THE STRUCTURE OF ICE

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The intermolecular forces which bind water in many kinds of compound, *e.g.*, hydrates, proteins, clays, and textiles, are of great interest and importance. Unfortunately, these systems are often complex, and the results of their investigation are not always reproducible or easy to interpret. The simplest solid compound containing water, ice, should present less difficulty, and its physicochemical properties are therefore now reviewed. Not all combined water, of course, is in the same state of combination as in ice : it is often bound more strongly. The heat of combination of water vapour with dry cellulose, for instance, is 16 kcal./mole,[1] while the heat of combination of water vapour with itself to form ice is only 11·5 kcal./mole : the binding in clay minerals may be stronger still. Nevertheless, a full understanding of ice would be a useful step forward in the study of these systems.

Polymorphism in Ice.—The published literature on ice abounds in contradictions,[2] and it is often difficult to decide which work is reliable. This is particularly true of observations on the crystalline form of ice, which has at different times been placed in most of the trigonal, rhombohedral, and hexagonal classes, with occasional references to cubic crystals. The reason for the discrepancies is not far to seek,[3] for although single crystals of ice are easily obtainable, *e.g.*, from hail-stones, clear sections of blocks of ice, or surface lake ice, or from the partly frozen water under the surface, yet they usually have little or no external form from which their symmetry can be decided. Snowflakes usually have no good crystal faces, and are too fragile for lengthy examination. Their symmetry usually seems to be holohedral hexagonal, class 6/*mmm*, but the form depends on the conditions of growth, and less symmetrical forms are common. Schaefer [4] describes a number of these, both natural and artificial : the unusual forms, which are caused by deliberately introduced impurities, all seed supercooled water to give hexagonal crystals, and presumably have the same internal structure as the normally formed crystals. The existence of occasional crystals of unusual shape is not sufficient to prove polymorphism.

A claim to have found two polymorphic forms of ice distinguishable by *X*-ray methods has been made by Seljakov.[5] Crystals of the first of these, α-ice, which formed between 0° and − 5°, had hexagonal symmetry, as

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[1] Neale and Stringfellow, *Trans. Faraday Soc.*, 1941, **37**, 525.

[2] Dorsey, " The Properties of Ordinary Water Substance ", Rheinhold Publishing Corpn., New York, 1940.

[3] Owston and Lonsdale, *J. Glaciol.*, 1948, **1**, 118.

[4] *Chem. Reviews*, 1949, **44**, 291.

[5] *Compt. rend. Acad. Sci. U.R.S.S.*, 1936, **10**, 293 ; **11**, 227 ; 1937, **14**, 181.

shown by their Laue pattern. No other examination of single crystals of this form was made, but some were powdered and then gave an X-ray diffraction pattern with no (0002) reflection observable. The β-form crystallised from water supercooled below $-5°$, giving crystals which had trigonal Laue symmetry and when examined as single crystals gave a strong (0002) reflection. When powdered, however, the β-form crystals gave the same X-ray pattern as the α-form, with the (0002) reflection absent. Seljakov therefore suggested that β-ice is converted into α-ice by being powdered. Neither of these forms was identical with that described by Barnes,[6] which had hexagonal Laue symmetry, like α-ice, and also gave strong (0002) X-ray reflections, like β-ice. Two criticisms may be made of Seljakov's work: first, that he did not carry out tests to ensure that the crystallites in the powdered specimens were randomly oriented, for if there were "preferred orientation" some X-ray reflections might be absent; secondly, that he confined his examination of single crystals (with one exception) to taking Laue photographs, which can be misleading. His experimental results do not appear to be sufficient to prove that the α- and β-forms are different from the form studied by Barnes.

The crystals made by Adams [7] by condensation from moist air were usually hexagonal prisms, sometimes showing asymmetrical etch-pits. This led him to conclude that ice belongs to a polar hexagonal class, but, since piezo- and pyro-electricity had never been demonstrated in ice,[8] that it is usually twinned on the (0001) plane. It is also possible, however, that the very small crystals (0·02 mm. long) used by Adams were affected by traces of impurities.

Several claims have been made to have produced ice of cubic symmetry by crystallisation from various solvents, especially alcohol, at about $-50°$. These crystals, however, have never been shown to be pure ice, or to be cubic except in appearance. More important are two recent claims to have produced a cubic form by condensation. Rau [11] has found that water vapour condensed into droplets on a metal mirror solidified below $-72°$ to give isotropic cubes, octahedra, or tetrahedra—*i.e.*, crystal shapes possessing cubic symmetry. These crystals melted at $-72°$, and on further heating re-solidified in hexagonal form. Cwilong [12] was unable to repeat these observations when the air in the apparatus was scrupulously clean: traces of organic vapour led to similar results to those described by Rau.

Similarly, König [13] condensed water vapour on a collodion film in an electron-diffraction apparatus at 10^{-4} mm. pressure. If condensation took place below $-80°$ the resulting crystals were cubic, changing into a hexagonal form above $-80°$. The electron-diffraction patterns show that the hexagonal form is ice-I; in the cubic form the oxygen atoms are arranged

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[6] *Proc. Roy. Soc.*, 1929, *A*, **125**, 670.

[7] *Ibid.*, 1930, *A*, **128**, 588.

[8] Hettich and Schleede, *Z. Physik*, 1928, **50**, 249; Wooster, quoted by Bernal and Fowler.[21]

[9] Bridgman, *J. Chem. Physics*, 1935, **3**, 597; 1937, **5**, 964.

[10] McFarlan, *ibid.*, 1936, **4**, 60, 253.

[11] *Schrift. Deut. Akad. Luft*, 1944, **8**, ii, 65.

[12] *J. Glaciol.*, 1947, **1**, 53.

[13] *Z. Krist.*, 1944, **105**, 279.

in the same way as the carbon atoms in diamond, and are 2·75 Å apart. In ice-I (see next section) the oxygen atoms are effectively the same distance apart, 2·76 Å, at 0°.

This work makes it probable that a cubic form of ice can exist at low temperatures, though Burton and Oliver [14] found no conclusive evidence of any form but hexagonal ice-I: in their work water vapour when condensed below − 110° did not crystallise, and above − 110° ice-I was found. Rau considered his cubic crystals to be metastable ice-VI, since the P–T curve for ice-VI when extrapolated indicates that it might be metastable below about − 70° at low pressure. This, however, conflicts with McFarlan's conclusion that ice-VI at atmospheric pressure and − 180° has a lower symmetry than ice-II or ice-III, which are hexagonal or orthorhombic. In addition, the density of König's cubic ice is 0·92 g./cm.^{3}, identical with that of ice-I, while the density of ice-VI at 22,400 kg./cm.^{2} pressure is 1·52 g./cm.^{3}. It may be, therefore, that the cubic form is a quite new modification.

St. John [15] has reported a hexagonal form, stable just below 0° and at atmospheric pressure, with lattice parameters $a = 4{\cdot}74$, $c = 6{\cdot}65$ Å; these do not agree with any other observations, and have not yet been explained.

Under special conditions polymorphism is shown by ice, and Bridgman [9] has described a total of six forms which are stable only at high pressures and quickly revert to a seventh form, the normal ice-I, at atmospheric pressure. Little is known of their structure and properties, though McFarlan [10] was able to show that in ice-II and ice-III the intermolecular distance was nearly the same as in ice-I.

We may conclude that the only forms of ice which undoubtedly exist are hexagonal ice-I, Bridgman's six high-pressure forms, and possibly a cubic form stable only at low temperatures. No other modification of ice has been examined sufficiently thoroughly for it to be accepted as authentic.

The Structure of Ice-I.—The X-ray work of Dennison,[16] W. H. Bragg,[17] and Barnes [6] leaves little doubt as to the mean positions of the oxygen atoms. Four of these in the positions $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{16})$ and $\pm(\frac{1}{3}, \frac{2}{3}, \frac{7}{16})$ are contained in a hexagonal unit cell of parameters $a = 4{\cdot}513_5\ kX$, $c = 7{\cdot}352\ kX$.[18] The molecules are then arranged in puckered layers parallel to the (0001) plane. Each molecule is tetrahedrally co-ordinated to four others, three in the same layer, and one in an adjacent layer, but all four the same distance, 2·76 Å, away (Fig. 1). The ready cleavage and gliding in this layer plane which is shown by ice near its melting point is thus easily explained.[19] It may be added that the structure proposed by König for his cubic modification also involves tetrahedral co-ordination. The positions of the hydrogen atoms are not easily found by X-ray diffraction methods, because of their low scattering power for X-rays, and various attempts have been made to deduce their positions by less direct means.

Barnes [6] believed that the molecule was fully ionised to ($2H^+ + O^=$)

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[14] *Proc. Roy. Soc.*, 1935, *A*, **153**, 166.

[15] *Proc. Nat. Acad. Sci.*, 1918, **4**, 193.

[16] *Phys. Review*, 1921, **17**, 20.

[17] *Proc. Physical Soc.*, 1921, **34**, 98.

[18] Megaw, *Nature*, 1934, **134**, 900.

[19] Bragg, *Proc. Roy. Inst.*, 1938, **30**, 283.

and that each hydrogen nucleus was equally distant from, and collinear (or nearly so) with, two neighbouring oxygen ions. An ionic structure, however, is more characteristic of solids of high melting point which melt to a highly conducting liquid, such as the alkali halides.[20]

In a full discussion of the evidence available in 1933, Bernal and Fowler [21] pointed out that ice must consist of discrete molecules. The infra-red and Raman spectra of water vapour and of ice show that there is little change in the vibration frequencies of the water molecule owing to the change of state. In the vapour the O–H bond-length is 0·958 Å, and the angle $\widehat{HOH}$ is 104° 31′;[22] it may be estimated from the changes in vibration frequencies that the O–H bond becomes about 1·0 Å long with the angle $\widehat{HOH} = 109\frac{1}{2}°$ in ice. The hydrogen atoms cannot therefore be near the centres of the oxygen-to-oxygen bonds, since this would imply an O–H bond-length of 1·38 Å. If the hydrogen atoms are partly charged, electrostatic forces will hold them along the O–O bonds, one to each bond, about 1·0 Å from one oxygen atom and 1·76 Å from the other. By assuming net effective charges of $+\frac{1}{2}e$ on each hydrogen atom and $-e$ on the oxygen atoms in this model, Bernal and Fowler were able to account for the dipole moment of the molecule and also the intermolecular forces (assumed to be mainly electrostatic) as measured by the heat of vaporisation of ice.

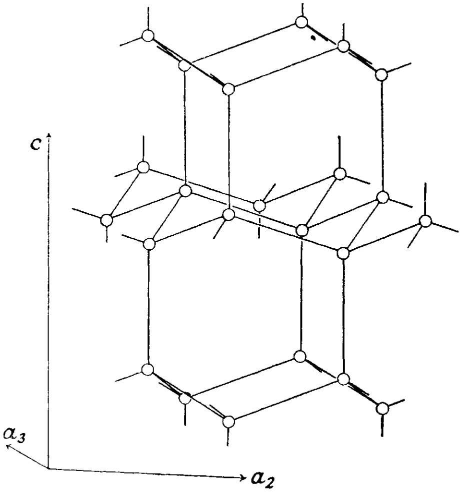

FIG. 1

The arrangement of the molecular centres in ice in layers perpendicular to the hexagonal axis, showing the tetrahedral co-ordination.

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[20] Kinsey and Sponsler, *Proc. Physical Soc.*, 1933, **45,** 768.

[21] *J. Chem. Physics,* 1933, **1,** 515.

[22] Darling and Dennison, *Phys. Review,* 1940, **57,** 128; Dennison, *Rev. Mod. Physics,* 1940, **12,** 188.

Verwey[23] has shown that, apart from the fact that the dimensions given in Bernal and Fowler's model are geometrically inconsistent, equally good agreement can be found by using a variety of models with formal charges on the atoms and an adjustable screening constant.

The difficulty immediately arises that, with the hydrogen atoms arranged in the way proposed by Bernal and Fowler, ice cannot both have a regular structure and also lack piezo- and pyro-electric properties unless the unit cell is improbably large, containing 96 molecules. This would not conflict with the X-ray determination of a unit cell containing only four molecules if the hydrogen atoms do not scatter X-rays, as was at that time believed. Bernal and Fowler, therefore, tentatively suggested that the positions of the hydrogen atoms might be irregular, or glass-like.

This suggestion was taken up by Pauling,[24] who showed that a crystal containing N molecules would have $(3/2)^N$ such irregular arrangements, and that if only the interaction of each molecule with its four nearest neighbours is considered all these arrangements would have the same energy. As a result, ice should have a residual entropy of $\boldsymbol{k}N \ln (3/2)$ or 0·805 cal./° c./mole, which would be found even at the lowest temperatures. The experimentally found residual entropy of ice is 0·82 cal./° c./mole,[25] with a possible error of ± 0·1 cal./° c./mole, in striking agreement with Pauling's calculation. If deuterium is substituted for hydrogen the residual entropy, which should theoretically be the same, is found to be 0·77 cal./° c./mole,[26] again remarkably close to the predicted value. This disposes of the alternative explanation of the residual entropy as being due to rotation of the water molecules at low temperatures, for then the values for H_2O and D_2O would be different.

It is not at first clear, however, that it is justifiable to assume that only the interaction of nearest neighbours is important. The structure assumed is a lattice of oxygen atoms arranged as described by Barnes[6] with one hydrogen atom along each O–O bond 1·0 Å from one oxygen atom and 1·76 Å from the other : the hydrogen atoms must also be arranged so that there are two to each oxygen atom. Any given H_2O molecule, A, can arrange itself in six different ways to satisfy these conditions (Fig. 2); once it is fixed its neighbour B has only three possible orientations; once B is fixed its neighbour C is in turn limited to three of its six possible arrangements; and so on. A chain of six molecules ABCDEF thus has 3^5 possible arrangements if A is fixed, and since 3^n is always odd, the six possible orientations of the last of the chain are not equally probable. In this particular case, out of 243 arrangements, three orientations of F occur 41 times, and the other three 40 times : the three which are favoured depend on the orientation of A. In a very long chain the directing effect of the molecule A would be even smaller. However, the structure consists, not

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[23] *Rec. Trav. chim.*, 1941, **60,** 887.

[24] *J. Amer. Chem. Soc.*, 1935, **57,** 2680.

[25] Giauque and Stout, *ibid.*, 1936, **58,** 1144 ; Giauque and Ashley, *Phys. Review*, 1933, **43,** 87.

[26] Long and Kemp, *J. Amer. Chem. Soc.*, 1936, **58,** 1892.

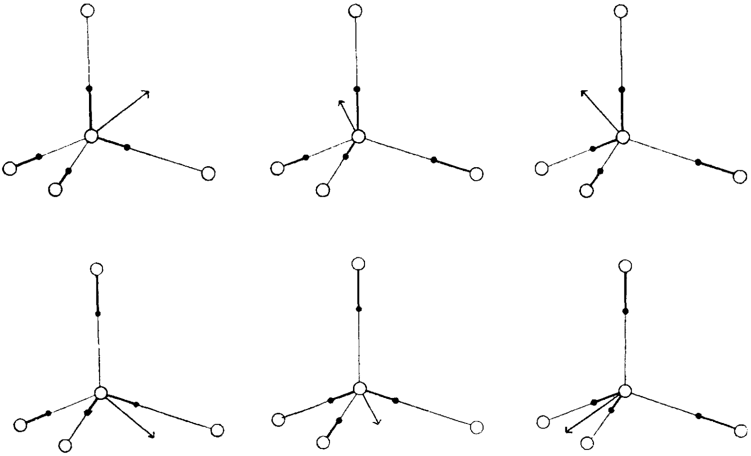

FIG. 2

The six possible arrangements of hydrogen atoms in the four bonds round each molecule, and the six corresponding directions of the resultant dipole moment. Fixing the position of any one hydrogen atom reduces the number of possible arrangements to three.

of chains, but of puckered rings each containing six molecules, so that in the series ABCDEF both B and F may be nearest neighbours of A (Fig. 3). Then A, on the one hand, restricts F to three orientations equally, but on the other hand, slightly favours three orientations (not usually the same three) in the proportion 41 : 40. These two effects of A on F are incompatible, and Pauling's assumption appears to this extent invalid. The discussion is further complicated by the fact that every molecule is a member

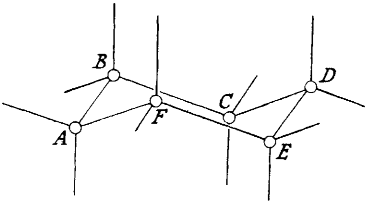

FIG. 3

A six-membered ring of H_2O *molecules.*

of twelve such six-membered rings, and Slater [27] concludes that Pauling's method of enumerating the possible arrangements is valid for a sufficiently large assembly of molecules though clearly wrong for a small number.

Pauling further suggested that at temperatures above about – 60° the hydrogen atoms do not remain vibrating about constant positions, but move, so that the crystal as a whole continually changes from one of the possible configurations to another. This could take place either by rotation of the molecules, or by movements of the hydrogen atoms between their

[27] *J. Chem. Physics,* 1941, **9**, 16.

two possible positions along the O–O bond, or by both of these processes. Since the hydrogen atoms are partly charged, we must examine the electrical properties of ice in considering this possibility.

The Electrical Properties of Ice.—The dielectric constant of ice near 0° is high (approximately 80) when an oscillating potential of low frequency (300 c/s) is used. It decreases with falling temperatures to a value of about 4 at – 60°, and at lower temperatures ice behaves as a non-polar solid : there is, however, no sharp transition at any temperature.[28] The values obtained can be satisfactorily explained as due to restricted rotation of the dipoles between certain relatively stable positions, and to their oscillation (" libration ") about those positions.[29] With decreasing temperatures these movements take place less readily and virtually cease below about – 60°. Since the molecules are less free to rotate in ice than in water, it is to be expected that the conductivity of ice should be much less than that of water, as is found. The relaxation time of the dipoles is about 10^{-6} sec. at 0°, rising to 10^{-5} sec. at – 20°, and 10^{-4} sec. at – 60°.[30]

It is important to note, however, that though the dipoles rotate it is not necessary for the *molecules* to rotate. In Pauling's model the dipole can move between six different but equivalent positions, by movements of hydrogen atoms without any hydrogen atom leaving its own O–O bond. Measurements of the dielectric constant, therefore, although showing that the molecules are sufficiently free at temperatures above about – 60° to allow changes from one configuration to another, yet do not show by which process the changes take place.

If both processes occur, electrolytic conduction would be observed when a constant or low-frequency alternating potential is applied to ice. Unfortunately, no reliable values of the conductance of ice are available. Two values of the order of 10^{-9} ohm^{-1} cm.$^{-1}$ at – 1° and – 10° have been reported,[28, 31] but the ice used was made from impure water of conductance approximately 10^{-6} ohm^{-1} cm.$^{-1}$. A much lower value, 10^{-10} ohm^{-1} cm.$^{-1}$, at – 2° has been reported, but the purity of the specimen was not stated.[30] Since the molecules are less free to rotate in ice than in water, it is to be expected that the conductivity of ice should be much less than that of water, as is found. It is not certain from the experimental evidence, however, whether the observed conductivity was really due to ice, or to impurities in the ice.

Quantum-mechanical Models.—In view of the unreliability of the experimental work on ice, theoretical treatments of the bonds between H_2O molecules have been concerned with liquid water rather than ice. There is good reason to suppose that similar considerations will apply in ice, and it seems useful to consider them here.

Bernal and Fowler showed that if conduction takes place in water by

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[28] Smyth and Hitchcock, *J. Amer. Chem. Soc.*, 1932, **54**, 4642.

[29] Bauer and Massignon, Faraday Soc. Discussion, " Dielectrics ", 1946, p. 12; Kirkwood, *ibid.*, p. 7.

[30] Murphy and Morgan, *Bell Syst. Tech. J.*, 1938, **17**, 640; 1939, **18**, 502.

[31] Johnstone, *Proc. Trans. Nova Scotian Inst. Sci.*, 1912, **13**, 126.

the Grotthus chain mechanism

$$H_3O^+ + H_2O \longrightarrow H_2O + H_3O^+$$

the extra mobility of the ion H^+ in water above its mobility in other liquids requires that a proton be able to pass from one molecule to another $2{\cdot}5 \times 10^{12}$ times per second. Using a rather crude potential-energy function, they showed that this is a reasonable value to expect if the relative orientations of the molecules are such as to permit proton transfer whenever necessary. At higher temperatures, however, favourable orientations are likely to exist for a smaller part of the time, owing to thermal agitation, yet the extra mobility is, in fact, higher at higher temperatures; Bernal and Fowler suggested that thermal rearrangements might also affect conduction. A further argument against their treatment is that if it were correct, the ion D^+ should have an extra mobility only about one-twentieth of that of H^+, thus making its extra mobility negligible, which is not the case.

An improved, but mathematically much more involved, treatment has been given by Wannier.[32] Using a potential-energy curve derived from spectroscopic data, he found that the time taken by a proton to move along its O–O bond from one molecule to another is less than 10^{-12} sec., whereas the time taken by a water molecule to rotate is $65{\cdot}5 \times 10^{-12}$ sec. at 0°, and $4{\cdot}8 \times 10^{-12}$ sec. at 156°. The electrical resistance of water is a function of the sum of the times of rotation and of proton transfer, and quite clearly depends almost entirely on the time of rotation since this is much the larger of the two, falling as the temperature rises. The transfer time for a deuteron is greater than that for a proton, but is still much smaller than the rotation time for the D_2O molecule. The difference in conductivity between water and heavy water is thus due almost entirely to the difference in the rotational inertia of the molecules. Wannier's calculated values of the conductivity of water do not agree closely with those observed experimentally, but their variation with temperature is correct, and the ratio between the mobilities of the ions H^+ and D^+ is correctly derived as 1·5 at 18°. It seems probable, therefore, that his explanation of the conductivity of water is qualitatively correct.

Using other spectroscopic data, Huggins [33] has calculated the potential energy of various arrangements of the system $O{-}H{\cdots}O$, taking account of the possible variations in the length of the bond and charges on the atoms. The curves show that an energy barrier of about 2·2 kcal./mole must be crossed to allow the hydrogen atom to move from one position of minimum energy 1·0 Å from one oxygen atom, to the other, provided that (*a*) the oxygen atoms remain 2·75 Å apart, and (*b*) the effective charges on the oxygen atoms remain equal, and unchanged by the movements of the hydrogen atom.

This energy barrier is not large, and the hydrogen nucleus in an isolated intermolecular bond could move from one position of minimum energy to the other quite readily. In ice, however, we cannot consider a single

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[32] *Ann. Physik,* 1935, **24,** 545.

[33] *J. Phys. Chem.,* 1936, **40,** 723.

bond in isolation, for the movement of a proton will affect the net charges on the oxygen ions, and so affect neighbouring bonds. For condition (*b*) above to hold, the protons in a ring of at least six bonds must move simultaneously at the same speed, and begin from corresponding points along the bonds. If these exacting conditions are not fulfilled, proton transfer will occur much less readily.

Huggins's hypothesis of synchronous group movements is one extreme possibility. The other extreme is to suppose that the hydrogen atoms move by a chain mechanism in which a proton is handed on from an ion $(H_3O)^+$ to the next H_2O molecule. Now, Stearn and Eyring[34] have pointed out that the proportion of dipoles rotating at any instant in ice at 0° is nearly the same, about one in 10^8 molecules, as the number of ions $(H_3O)^+$ in water at 0°. This suggests that the ion is the intermediate " activated complex " in dipole rotation, and hence that the dipole rotates because of movements of hydrogen atoms along the bonds. It does not follow, however, that they move independently, one at a time. Any movement in one bond affects the next, and a rearrangement may take the form of a disturbance crossing the crystal, involving at any time only a small group of atoms whose movements are not synchronous.

It has been pointed out to the Reviewer that Stearn and Eyring's calculation of the ratio of $(H_3O)^+$ ions to un-ionised molecules in water is incorrect. The expression $e^{-\Delta F/2RT}$, where ΔF is the standard free energy of ionisation of water, does not give this ratio : since water has very nearly unit activity in dilute aqueous solutions, the expression gives the molality of hydrogen ions, $3{\cdot}5 \times 10^{-8}$ g.-ion per 1000 g. of water at 0°. The proportion of molecules which have ionised to give $(H_3O)^+$ is then 1 in $1{\cdot}6 \times 10^9$. This does not affect the point that the similarity between the free energy of activation of dipole rotation in ice and half the free energy of ionisation of water suggests that the two processes may be basically the same. It may also be mentioned that although Stearn and Eyring discuss electrolytic conduction in water on the assumption that proton transfer occurs less readily than molecular rotation, this is only an assumption, and leads, as they point out later, to inconclusive results.

From a consideration of the variation of the dielectric constant of ice with temperature and frequency, Powell and Eyring[35] have calculated the entropy of activation of the dipole relaxation process to be 22·5 cal./° c./mole. This they state to be seven times the entropy of fusion of ice, and hence conclude that a group of seven molecules must free themselves from their neighbours in order to allow one dipole to rotate. Apart from the fact that the entropy of fusion of ice is 5·26 cal./° c./mole, which is one-quarter of the calculated entropy of activation, not one-seventh, their conclusion cannot be admitted. It assumes that on fusion all the molecules become free and independent, whereas water near 0° is, in fact, highly associated.

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[34] *J. Chem. Physics*, 1937, **5**, 113.

[35] " Advances in Colloid Science ", Vol. 1, p. 183 ; Interscience Publishers Inc., N.Y., 1942.

Magat and Bauer,[36] on the other hand, calculated ΔS to be 8·6 cal./° c./mole, and the energy of activation 12·9 kcal./mole. The thermodynamic quantities deduced by these different workers are shown in Table I, together with the corresponding values for the fusion and vaporisation of ice, and for ionisation in water.

TABLE I

Changes in free energy (ΔF), *heat content* (ΔH), *and entropy* (ΔS) *for processes in ice at* 0°

	ΔF, kcal./mole.	ΔH, kcal./mole.	ΔS, cal./° c./mole.
Dipole relaxation (activation) [35] . . .	8·39	14·5	22·5
,, ,, ,, [36] . . .		12·9	8·6
A.C. Conduction (activation) [38] . . .	—	11·5	—
Fusion [2]	0	$1{\cdot}43_5$	5·25
Vaporsiation [2] *	0	12·23	44·78
Ionisation in water [2]	18·65	14·62	14·76

* At the vapour pressure of ice.

The difficulties of interpreting dielectric data are shown by Murphy,[31] who lists no less than eight models, which when set up with the appropriate constants would have dielectric behaviour similar to that of ice. It can be seen from the table that no clear picture of the processes in ice can be obtained from the available data. They show only that the movements suggested by Pauling can occur in ice and require an activation energy of about 12 kcal./mole : a similar energy is required for ionisation, or for the complete freeing of the molecule from its neighbours. The ready reorientation of molecules at temperatures near the melting point, as shown by the phenomena of regelation and recrystallisation in glaciers,[37] indicates that molecular rotation occurs, while Murphy's work [38] on the a.c. conductance of ice, at fairly high frequencies, suggests that proton transfers occur equally readily. Reliable work on the d.c. conductance of ice is needed to prove conclusively whether or not both processes occur.

The Vibrations of the Atoms about their Mean Positions.—As has already been pointed out, Huggins's potential-energy curves require the proton to cross a potential barrier of 2·2 kcal./mole on moving from one molecule to the next, if the charges on the oxygen atoms remain equal. The energy required to move the proton if all other atoms remain stationary and so have their effective charges altered when the proton moves, however, is much more, of the order of 10 kcal./mole. The same energy is required to shorten the bond by 0·1 Å, enough to remove the potential-energy barrier, and cause the most stable position of the proton to be at the centre of the bond. This suggests the possibility that the movements of the protons

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[36] Magat, *J. Chim. physique*, 1948, **45**, 93 ; Bauer, *Cahiers de Phys.*, 1944, No. **20**, 1 ; No. **21**, 21.

[37] Perutz and Seligman, *Proc. Roy. Soc.*, 1939, *A*, **172**, 335.

[38] *Phys. Review*, 1950, **79**, 396.

might be chance occurrences depending on the relative movements of the oxygen atoms to reduce the barriers and allow movements to take place freely. It will be seen from Table I that both dipole relaxation and conduction require activation energies of this order, 10 kcal./mole.

A simple method of calculating the root-mean-square amplitude of thermal vibration of atoms in a crystal has recently been pointed out.[39] The Debye characteristic temperature is obtained from the molar specific heat C_v at a very low temperature T by the equation

$$\Theta = T\sqrt[3]{12\pi^4 \boldsymbol{R}/5C_v}$$

Giauque and Ashley's values [25] of the specific heat near 10° K. being taken, Θ is found to be 192° K. for ice: the experimental figures were, in fact, found at constant pressure, but at low temperatures the difference between C_p and C_v is immeasurably small. The mean-square amplitude of vibration is then

$$\overline{u^2} = \frac{9\boldsymbol{h}^2}{4\pi^2 \boldsymbol{k} m\Theta}\left\{\frac{\phi(x)}{x} + \frac{1}{4}\right\} = \frac{4{\cdot}36 \times 10^{-14}}{A\Theta}\left\{\frac{\phi(x)}{x} + \frac{1}{4}\right\}$$

where A is the atomic weight, $x = \Theta/T$, and $\phi(x)$ is the Debye function

$$\frac{1}{x}\int_0^x \frac{\xi . d\xi}{e^{\xi} - 1}$$

with $\xi = \boldsymbol{h}\nu/\boldsymbol{k}T$. If we assume the molecules to move rigidly, this gives in ice a root-mean-square amplitude of 0·41 Å at 0°. The relative movements of two neighbouring molecules will be less than this, but may still be considerable and enough to reduce the potential-energy barriers.

This value cannot be exact, since the calculation of Θ assumes the substance to be elastically isotropic, which is not in general true of crystalline substances, even when they crystallise in the cubic system. The application of this calculation to ice, therefore, requires closer consideration.

The Physical Anisotropy of Ice.—No determinations of the elastic constants of single crystals of ice have been made, and there appear to be few reliable measurements of the elastic properties of polycrystalline ice.[2] Those made by static methods ignore the plastic deformation which always occurs, and where methods involving the measurement of the velocity of vibrations have been used, results have varied by 10% even when supposedly identical specimens have been used at carefully controlled temperatures.

The most recent, and probably most reliable, work shows that artificial polycrystalline ice and natural river ice, in which the hexagonal axis is usually vertical, are both elastically isotropic, within the limits of experimental error. The results are shown in Table II. The only direct determination of the compressibility [43] gives $1{\cdot}2 \times 10^{-11}$ dyne^{-1} at − 7°, which agrees quite well with Northwood's indirectly determined value [42] of $1{\cdot}02 \times 10^{-11}$ at − 15°. Bridgman's value of $3{\cdot}0 \times 10^{-11}$ is not reliable, as he himself has agreed. These data are not sufficient to determine the five elastic constants of monocrystalline ice, but it seems reasonable to suppose that ice is elastically isotropic within 10% error.

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[39] Lonsdale, *Acta Cryst.*, 1948, **1**, 142.

TABLE II

Elastic constants of ice

Temp.	Young's modulus, dynes/cm.^{2} ($\times 10^{-10}$).	Rigidity modulus dynes/cm.^{2} ($\times 10^{-10}$).	Poisson's ratio.	Compressibility, cm.^{2}/dyne ($\times 10^{11}$).	Ref.
− 10° . .	9·5				40
− 30 . . .	10·2				
− 35 . . .	10·9				
− 5 to − 15 .	9·2	3·38[a]	$0{\cdot}36_5$	0·88[b]	41
− 15 . . .	9·8	3·68	0·33	1·02[b]	42
− 7 . . .				1·2	43

[a] Wrongly quoted by Dorsey.[2]

[b] Calculated from the values of Young's modulus and the rigidity modulus.

The optical birefringence of ice, 0·0013, is low,[2] and the magnetic anisotropy immeasurably small.[44] The coefficient of thermal expansion is $(29 \pm 10) \times 10^{-6}$ along the hexagonal axis, and $(17 \pm 10) \times 10^{-6}$ along the direction perpendicular to it.[18] The difference between these two values is small, and was in fact considered by Megaw to be insignificant. The thermal conductance of ice has not been accurately determined, but it is probably nearly the same in all directions in the crystal.[2]

It seems, therefore, reasonable to suppose that ice is an unusually isotropic substance, and that Debye's treatment of lattice vibrations and determination of Θ is more justifiable for ice than for many cubic compounds.

The Diffuse Scattering of X-Rays by Ice.—The thermal movements of the atoms in a crystal not only weaken the normal X-ray pattern, but also result in a diffuse second-order pattern, whose intensity depends on the amplitude of the vibrations. The strongest parts of this pattern, called diffuse spots, are caused by vibrations controlled by the macroscopic elastic forces. In ice their intensity is comparable with those from metallic sodium, in which the atoms have a r.m.s. amplitude of 0·5 Å.[39, 45] The value of 0·4 Å for the atoms in ice is thus at least approximately correct.

There also occur in this diffuse X-ray pattern weaker " diffuse streaks " which appear to indicate strong local disturbances not controlled by the ordinary elastic forces. These disturbances are strictly confined to the planes which contain the intermolecular bonds, and seem to require a relative movement of neighbouring oxygen atoms of about 0·1 Å. These diffuse streaks are not fully explained, however, and since they occur also

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[40] Boyle and Sproule, *Canadian J. Res.*, 1931, **5**, 601.

[41] Ewing, Crary, and Thorne, *Physics*, 1934, **5**, 165.

[42] Northwood, *Canadian J. Res.*, 1947, **25**, 88.

[43] Richards and Speyers, *J. Amer. Chem. Soc.*, 1914, **36**, 491.

[44] Lonsdale, *Nature*, 1949, **164**, 101.

[45] Owston, *Acta Cryst.*, 1949, **2**, 222.

with substances which have no directed bonds (*e.g.*, metals), care must be taken in interpreting them. In particular, there seems no justification for assuming that they are directly caused by movements of the hydrogen atoms, as has been suggested,[46] or indeed by any peculiarity of ice.[45]

Spectroscopic Evidence relating to Atomic Movements.—The Raman and infra-red spectra of water have been much studied, but for ice the data are less complete. Those shown in Table III are collected from a number of sources, and so are not entirely consistent.[22, 47, 48, 49]

TABLE III

Spectroscopic frequencies (*cm.*$^{-1}$).

State.	ν_1.	ν_2.	ν_3.	Combination band.	Hindered rotation about *CX*.	Hindered translation.	Hindered rotation about *CY*.
Vapour . .	3650	1595	3755				
Liquid at critical point (d 0·4), d_{O-O} = 4·7 Å	3600						
Liquid at 70° .	3448	1642 (K = 22)	3434 (K = 50)	2092 (K = 2·8)			
Liquid at 40° .	3440	1656		2167	320—1020	200	
Liquid at 3° .	3448	1642 (K = 18)	3397 (K = 58)	2149 (K = 3·6)	500	152—225	60
Ice near 0°	3156	1644 (K = 11)	3259 (K = 120)	2222 (K = 7·8)	610	210	54
Ice at − 183°	3090 3135						

K = Absorption coefficient.

In water vapour the three principal modes of vibration result in three sharp lines. Owing to molecular interaction the lines become more diffuse as the gas is cooled or condensed : this is noticeable even in water vapour above the critical point. In water the lines become broad diffuse bands whose maxima are at the frequencies recorded. In ice near 0° the bands are less broad, and at low temperatures (— 183°) only one sharp intense line (with a sharp but weak satellite) appears. The diffuseness of the bands at higher temperatures is presumably due to dipole interaction, since at — 183°, where dipole rotation is unimportant,[28] the lines are sharp. It is not due to mere movements of the atoms since these are still quite large (r.m.s. amplitude 0·25 Å) at — 183°. Born [50] does not agree that the diffuseness

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[46] Lonsdale, *Nature*, 1946, **158**, 582.

[47] Sutherland, *Proc. Roy. Soc.*, 1933, *A*, **141**, 535 ; Barker and Sleator, *J. Chem. Physics*, 1935, **3**, 660 ; Ukholin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1935, **26**, 395 ; Cross, Burnham, and Leighton, *J. Amer. Chem. Soc.*, 1937, **59**, 1134 ; Fox and Martin, *Proc. Roy. Soc.*, 1940, *A*, **174**, 234.

[48] Magat, *Trans. Faraday Soc.*, 1937, **33**, 114.

[49] Cartwright, *Phys. Review*, 1935, **49**, 470 ; Cartwright and Errera, *Proc. Roy. Soc.*, 1936, *A*, **154**, 138.

[50] *Nature*, 1946, **158**, 830.

is due to dipole interaction, but his arguments have been strongly criticized,[51] and have found no support.

The symmetrical stretching frequency of both O–H bonds ν_1, decreases on association, showing that the O–H bond length increases from 0·96 Å in the vapour to $\sim$ 1·0 Å in ice at 0° (Fig. 4). The amplitude of this vibration does not appear to have been estimated, though Wannier considered that it might be as much as 0·4 Å in water, or enough to bring a hydrogen atom to the centre of an O–O bond.

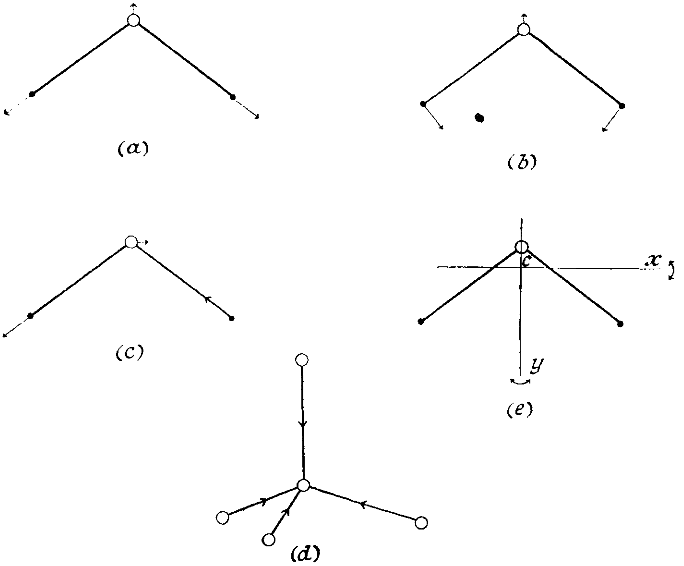

FIG. 4

Modes of vibration : (a) ν_1, (b) ν_2, (c) ν_3, (d) *hindered translation, or contraction of the five-molecule tetrahedron,* (e) *hindered rotation about* CX *and* CY, *where* C *is the centre of gravity of the molecule.*

The frequency of deformation of the bond angle $\mathrm{H\hat{O}H}$, ν_2, varies little with change of state : the intensity of the band is less in ice than in water.

The simultaneous shortening of one bond and lengthening of the other, ν_3, has, like ν_1, a lower frequency in ice than in water or water vapour. The intensity of this band is greater in ice than in water, which is interesting since this vibration, if of sufficient amplitude, could lead to the transfer of hydrogen atoms from one molecule to the next.

Vibrations of still lower frequency occur in water, and in ice the bands are sharper and stronger. One of these bands has a frequency of 210 cm.$^{-1}$ and is attributed [49] to hindered translation, *i.e.*, to stretching of the O–O bonds (Fig. 4*d*). In water, the amplitude of this vibration has been estimated as 0·15 Å, but no estimate has been made for ice. The assignment of this band is confirmed by the fact that it does not appear with

[51] Martin, *Nature*, 1947, **159**, 503.

mixtures of water and dioxan, in which the hydrogen-bond system is broken down, and by the fact that a similar band occurs in liquid formic acid at 180 cm.$^{-1}$. This frequency gives $2{\cdot}7 \times 10^4$ dynes/cm. as the force constant of the hydrogen bond O—H···O in formic acid, which may be compared with $\sim 6 \times 10^5$ dynes for the force constant of the covalent O–H bond, *i.e.*, for the constant controlling the ν_1 vibration.[52]

A second band occurs at 610 cm.$^{-1}$, and is attributed by Magat to hindered rotation or " libration " of the molecule about the axis CX (Fig. 4*e*). These oscillations have an amplitude in water of ± 27°,[49] but here again no estimate appears to have been made for ice. Both these frequencies of 610 cm.$^{-1}$ and 210 cm.$^{-1}$ are found, appropriately modified, in heavy water and heavy ice. Their variation with temperature does not appear to have been studied. A third band, at 60 cm.$^{-1}$, has been found in the Raman spectra of water and ice, and is attributed by Magat to rotation of the molecule about the dipole axis CY (Fig. 4*e*).

Unfortunately, none of these low-frequency bands, which are the most important for studying the intermolecular vibrations, have been fully examined: the available information on them has been summarized by Magat.[36]

The " Statistical " Structure of Ice.—The random structure proposed by Pauling—" random " here having a special, restricted meaning—requires that over a sufficiently long time interval, each of the two available hydrogen positions along each bond is occupied for half the time. In many kinds of experiment it will thus appear that there is half a hydrogen atom in each of the two positions (Fig. 5).

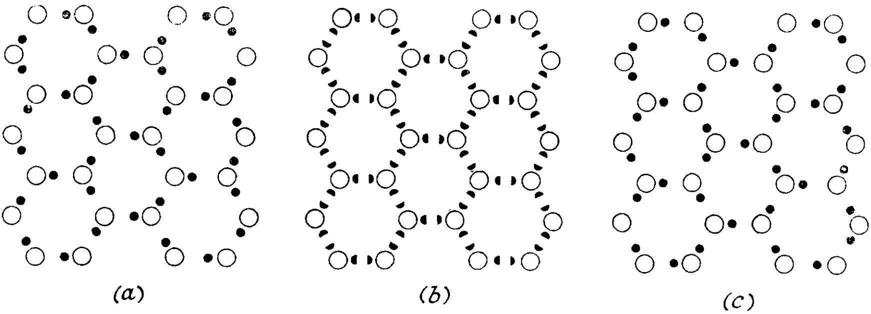

FIG. 5

Part of a layer of molecules viewed along the hexagonal axis : (a) *and* (c) *Possible instantaneous configurations before and after a co-operative movement in which all the dipoles rotated.* (b) *The " statistical " or " half-hydrogen " structure, the time average of all configurations such as* (a) *and* (c).

This should apply to neutron diffraction, which should be able to give the most direct evidence of the positions of atomic nuclei. So far, however, it has only proved possible to examine crystalline powders, not single crystals, and to achieve rather poor resolution. Hydrogen compounds

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[52] Davies, *Ann. Reports*, 1946, **43**, 5.

have the disadvantage that they give a strong incoherent background scattering which obscures the diffraction maxima, but the deuterium analogues can be used instead. The results of a study of D_2O are in general agreement with the " half-hydrogen " structure, though some important lines in the diffraction pattern were not clearly resolved.[53] Other structures considered and found unsatisfactory were : (*a*) Barnes's structure, with the hydrogen atoms midway between the oxygen atoms ; (*b*) Bernal and Fowler's structure, a static ordered arrangement which is one of Pauling's $(3/2)^N$ arrangements ; (*c*) a model in which the hydrogen nuclei rotate *continuously* round the oxygen atoms.

Another promising method of finding the positions of atomic nuclei which have spin is that involving nuclear magnetic resonance, and in one case of a crystal containing water, *viz.*, gypsum, $CaSO_4,2H_2O$, it has been found possible to show that the hydrogen atoms are in the positions along the hydrogen bonds which would be expected from Bernal and Fowler's work.[54] A fixed magnetic field and an alternating magnetic field are applied to the specimen in two directions at right angles, and at the appropriate frequency of alternation the nuclear magnetic moment rotates in resonance with the applied field : a maximum is then observed in the voltage induced in a coil whose axis is at right angles to the directions of the two applied fields. Fine structure in this resonance peak is caused by interaction between nuclei, and since it varies with the direction of the applied field relative to the crystal axes, it is possible to find the distance between nuclei which have spin and the directions of the lines joining them. In the case of ice no such fine structure is found, indicating that the hydrogen nuclei have no fixed position : and the resonance maximum is very sharp, which would agree with " shuttling " of the nuclei along the bonds. This resonance, once set up, persists after the fixed field is switched off, until destroyed by thermal agitation : the half-life of the resonance state is related, in ice, to the time of dipole relaxation, as would be expected.[55]

In *X*-ray or neutron diffraction, experiments usually last for some hours, and the structure thus revealed is an average one : its unit cell is identical in size with that found by Barnes, and has sixteen equivalent positions in the space group $C6/mmc$ occupied by half a hydrogen atom. This would be expected whether the randomness of position of the hydrogen atoms were static or dynamic, though the dielectric behaviour of ice seems to leave no doubt that it is dynamic.[46] As a result, all four bonds linking any molecule to its neighbours appear, in this statistically average structure, to be identical. The molecules appear to have full tetrahedral symmetry and no distinction is possible between the two " incoming " and the two " outgoing " hydrogen bonds.

Intermolecular Forces.—We have seen that for some purposes we must consider the crystal as a whole, since no unique structure is possible, while for others a statistically average unit cell containing four molecules is

[53] Wollan, Davidson, and Shull, *Phys. Review*, 1948, **73**, 842.
[54] Pake, *J. Chem. Physics*, 1948, **16**, 327.
[55] Bloembergen, Purcell, and Pound, *Phys. Review*, 1948, **73**, 697.

adequate. The unit we wish to understand, however, is the individual molecule as it exists in the bound state, and its bonds with its neighbours.

The term " the strength of a hydrogen bond " needs careful definition,[56] but is usually represented by the overall change in energy which occurs when the bond is formed. In ice this is 5·8 kcal./mole, half the heat of vaporisation of ice at 0° K. This may be compared with the mean heat of formation from its atoms of the covalent O–H bond in water, 110 kcal./mole. The force constants $\sim 3 \times 10^4$ dynes/cm. and $\sim 6 \times 10^5$ dynes/cm. for the corresponding bonds in formic acid have already been mentioned.

It is fairly well established that the attractive forces in hydrogen bonds are mainly electrostatic. The net force between two water molecules can be explained in terms of various models in which the charge distribution is approximately represented by a set of point charges. Bernal and Fowler assumed that the hydrogen atoms have partly lost control of their electrons so as to leave charges of $-e$ on the oxygen atom and $+\frac{1}{2}e$ on each hydrogen atom. Verwey [23] took more careful account of the screening effect of the electrons, arriving at quite similar results when calculating the dipole moment of the water molecule, 1·84 D., and the net interaction energy between molecules. This type of treatment can give results in good agreement with experiment, but this is admittedly often fortuitous, owing to a cancellation of errors or to the use of parameters whose values, though reasonable, are somewhat arbitrarily chosen.[21]

The experimental determination of the exact charge distribution has unfortunately not yet been achieved, apart from the arrangement of the atomic nuclei. *X*-Ray diffraction measurements on water vapour have been made and agree with a distribution of electrons intermediate between two possibilities, *viz.*, (*a*) that all the electrons become attached to the oxygen atom which then scatters exactly like a spherically symmetrical neon atom, and (*b*) that the hydrogen atoms retain their electrons in spherically symmetrical orbits round their own nuclei, as if no chemical bonding at all had occurred.[57] At best, however, work on the vapour can give only a mean spherically symmetrical electron distribution, averaged over all possible orientations of the molecule.

We have already seen that *X*-ray diffraction by ice indicates a molecule which has at least tetrahedral symmetry whatever the instantaneous configuration of the molecule may be. Barnes's work, however, shows the electron distribution to be spherically symmetrical round the oxygen atoms. This conclusion rests upon the absence of a certain group of *X*-ray reflections, which are in fact found on closer examination to be present, though weak. The molecular centres therefore are arranged as described by Barnes, but the electron distribution round these centres has tetrahedral symmetry, on the average.[58] A quantitative study of the distribution is not yet complete, however.

The idea has frequently been put forward on wave-mechanical grounds

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[56] Fox and Martin, *Trans. Faraday Soc.*, 1940, **36**, 897.

[57] Thomer, *Physikal. Z.*, 1947, **38**, 48 ; Pirenne, *J. Chem. Physics*, 1939, **7**, 144.

[58] Owston, *Brit. J. App. Physics*, 1950, **1**, 314.

that the instantaneous configuration of the electron distribution is to a large extent tetrahedral.[59] In its most extreme form the ten electrons of the molecule are supposed to lie, two in the inner *s* shell, and eight in four equivalent tetrahedrally directed orbitals, in a way analogous to the sp^3 hybridisation of carbon : two hydrogen nuclei lie along two of these otherwise identical directions. The same electron distribution should be found for all the iso-electronic series, Ne, HF, H_2O, NH_3, CH_4.

This picture is, of course, over-simplified, and it is found experimentally that Ne, H_2O, NH_3, and CH_4 have not the same electron distribution.[57] Theoretical treatment also indicates that it is not entirely correct so far as an individual water molecule is concerned,[60] but that in water or ice the effect of neighbouring molecules is to increase this tendency to a tetrahedral distribution. The electrostatic forces between two molecules are then regarded as being mainly due to attraction between a lone pair of one molecule and a hydrogen nucleus of the other. The calculated values of interaction energies, dielectric constant, dipole moment, and bending-force constant of the hydrogen bond are in good agreement with experiment. An electron distribution of the kind just described was found necessary to calculate the bending-force constant, rather than systems of point charges which make the bonds in the model much too directive.[60]

The flexibility of the hydrogen bonds permitted in this model may well explain why crystals of ice near 0° retain their unusual perfection and regularity of structure [61] in spite of the violent thermal agitation of the molecules, and also why ice, though highly crystalline, can flow under pressure like a viscous liquid.

Summary.—The conclusions which may be drawn concerning the structure of ice-I may be divided into three main parts :

(*a*) The positions of the atomic nuclei.
(*b*) The distribution of the electrons.
(*c*) The inter-atomic and inter-molecular forces.

It is with the first of these that much previous work has been concerned, and it is found that the usual view of a crystal as a rigid, static assembly of molecules of mathematically precise regularity is inadequate. This view is not correct for any real crystal, except perhaps at 0° K., and cannot be correct for ice even at 0° K. The main molecular centres, which lie very near to the oxygen nuclei, are arranged in an orderly way, so that each is equally distant from its four nearest neighbours, which are arranged in a tetrahedron around it : the symmetry of the whole assembly is hexagonal, space-group *C*6/*mmc*. The precise order is disturbed by thermal vibrations, which have an r.m.s. amplitude of 0·4 Å at 0°, and 0·25 Å at − 183°. Round each molecular centre are four positions, 1·0 Å away from the centre, and lying one on each of the four tetrahedrally directed lines joining the centre of its four nearest neighbours. These positions may be occupied by

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[59] Mulliken, *Phys. Review,* 1942, **41,** 756 ; *J. Chem. Physics,* 1934, **3,** 506, 514.
[60] Lennard-Jones and Pople, *Proc. Roy. Soc.*, 1951, *A*, **205,** 155 ; Pople, *ibid.*, p. 163.
[61] Lonsdale, *Phil. Trans.,* 1947, *A*, **240,** 219.

hydrogen nuclei, subject to the restrictions that there may be only one hydrogen nucleus on each intermolecular line, and that only two of the positions next to any centre may be occupied. This arrangement of hydrogen nuclei is not only not regular, but also is not static. During the stronger thermal vibrations, the hydrogen nuclei may move from one possible position to another, either by rotation of an H_2O molecule, or by transfer of a proton from one molecule to another. When this occurs, hydrogen atoms in neighbouring molecules must move, so that co-operative or group movements occur. These co-operative movements may consist of the simultaneous readjustment of a local group of molecules or of a chain reaction. The changes of orientation of the molecules are relatively infrequent, for only 1 in 10^9 molecules is changing at any instant at 0°, and about 1 in 10^{11} at $-60°$, but they are enough to control the dielectric properties of ice.

Because of the irregularity of position of the hydrogen nuclei, the average arrangement of all the molecules in a crystal consists of four " half-hydrogen " nuclei vibrating about the four positions permitted to hydrogen nuclei, and an oxygen nucleus vibrating about the mean molecular centre. This is also the average arrangement of any individual molecule, since each permitted hydrogen position is occupied, on the average over a sufficient time, for half the time.

The electron distribution in this hypothetical " average molecule " is not spherically symmetrical about the mean molecular centre, but is to some extent distorted in the directions of the oxygen-to-oxygen bonds. The extent of this tetrahedral distortion is not known, but theoretical reasons have been advanced for supposing it to be considerable. It is in fact suggested that the electron distribution of the individual molecules in ice is mainly tetrahedral all the time, and is little affected by changes in position of the hydrogen nuclei.

The forces between the oxygen and hydrogen atoms in the H_2O molecule in ice are not markedly different in kind or strength from those in the free vapour molecule, and are due to strong, essentially covalent bonds. The angle between the two O–H bonds appears to increase from $104\frac{1}{2}°$ in the vapour to $109\frac{1}{2}°$ in ice : this change may be real, or may be apparent, since the bond angle between the mean nuclear positions in the " average molecule " must be the tetrahedral angle, even if the bond angle in each molecule differs slightly from $109\frac{1}{2}°$: the small difference in ν_2 in vapour and ice (Table III) suggests that the change in bond angle may be negligible.

The forces between the molecules are of the " hydrogen-bond " type and have a force constant and energy of formation approximately one-twentieth as great as those of the inter-atomic bonds. They appear to be due to electrostatic interaction between the molecules, though various suggestions about the nature and positions of the interacting charges have been made. In the most recent, and apparently so far the most satisfactory suggestion, there are supposed to be positive point-charges at the mean nuclear positions, with the electrons distributed in a tetrahedrally symmetrical negative cloud. Such forces would be little affected by bending of the intermolecular bonds, or by changes in the positions of the hydrogen nuclei (except whilst they are changing). This might explain the apparently viscous properties of ice, and why, in spite of its random structure, it attains such unusual crystalline perfection.

These conclusions about the nature of the water molecule apply only to the molecules in ice, and perhaps, in a slightly modified form, in liquid water. The co-operative movements in particular can occur only in a system of molecules linked by hydrogen bonds, forming at least a ring of six. The tetrahedral symmetry of the molecule is due, in part at least, to the tetrahedral symmetry of its environment in ice, though McFarlan's work on the high-pressure forms ice-II and ice-III suggests that the tendency to form four equal tetrahedrally-directed bonds is strong. In an environment very different from that in ice, however, *e.g.*, in a strong electrostatic field when linked as water of hydration to an ion, its structure and behaviour may be much altered.

The preparation of this Review was begun while the author was in receipt of a research grant from the Agricultural Research Council, and completed during the tenure of an I.C.I. Research Fellowship of the University of London.