complicates the problem very greatly. The values given in Table 1 are derived indirectly from experiment and, while somewhat uncertain, give an idea of the magnitudes involved. While the concentrations of interstitials, vacancies and ion states are all small and of the order found in other solids, the concentration of valence defects is quite large - nearly 1 in 10^6 of the bonds being affected.

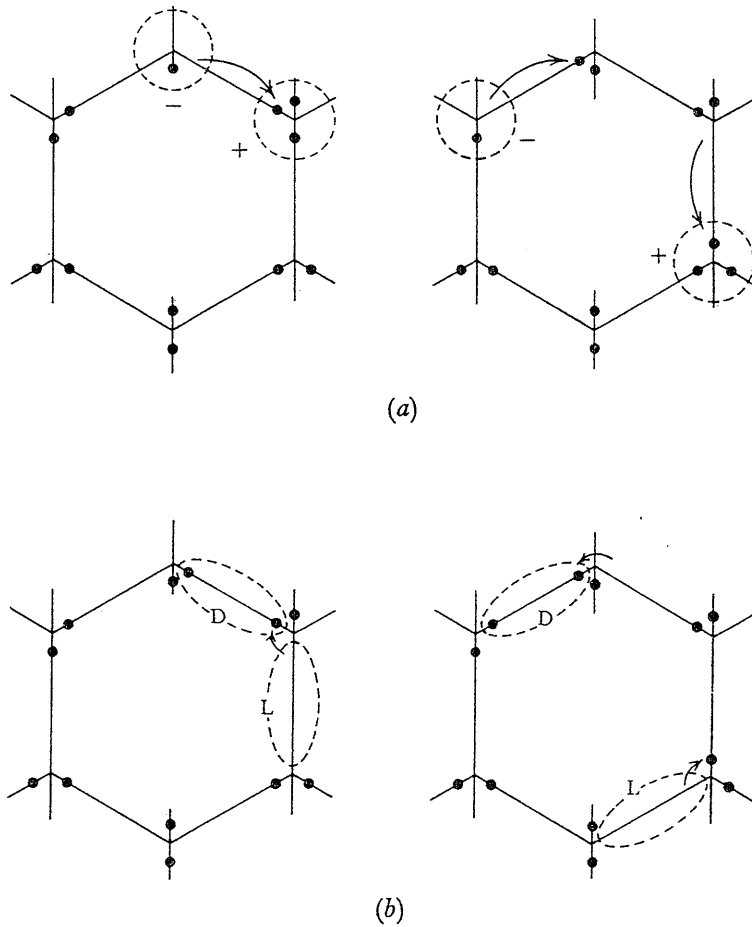


Figure 9 (a) The formation of two ionic defects by the jump of a proton along a bond, and the separation of these defects by further similar jumps, (b) the formation and separation of two Bjerrum (valence) defects by the oblique jump of a proton, or equivalently by the rotation of a molecule about one of its bonds (after Fletcher 1970).

The ice structure can also accommodate impurity atoms or molecules, either interstitially or substitutionally, but the equilibrium solubilities are very small, as evidenced by the purity of ice found on the earth's surface. Even in ice formed from sea water, the salt occurs predominantly in small liquid saline inclusions in a much purer ice matrix. Most dissolved impurities have little effect on the properties of ice, but there is an important class of exceptions exemplified by substances such as NH_3 and HF . These molecules are very

Table 1 Point defects in pure ice at -10°C

Concentration of valence defects (D,L)	10^{16} cm^{-3}
Concentration of ion states (\oplus,\ominus)	$10^{10} - 10^{11}\text{ cm}^{-3}$
Concentration of interstitials	$10^{10} - 10^{11}\text{ cm}^{-3}$
Concentration of vacancies	10^{12} cm^{-3}
Mobility of L defects	$2 \times 10^{-4}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$
Mobility of D defects	$1 \times 10^{-4}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$
Mobility of \oplus ion states	$10^{-1}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$
Mobility of \ominus ion states	$< 10^{-2}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$

similar in size to the water molecule and enter the ice structure substitutionally, with their protons participating in the hydrogen bonding. Clearly, however, NH_3 brings with it an excess proton while HF has a missing proton, and this has a profound effect.

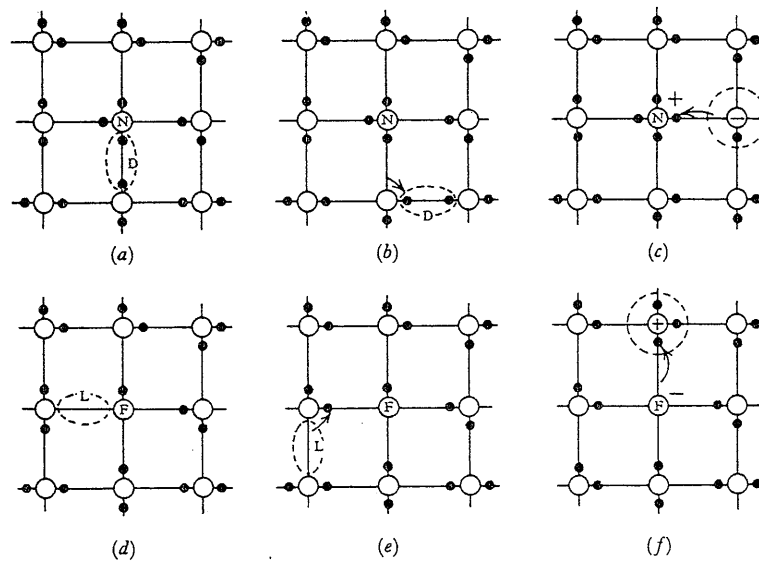


Figure 10 (a) A proton donor impurity centre NH_3 shown schematically in a 2-dimensional analog of the ice structure; (b) liberation of a D defect by proton-jump diffusion; (c) subsequent liberation of a negative ion state \ominus ; (d) a proton acceptor impurity centre HF in the same structure; (e) liberation of an L defect; (f) liberation of a positive ion state \oplus (after Fletcher 1970).

What happens is shown schematically in Fig. 10, which is a 2-dimensional analog of the 4-bonded ice structure. An NH_3 molecule inserted substitutionally in the lattice, as shown in Fig. 10a, results in one of its bonds having two protons on it, thus creating a D defect. This D defect can migrate away in the usual way, as shown in Fig. 10b, but in addition it is energetically favourable for an electron transfer to occur along one of the other bonds, as shown in Fig. 10c, giving a free negative ion state OH^- and an immobile substitutional ion NH_4^+ . The net result is the release of a D defect and a \ominus ion state for each incorporated NH_3 molecule. For a substitutional HF molecule, as shown in Fig. 10d-f, the result is an immobile F^- ion together with a free L defect and a free \oplus ion state H_3O^+ .

In reality, of course, there is an activation energy associated with these defect liberation processes, that for the ion states (0.6 to 0.7 eV) being substantially higher than that for the L and D defects (about 0.01 and 0.3 eV respectively). These values mean that the valence defects are substantially all liberated for temperatures approaching 0°C , while there is only a small fractional liberation of the associated ion states.

It is helpful to think of materials like NH_3 as proton donors and those like HF as proton acceptors, by analogy with electron donors and acceptors in electronic semiconductors. In the next section we shall see that the analogy goes quite deep. For the present we note that it is possible to incorporate into the ice structure concentrations of these materials as high as 10^{20} cm^{-3} , or a few tenths of one percent. Even an impurity concentration of less than one part per million has an immense effect on the equilibrium concentration of mobile point defects, however, and thus on the detailed physical properties of the sample. Again, the analogy with electronic semiconductors is clear.

ELECTRICAL PROPERTIES - A PROTONIC SEMICONDUCTOR

Although ice is a more-or-less insulating material, it is far from being devoid of interesting electrical properties. It has a high dielectric constant - around 100 at low frequencies - and an electrical conductivity of order $10^{-9}\text{ ohm}^{-1}\text{ cm}^{-1}$ which depends greatly upon purity and which tends to increase exponentially with temperature.

Let us consider in detail the effect of a steady electric field on an ice crystal. The D defects and \oplus ion states, having positive charges, tend to migrate in the direction of the field by successive proton jumps, while the L defects and \ominus ion states migrate in the opposite direction. It is important to note that these proton jumps are in each case between two states of equivalent energy, apart from the bias produced by the external field. The energy diagram for the proton

is as shown in Fig. 11 and can be calculated, at least in principle, from first principles. In the case of proton transfer along the bond directions, as required for ion-state motion, the two energy minima are only about 0.8 Å apart and the transition is thought to occur by a quantum-mechanical tunnelling effect. This gives a very rapid transfer rate which is essentially temperature independent and this accounts for the very high mobility of the ion states, particularly the \oplus state. Motion of the valence defects, on the other hand, requires oblique motion between two proton positions which are about 1.8 Å apart. Quantum tunnelling over this distance is very slow, and proton transfer takes place by classical thermal activation over the intervening barrier, which has a height of about 0.24 eV. Diffusion of these defects is therefore a good deal slower than that of ion states. Values for the mobilities of the different defects at -10°C are given in Table 1.

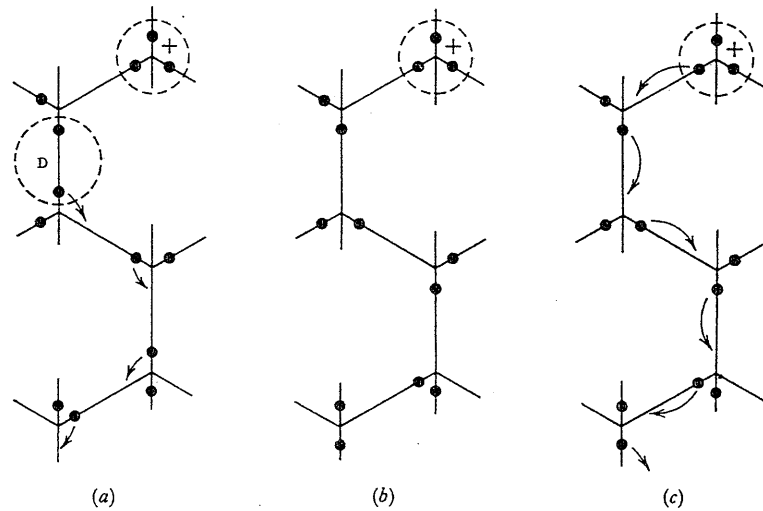


Figure 11 Proton jumps associated with the motion of a D defect along a chain of bonds, as in (a), leave this chain polarised, as in (b), so that no other D defect can traverse the same chain in the same direction. Proton jumps associated with motion of a positive ion state along the same chain of bond in the same direction, as in (c), restore the original proton configuration (after Fletcher 1970).

Suppose now we follow the motion of D defect along a chain of bonds as shown in Fig. 11a. After passage of the defect, the bonds of the chain have all been reoriented in such a way that no further defect can use the same chain, as shown in Fig. 11b. The same polarisation results from L defects passing through the crystal in the opposite direction. This means that motion of the

very numerous valence defects through the crystal under the influence of an electric field can lead to electric polarisation through reorientation of the water molecules, but cannot give a steady electric current.

Fig. 11c shows, however, what happens when a positive ion state is allowed to follow the D defect through the crystal - it has the effect of reorienting all the bonds back to their original configuration. The same thing happens for a negative ion state moving in the opposite direction. Thus a combination of valence-defect motion and ion-state motion can give a steady electric current, with the conductivity being determined by whichever mechanism is less efficient. From the concentrations and mobilities given in Table 1 it is clear that, in pure ice near -10°C , valence defects (and particularly L defects) are primarily responsible for dielectric polarisation effects, while electrical conductivity is limited by the motion of positive ion states.

A complete theory of the electrical effects associated with defect motion has been worked out on the basis of contributions from many people, and is usefully summarised by Jaccard (1959). On the argument given above, we can write for the number current density j_D of D defects under the influence on an electric field E the relation

$$j_D = n_D \mu_D E + \Omega_D n_D \int_0^t (j_+ - j_- + j_L - j_D) dt$$

where n_D and μ_D are respectively the number density and mobility of the D defects and Ω_D is a quantity measuring the extent to which the currents that have already passed through the crystal may block the paths of the D defects. Three similar equations can be written for the number current densities j_L , j_+ and j_- of the other defects. If the applied field varies as $\exp(i\omega t)$, then $\int dt$ in the expression above can be replaced by $1/i\omega$.

For high frequencies the integral can be neglected and we have a simple set of equations

$$j_i = n_i \mu_i E$$

which lead to the high-frequency conductivity

$$\sigma_{\infty} = \sigma_+ + \sigma_- + \sigma_D + \sigma_L$$

where

$$\sigma_i = n_i \mu_i e_i$$

and e_i is the effective charge, either positive or negative, associated with defect i . This implies that each carrier moves over such a small distance that interactions are unimportant and their conductivities can be simply added. The effective charges e_i must satisfy the relation

$$|e_+| + |e_{DL}| = e$$

and in fact they all turn out to be close to $0.5e$, with small anisotropy corrections.

At very low frequencies, conversely, the integral term dominates and the static conductivity is essentially given by

$$\sigma_s^{-1} = A(\sigma_+ + \sigma_-)^{-1} + B(\sigma_D + \sigma_L)^{-1}$$

where the constants A and B are unity in this approximation, but should be determined in detail by solving the equations properly.

A proper solution of the equations for a finite frequency gives an expression for the complex conductivity, or equivalently for the complex dielectric constant. The dielectric constant is high at low frequencies, where there is time for substantial molecular reorientation through defect motion, but decreases at high frequencies, going through a Debye relaxation behaviour at a frequency which is in the audio-frequency range. When this analysis is supplemented by inclusion of molecular distortion and electronic polarisability, the general form of the dielectric behaviour is as shown in Fig. 12. The large dielectric constant at low frequencies results from cooperative orientation of molecules in the electric field, since the hydrogen bonding requirements impose some correlation upon neighbouring molecules. Even in very strong fields, however, the extent of the molecular orientation is very small (of order 10^{-4} for a field of 1000 V cm^{-1}).

It is interesting to compare this general behaviour with that of water, which also has a substantially 4-bonded structure but effectively a very large concentration (of order 10 atomic percent) of valence defects which allow the configuration to relax very rapidly. The low-frequency dielectric constant is high (about 80), for the same reason as in ice, but the relaxation time is of order 10^{-11} s so that the dielectric constant remains high up to microwave frequencies (about 10 GHz, corresponding to 3 cm wavelength). Water drops are therefore easily seen on meteorological radars (wavelength 3 to 10 cm) while snow flakes of comparable size are not. Indeed the radars show a bright band of reflections when the snow flakes fall through the melting level and acquire a thin coating of liquid water. Hailstones, fortunately, are generally clearly visible because their rapid growth by coalescence with water droplets gives them a thick coating of liquid water.

It is clear from our discussion, of course, that proton-donor and proton-acceptor impurities will have a large effect upon the electrical properties of ice. In this sense they act in very much the same way as donors and acceptors in electronic semiconductors. These impurities generally raise the static conductivity of ice. Their effect on the low-frequency dielectric constant is more complicated and depends on the complementary roles played by ion states

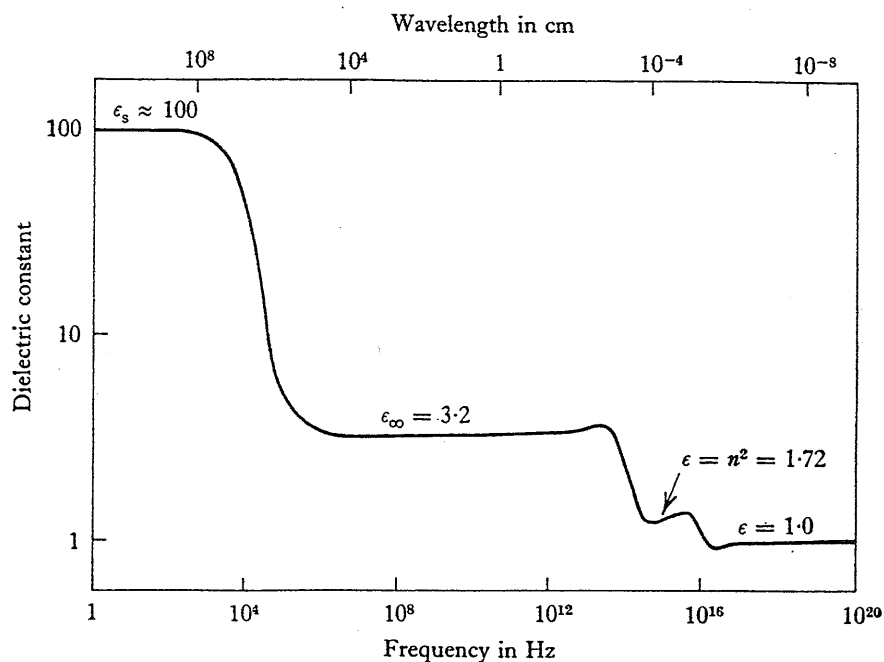


Figure 12 Behaviour of the dielectric constant of pure ice at about -10°C as a function of frequency. At low frequencies the main effect is from dipole reorientation, at higher frequencies from molecular distortion, at still higher frequencies from electronic polarisation. The dielectric loss has maxima near those frequencies where the dielectric constant is changing sharply (after Fletcher 1970).

and valence defects. To examine this in a little more detail, we recall that, for addition of HF, for example, the L defects are essentially all liberated because of their low binding energy. We can therefore write

$$n_L \approx n_L^0 + n_{HF}$$

$$n_+ \approx n_+^0 + B n_{HF}^{1/2}$$

where B is a constant and the meaning of the other symbols is clear. When the mobilities of the carriers are taken into account, the partial conductivities σ_L and σ_+ behave as shown in Fig. 13.

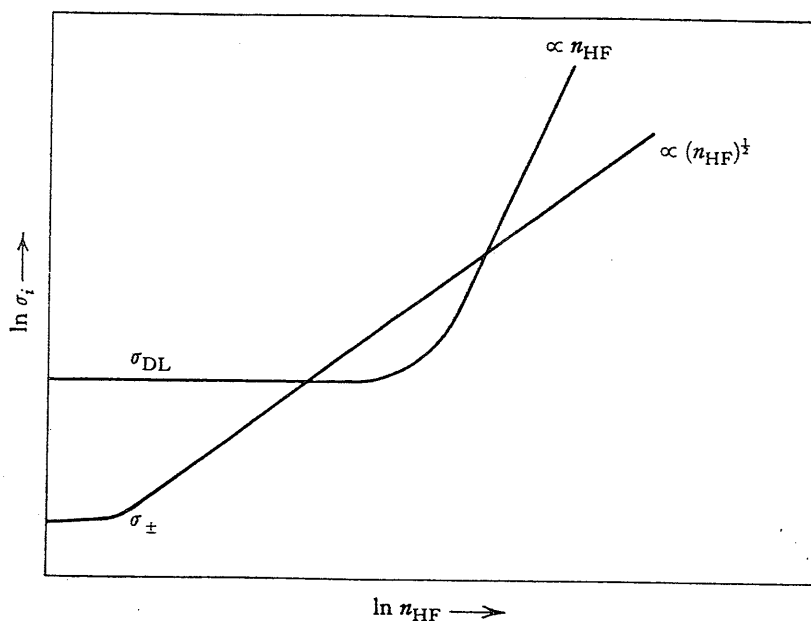


Figure 13 Dependence of the partial conductivities of L defects and \oplus ion states upon the concentration of added HF in an ice crystal.

In Fig. 13 there are two concentrations of added HF for which the partial conductivities of L defects and \oplus states are equal. When this occurs, there is no net polarisation, and the static dielectric constant falls to the high-frequency value, as shown in Fig. 14 (Steinmann 1957).

The analogy with electronic semiconductors is, in fact, quite extensive, though the phenomena are complicated by the presence of four interacting carriers. Ice samples can be designated as *p*-type or *n*-type depending upon whether they contain proton donors or proton acceptors, (though *p*-type ice then contains D and \ominus defects while *n*-type contains L and \oplus) and contacts between materials of different polarity have rectifying properties. The Hall effect in ice can be measured, and it is even possible to work out a band picture for the behaviour of ion states in ice. The band gap is the energy of formation of ion-state pairs, about 1 eV, and the total conduction band width turns out to be only about 10^{-3} eV, which is about what one might expect from the relative masses of protons and electrons.

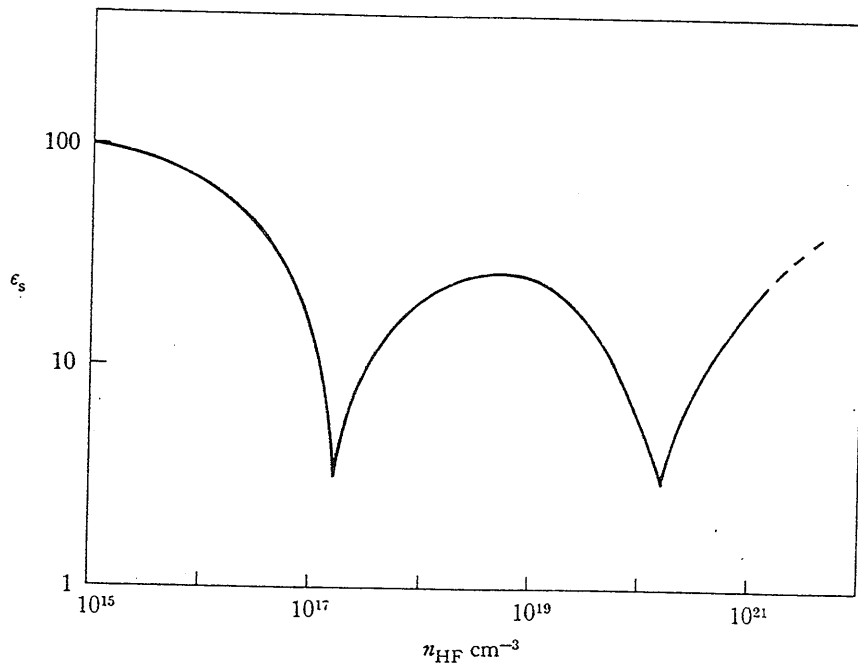


Figure 14 Dependence of the static dielectric constant of ice upon the concentration of HF impurity (after Steinmann 1957).

The thermoelectric effect in ice is likewise rather similar to, though more complex than, the thermoelectric effect in electronic semiconductors, and has a similar large magnitude. Jaccard (1963) has provided a theoretical analysis of the effects to be expected, and this has been verified in considerable detail by Bryant & Fletcher (1965). Their measured results, along with those of several other workers, are shown in Fig. 15. The behaviour arises from diffusion of carriers down the thermal gradient, balanced by back-diffusion caused by concentration gradients and resulting electric fields. For concentrations of HF or NH_3 less than about 10^{16} cm^{-3} , only the concentration of ion states is significantly affected, while for much larger concentrations the number of orientational defects also changes. These circumstances give rise to the various plateaus seen in the curve.

Finally in this section we should note that electrical properties constitute one area in which there is a significant difference between the behaviour of ordinary ice, H_2O , and heavy ice D_2O . This comes about because the change of a factor 2 in mass between the proton and the deuteron has a considerable effect on the rate of quantum tunnelling along bonds, and therefore on the

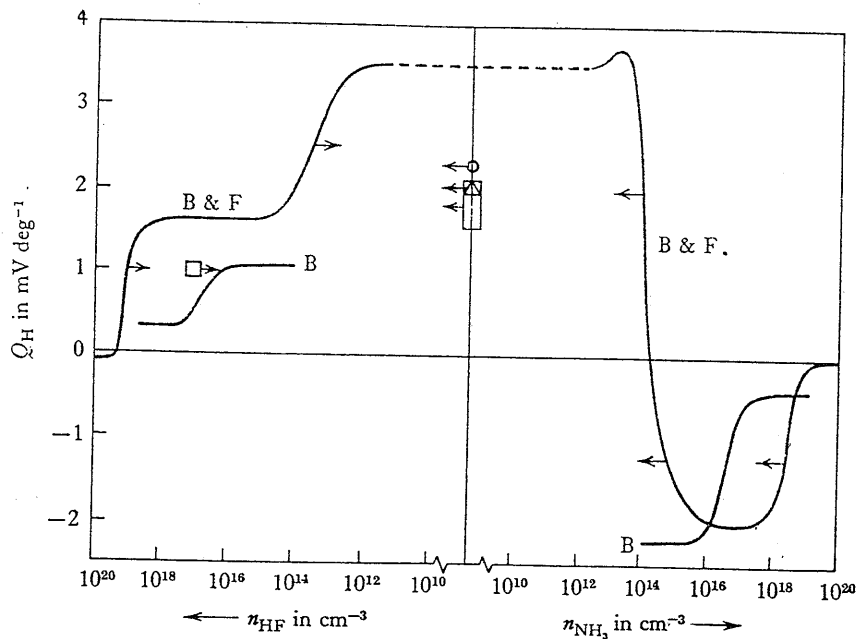


Figure 15 The homogeneous thermopower of ice containing various concentrations of HF or NH_3 . The curve is from Bryant and Fletcher (1965) and points from other investigators.

mobility of \oplus and \ominus ion states. Details are unfortunately scanty. In nearly every other respect the physical properties of heavy ice are closely similar to those of ordinary ice.

OTHER HYDROGEN-BONDED SOLIDS

While ice is the very archetype of hydrogen-bonded solids, it is extreme in its properties because its molecules form a completely bonded 3-dimensional structure. In no other materials is the extent of hydrogen bonding so complete. Nevertheless, ice does provide an exemplar of the sorts of properties to be found in other solids of this class. It also provides a guide to the sort of properties we should expect in water molecules immobilised near surfaces, in pores, and perhaps even in more closely bonded situations. Such molecules are vitally important for many processes in biological systems, all of which are aqueous, and most of which depend critically upon the properties of water near membranes.

Chief among the points to be noted from our survey of the physics of ice are the persistence of hydrogen bonds even in highly distorted situations, the

importance of molecular orientation effects, and the ease with which protons can be transferred from one end of a bond to the other, thereby transferring either a charge or a polarisation through the whole hydrogen-bonded structure, without the necessity for physical transport of a single entity from one end to the other.

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