STRUCTURE AND PROPERTIES OF ICE

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BY

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I

THE POSITION OF THE HYDROGEN ATOMS AND THE ZERO-POINT ENTROPY OF ICE

1. Historical introduction.

In the middle of the thirties, a certain finality appeared to have been reached with regard to the opinion on the structure of ice. BARNES[1]) had shown that the oxygen nuclei lay in puckered hexagonal layers, in which oxygen atoms were raised and lowered alternately (see fig. 1). Adjacent layers were mirror-images and
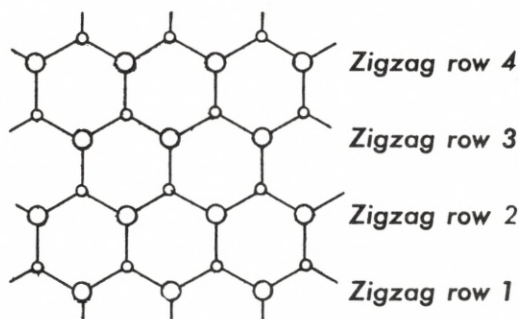

Fig. 1. Projection of a layer of oxygen atoms in an ice crystal. The small circles are oxygen atoms below the level of the paper, and the large circles, oxygen atoms above the level of the paper.

the parameters were adjusted so that each oxygen nucleus was surrounded by 4 oxygen nuclei in a regular tetrahedral arrangement at a distance of 2.76 Å. BERNAL and FOWLER[2]) had shown that it is probable that the *protons* lie on the linkages between the oxygen nuclei, ca. 1 Å. from one and 1.76 Å. from the other. One and only one proton lies on each linkage, and the arrangement is such that each oxygen nucleus has two and only two protons at a distance of ca. 1 Å. from it. In this way the ice is built up of molecules closely approaching the form and size, which MECKE[3]) has calculated for the molecule of water vapour from the infra-red spectrum (isosceles triangle with the oxygen nucleus at the apex, apical angle ca. 106° and sides 0.97 Å.). An

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extremely large number of such proton arrangements are possible. BERNAL and FOWLER tended to assume that the arrangement in ice was irregular, in any case in the region of the melting point. They write: "In that case ice would be crystalline only in the position of its molecules, but glass-like in their orientation."

Finally, in 1935 PAULING[4]) pointed out that DEBYE's investigations on the dielectric properties of ice showed that the configuration of ice must alternate between the many alternatives given by BERNAL and FOWLER. PAULING calculates the number of possible configurations of an ice crystal to $(^3/_2)^N$, where N is the number of molecules in the crystal, and by assuming that all these configurations, even at low temperature, are equally probable, he arrives at the result that ice must have a zero-point entropy of $k \ln(^3/_2)^N = R \ln(^3/_2) = 0.806$ kcal/gmol/degree. This value agrees extremely well with the value of 0.82 ± 0.15 kcal/gmol/degree found experimentally by GIAUQUE[5]). On account of this excellent agreement, the problem of the structure of ice had since generally been considered as solved.

The way in which PAULING develops his formula for the number of configurations only gives the formula as an approximation. PAULING considers the proton-condition for a first, randomly chosen, oxygen atom in the lattice, while an exact development requires that also, and especially, the conditions for the other atoms should be considered. For these the proton-position in the direction of the previously considered adjacent atoms is already defined.

An exact development of the formula can be obtained in the following way: We have an ice crystal, in which the position of all the oxygen atoms is known, and we will now determine the number of possible proton configurations. Let us imagine that we have decided on the proton configurations around all the oxygen atoms in and beneath one of the puckered hexagonal layers. Let us furthermore assume that we have decided on the situation around the oxygen atoms in a zig-zag row above this layer, and are now going to investigate the number of configurations during the construction of an adjacent zig-zag row. It can easily be seen that, if the crystal is large, it is only the conditions during this construction that must be investigated in order to solve the problem. We will now choose to place the new zig-zag

row at that side of the first, where the low-lying molecules are present. In fig. 1, this means that the new zig-zag lines must be placed in the order 1, 2, 3, 4. When we do this, the new oxygen atoms, for which the proton configuration must be decided, will always have two adjacent atoms already in position, for which the configuration is decided. If these two adjacent atoms both have protons in the direction towards the atom considered, or if they both have no protons in this direction, then the proton placing around the atom considered is unambiguously decided. On the other hand, if the proton situation is different towards the two adjacent atoms, the proton placing can be performed in two ways.

Let us call the number of configurations in the system so far constructed, $A + B$, where A is the number of configurations, in which the two adjacent atoms show the same proton situation, and B, the number of configurations in which they show different proton situations towards the new oxygen atom. Hence the number of possible configurations rises from $A + B$ to $A + 2B$, when this atom is included in the system. Around each oxygen atom, and hence also around the oxygen atom last added, two protons can be placed in six different ways. In the group of configurations, the number of which we have calculated above to be $A + 2B$, the 6 ways occur in the following numbers: $A/2$, $A/2$, $B/2$, $B/2$, $B/2$ and $B/2$. Since, for reasons of symmetry, these numbers must be equally large, A must be equal to B. As a result, the number of possible configurations for each oxygen atom in the ice crystal rises in the ratio $(A + 2B)/(A + B) = {}^3/_2$ and the total number of configurations becomes $({}^3/_2)^N$.*

2. Mirror symmetric and centric symmetric atom pairs in ice.

In PAULING's calculation of the zero-point entropy of ice it is assumed that all the possible configurations are so similar in energy that, even at the temperature at which they are fixed by freezing, they can be considered as equally probable. PAULING

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expressed this (in "Nature of Chemical Bond" 2nd ed. 1945 p. 302) in the following words: "and that under ordinary conditions the interaction of non-adjacent molecules is such as not to stabilize appreciably any one of the many configurations satisfying these conditions with reference to the others." The excellent agreement found by PAULING between the calculated and the found zero-point entropy of ice made such a great impression that this assumption was accepted without any serious examination. It is, however, possible that too great emphasis has been laid on this agreement. GIAUQUE's value for the zero-point entropy occurs as a small difference between two large values: GORDON's[6]) spectroscopic value for the entropy of water vapour at $25°$ C and 1 atmos. (45.1 ± 0.1) and GIAUQUE's[5]) thermically determined value for the difference between the entropy of water vapour at $25°$ C and 1 atmos. and of ice at $0° K$ (44.28 ± 0.05). It is perhaps possible that these values are not so accurately determined as the authors themselves think. In addition to the random errors, which are given in the above expressions, there may be systematic errors. We will therefore now try to investigate whether the assumption of PAULING has been justified.

As an introduction to the investigation of the energy content of the different configurations, we will attempt to find an explanation for the reason why ice crystallizes differently from diamond, although the arrangement of the 4 adjacent atoms around an atom is the same in both cases, when we consider only the carbon and oxygen atoms and disregard the protons. The difference between the two arrangements can first be seen, when the six adjacent atoms around an atom pair are considered. The same circumstances, which cause the oxygen atoms in ice to be arranged in another way than the carbon atoms in diamond, can also be expected to make the configurations in ice energetically different.

In diamond, the arrangement around an atom pair is always *centre symmetric* (see fig. 2). If the 6 adjacent atoms are projected onto a plane at right angles to the linkage between the two atoms, the 6 atoms form a regular hexagon.

In an ice crystal, the arrangement around oxygen atom pairs, which lie in the same puckered hexagonal layer, is centre symmetric, as in diamond; but around atom pairs, whose atoms lie

in different layers, the arrangement is *mirror symmetric* (see fig. 2). If the 6 adjacent atoms are projected onto a plane perpendicular to the linkage between the two atoms, the adjacent atoms coincide in pairs. In ice $1/4$ of the atom pairs are in mirror symmetric and $3/4$ in centric symmetric positions. It is probably not possible
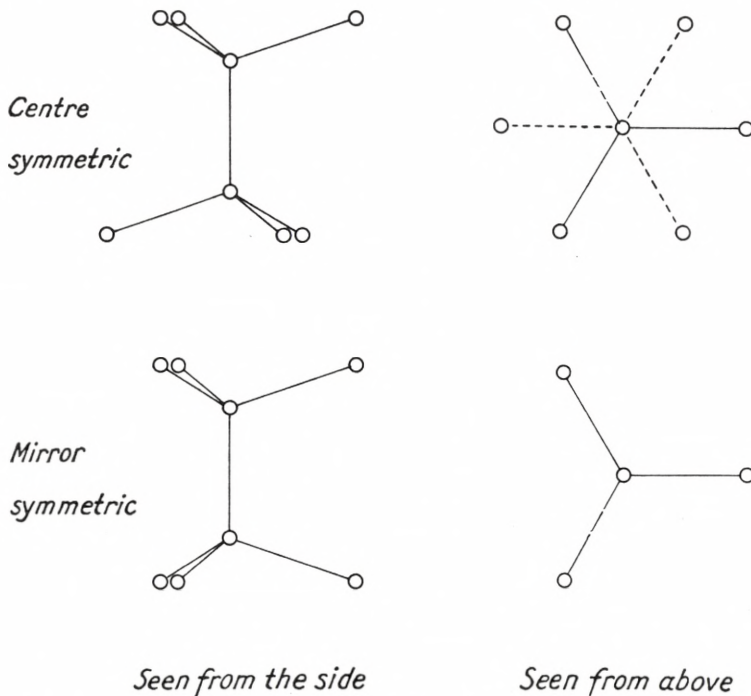

Fig. 2. Centre symmetric and mirror symmetric positions of oxygen atoms in ice.

to construct a crystal in which more than $1/4$ of the atom pairs are in mirror symmetric positions, if the arrangement around all the atoms is to be regularly tetrahedral. In an ice crystal, there are presumably as many mirror symmetric atom pairs as possible present.

The centric symmetric arrangement in diamond can be explained as a result of the repulsion between the electrons around the 6 adjacent atoms. But why does the mirror symmetric arrangement occur in ice and even in as high a proportion as possible? This suggests that the mirror symmetric position for water molecules is more stable and poorer in energy, than the centric sym-

metric. If this is actually the case, then the distance between the atoms in mirror symmetric atom pairs ought to be less than the distance between atoms in centric symmetric atom pairs.

Accurate measurements on ice crystals have been carried out by HELEN D. MEGAW[7]). She made her measurements in order to investigate whether there was a difference between ice from heavy and from light water, but she found no difference. From her measurements it is possible to calculate the ratio c/a between the hexagonal main axis and the secondary axes perpendicular to the main axis to 1.6283, varying between 1.6276 and 1.6287 for both heavy and light ice. In the ideal structure, with equally large distances and equally large angles everywhere, the ratio is $c/a = \sqrt{\dfrac{8}{3}} = 1.6330$. The deviation from this figure is small, but must be considered as indubitably significant. If the deviation is to be explained by differences in atomic distances, the distances in mirror symmetric atom pairs must be 0.55 $^0/_0$ shorter than the distance in centre symmetric atom pairs. $\left(\left(\dfrac{2}{3}+2x\right):\sqrt{\dfrac{8}{3}}=1.6283\right.$ gives $x = 0.9945$). A little of the deviation may perhaps be explained by inequality in the angles between the linkages of the atoms; but this inequality can scarcely be considerable, since no reasonable cause for this can be seen. The mirror symmetric linkages must therefore be several $^1/_{10}$ $^0/_0$ shorter than the centre symmetric. In consideration of the slight compressibility of ice $(1.2 \cdot 10^5$ per bar) this is not an inconsiderable difference.

If the mirror symmetric linkage between the H_2O molecules is shorter than the centric symmetric, this linkage must also be more stable and poorer in energy than the centre symmetric. This gives us a cause for the fact that ice crystallizes hexagonally and not regularly.

3. An electrical model of the H_2O molecule.

One may well ask, why the mirror symmetric linkage is firmer than the centric symmetric. In order to attempt to find an explanation for this, we will consider the forces which hold the molecules together in ice crystals. A H_2O molecule is an electrical dipole. Assuming that electrostatic forces hold the molecules

together in ice just as electrostatic forces are responsible for holding the ions together in sodium chloride, we will attempt to calculate, from plausible assumptions, the electrostatic internal energy.

Our assumption is not a contradiction of the general practice of designating the bonds between molecules in ice as hydrogen bonds. The so-called hydrogen-bonds must principally be considered to be of electrostatic nature.

In order to calculate the effect of the electrostatic forces between molecules of ice, we must construct an electrical model of a water molecule. We know that the *positive* charges on the nuclei form an isosceles triangle with the oxygen nucleus at the apex and the two protons on the base line. In the water vapour molecule, according to MECKE[3]) the sides are 0.97 Å., but in the molecules of ice, according to CROSS, BURNHAM and LEIGHTON[8]) and PAULING[4]) they are slightly larger, ca. 0.99 Å. The apical angle in the water vapour molecule, according to MECKE, is ca. 106°, hence nearly equal to the tetrahedral angle 109.5°. Even if it is not certain that the protons in an ice crystal lie exactly on the linkages between the oxygen atoms, they must lie very close to them, and in our model, we will assume that they lie on the linkages (fig. 3 a). The three nuclei are encircled by 10 *electrons*. Two of the orbits are quite close to the oxygen nucleus at the apex, and the 8 remaining electrons circle in pairs in 4 eccentric orbits, which radiate tetrahedrally from the oxygen nucleus (comp. BARNES[1]), MULLIKEN[9]) and BERNAL and FOW-LER[2])) (fig. 3 b). The two protons lie within two of these eccentric orbits. The electron orbits completely screen the positive charge of the oxygen nucleus. They also screen a considerable part of the charge of the protons, but give an excess of negative charge in the two eccentric orbits which do not contain protons. We will therefore consider an ice molecule from the electrostatic view-point as a regular tetrahedron of radius 0.99 Å. with positive charges in two corners and negative charges in the other two (figs. 3 c and 3 d). As we shall see later, it is of little importance for our calculations whether the tetrahedron-model should in fact have deviated somewhat from regularity.

It is known from measurements of the dielectric constant of

water vapour that the dipole moment of the water molecule is
1.87 Debye. If the tetrahedral model is to have this dipole moment,
the electrical charges in the corners must be $\pm\, 0.171\, e$ ($e =$ the
electronic charge). Hence the electrons screen most of the elec-
trical charge of the protons, and only give small negative charges
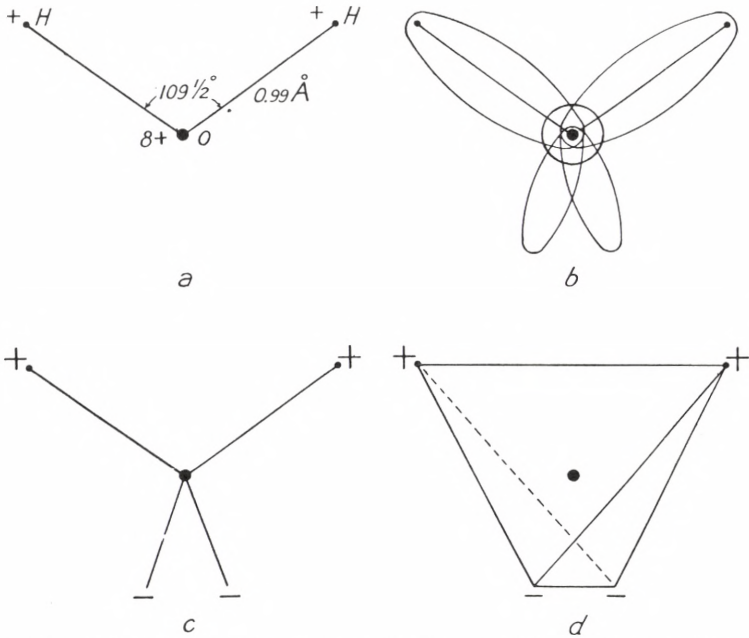in the remaining corners. In ice these tetrahedra are placed

Fig. 3. Electrostatic model of a water molecule: a position of the positive charges
in a molecule, b the electron orbits, c and d two different representations of the
regular tetrahedron model used.

at a mutual distance of 2.76 Å., calculated from their centres.
We will therefore imagine an ice molecule as a sphere of radius
1.38 Å., inside which 4 electrical charges are placed in a regular
tetrahedral arrangement, as described above.

This molecular model of course only represents a rough ap-
proximation to the actual molecule with the negative electricity
of the electrons distributed over large volumes. The simplicity of
the model, however, permits many calculations to be performed
with it, and if these give results, which agree with experience,
it is probable that the model gives us a good representation of
the electrical structure of the H_2O molecule.

4. The electrostatic energy between adjacent molecules in ice.

Two adjacent molecules in ice can have 6 different positions relative to each other. These are presented in figure 4. Position no. 1 can suitably be designated as *inverse* mirror symmetric (ms_1) because the electrical charges at symmetrical places have

1. *Inverse*
mirror symmetric

2. *Oblique*
mirror symmetric

3. *Oblique*
mirror symmetric

4. *Inverse*
centre symmetric

5. *Oblique*
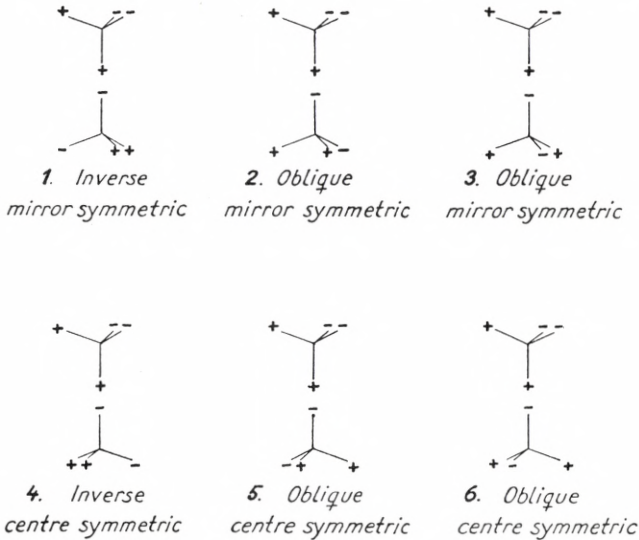*centre symmetric*

6. *Oblique*
centre symmetric

Fig. 4. The 6 positions relative to each other of two adjacent molecules in ice.

opposite signs. No. 2 and no. 3 are energetically alike and can be designated as *oblique* mirror symmetric (ms_2 and ms_3).

Similarly, two molecules in centric symmetric positions can have three different relative positions (see fig. 4). No. 4 will be designated as *inverse* centric symmetric (cs_1) because the electrical charges at symmetrical places have opposite signs. The two remaining (no. 5 and no. 6) are energetically alike and can be designated as *oblique* centric symmetric (cs_2 and cs_3).

The electrostatic energy, to be overcome on separating two electrical molecular models (A and B) is $E_{AB} = (0.171\ e)^2 \Sigma\ 1/r$, where r is the distance between two charges, and the summation must include all 16 combinations of two charges, one from each molecule.

These energies are given in table 1, column 2, headed tetra-
hedron, $r = 0.99$ Å. It can be seen that the energy is rather
different for the 4 possible positions. These E_{AB} values given in
italic type are those with which we shall deal in the following
section.

TABLE 1.

*Electrostatic energies E_{AB} between adjacent molecules in ice, given
in 10^{-12} erg.*

	Tetrahedron					triangle
	$r =$ 0.99 Å	$r =$ 0.69 Å	$r =$ 0.46 Å	$r =$ 0.276 Å	infinit. small	$r =$ 0.99 Å
Mirror sym. inverse (ms_1) ..	*0.5067*	0.312	0.261	0.240	0.220	0.387
— — obliq. (ms_2, ms_3)	*0.4319*	0.217	0.144	0.105	0.055	0.309
Centric sym. inverse (cs_1)...	*0.4117*	0.191	0.111	0.058	0.000	0.290
— — obliq. (cs_2, cs_3).	*0.4792*	0.279	0.233	0.195	0.165	0.355

In order to obtain some idea of the significance of taking the
radius to be 0.99 Å., the other columns in table 1 give the energies
for smaller tetrahedra ($r = 0.69$, 0.46 and 0.276 Å. respectively)
and for an infinitely small dipole. In all cases, it was of course
assumed that the electrical charges had such a size as to give
the dipole moment 1.87 Debye. It will be seen that the energy
falls, when the model is made smaller. The fall is initially rapid,
but later becomes slow. On the other hand, the differences
between the energies of the different positions increase, but
this increase is rather slow. The figures show the importance
of not being satisfied with assuming an infinitely small dipole,
but using a more developed picture of the distribution of the
charges.

The last column in table 1 shows the energy values obtained
by using as model a triangle with apical angle 109.5° and sides
0.99 Å., and with two equally large charges (0.342 e) placed on
the base, and a negative charge, twice as large (—0.684 e) at the
apex. It can be seen that this triangular model gives slightly less
energy than a tetrahedron of radius 0.99 Å., but the differences
between the energies are about the same. Triangular models,
placed in the tetrahedral orientation, which is, however, not very

probable for them, thus give similar energies as tetrahedron models. Hence it may be concluded that the results, drawn from the following discussion, would not have been altered appreciably, if another tetrahedral model had been used, in which the two negative charges had been moved slightly nearer to the centre and the tetrahedron had thus not been regular. It would have been reasonable to use such a model, if it had not made the calculations more difficult.

BERNAL and FOWLER[2]), who first tried to calculate the electrostatic energies of ice crystals, used, for their calculations, a triangular model with positive charges $(0.49 \, e)$ on the base and a negative charge, twice as large, placed on the bisector of the apical angle, slightly below the apex. This model does not fit our views on the electrons in the water molecule, and can not explain the tetrahedral layering of the molecules in ice. It is not easy to see why BERNAL and FOWLER have used this triangular model. They themselves point out the tetrahedral placing of the 8 external electrons of the molecule and the possibility of using this to explain the tetrahedral grouping of the molecules in ice.

5. The electrostatic lattice energy of ice crystals.

The differences between the energies of inverse and oblique positions are, according to table 1, considerable:

$$E_{AB} ms_1 - E_{AB} ms_2 = 0.0748 \; 10^{-12} \; \text{erg.}$$
$$E_{AB} cs_2 - E_{AB} cs_1 = 0.0675 \; 10^{-12} \; \text{erg.}$$

Since, at $273° \, K$, kT is equal to 0.0374×10^{-12} erg., it must be expected that at the melting point ms_1-positions will be present in greater amount than ms_2 and ms_3 and that cs_2- and cs_3-positions will be present in greater amount than cs_1-positions, and the preferences must be expected to be even more pronounced at lower temperatures. The size of this temperature dependence will be considered later. We will here just assume that at low temperature the inverse position (ms_1) will be predominant among the centric symmetric, while at high temperature the inverse and the two oblique positions will approach equal probability.

This result is not in opposition to the observations made by

WOLLAN, DAVIDSEN and SHULL[10]) on the diffraction of neutron beams. These authors have shown that in ice "on the average two hydrogen atoms will be found close to a given oxygen atom", and that the arrangement on the whole is irregular. This does not contradict the view given above, as according to that view there should be no periodic regularities in the placing of the protons in the crystal lattice of ice.

At low temperature the mean electrostatic lattice energy between adjacent molecules in an ordinary *hexagonal* ice crystal will be in mean $^1/_4 E_{AB} ms_1 + ^3/_4 E_{AB} cs_2$ and at high temperature (which, however, is far from being reached at the melting point of ice) it will be: $^1/_{12} E_{AB} ms_1 + ^1/_6 E_{AB} ms_2 + ^1/_4 E_{AB} cs_1 + ^1/_2 E_{AB} cs_2$. In a hypothetical ice crystal with diamond structure, in which all positions are centric symmetric, the electrostatic energy between adjacent molecules would be in mean: at low temperature $E_{AB} cs_2$ and at high temperature $^1/_3 E_{AB} cs_1 + ^2/_3 E_{AB} cs_2$. The total lattice energy between all adjacent molecules is obtained by multiplying these mean values by $2N$, where N is the number of molecules. In table 2 are presented the lattice energies thus calculated, given in kcal/gmol.

TABLE 2.

The electrostatic lattice energy of ice crystals, calculated from the energies between adjacent molecules.

	Ordinary hexagonal ice crystal	Hypothetic ice crystal with diamond structure
At low temperature	14.04 kcal/gmol.	13.88 kcal/gmol.
At high temperature	13.21 —	13.23 —

The electrostatic lattice energy must be assumed to constitute the main part of the heat of sublimation of ice. The values for hexagonal ice in table 2 are somewhat higher than the experimentally determined heat of sublimation of ice: 12.14 kcal/gmol at 0° C. In order to obtain from the electrostatic lattice energy an accurate value for the heat of fusion of ice, it is, however, necessary to subtract the potential of the repulsive forces, which hold the molecules in place at a distance of 2.76 Å. and to add the potential of the VAN DER WAAL's forces, hence a better agree-

ment could scarcely be expected. BERNAL and FOWLER[2]) have shown that it is possible to obtain a heat of sublimation of the right order of magnitude by electrostatic calculation from their triangular molecular model. Using their estimated corrections for the repulsive forces (— 6.8), for the VAN DER WAAL's attraction (+ 4.1) and for the attraction of next neighbours (+ 1.1), the latter however with opposite sign, we calculate for the heat of sublimation of ice:

at low temperature............ $14.0 - 6.8 + 4.1 + 1.1 = 12.4$
at high temperature........... $13.2 - 6.8 + 4.1 + 1.1 = 11.6$

The electrostatic lattice energies in table 2 give us a possibility of obtaining a better understanding of the reason why ice crystallizes hexagonally and not as diamond cubically. Admittedly the energies at high temperature are practically speaking the same for the hexagonal and for the cubic lattice, but at low temperature the lattice energy is 0.16 kcal/gmol higher for the hexagonal than for the cubic lattice, and as we shall see later, the melting point of ice must, in this connection, be considered as a low temperature. A difference in the lattice energies of 0.16 kcal/gmol is perhaps rather small to explain why the hexagonal lattice is to be preferred; however, it will later be shown that the difference increases to 0.42 kcal/gmol, when the electrostatic energies between molecules, which are separated by a single molecule, (next neighbours) are taken into consideration (table 4). For polymorphous compounds having a temperature of transformation in the region of ordinary temperatures, the heat of transformation is often no greater. Thus the heats of transformation between the different known modifications of ice lie within values of from 0.016 to 0.304 kcal/gmol, and the heats of transformation for the solid modifications: of HCl is 0.248, of HBr 0.165 and 0.113, of HJ 0.126 and of H_2S 0.108 and 0.361. For NH_4Cl the two heats of transformation have been found to be: 0.200 and 0.427, for NH_4NO_3 0.402 and for $CaCO_3$ 0.30, all figures in kcal/gmol and according to Landolt-Börnstein, 3rd suppl. The heat of transformation for transformation of rhombic sulphur to monoclinic sulphur is 0.84. The molecule of sulphur is, however, also rather large, S_8.

6. The electrostatic energies between molecules of ice, which are separated by one or more molecules.

The electrostatic energies between molecules which are not adjacent have been ignored in the considerations so far described. However, the orientation of the other molecules around an adjacent molecular pair may be dependent on whether this pair is in centric symmetric or mirror symmetric position and whether this position is inverse or oblique. It is therefore possible that the electrostatic energies of the surrounding molecules could neutralize the differences in energy found for the 4 different positions of a molecular pair. If this was the case, the inverse and the two oblique positions would be equally probable and the proportion between them would be independent of temperature. We will therefore examine the electrostatic energies between molecules which are not adjacent, more closely.

The electrostatic energies (E_{AC}) between two molecules, (A and C), which are separated by a single molecule (B), are far lower than the energies E_{AB} between adjacent molecules, and the electrostatic energies (E_{AD}) between two molecules (A and D), which are separated by two molecules (B and C), are even lower still. These molecules lie farther from each other and they are in addition more randomly orientated. A completely random orientation would reduce their contribution to zero.

Table 3 gives the result of a calculation of the electrostatic energies (E_{AC}) between molecules, which are separated by one molecule.

The three molecules A, B and C can have a total of 72 different positions relative to each other. The energy for all these positions can be read off in the table.

A and C present either a positive or negative corner to B. Since the energy of the system can not be changed, when we invert all charges, however, we only need to examine the two possibilities: that A and C present differently charged corners to B and that they present similarly charged corners to B. In the first case, when the energy is positive, we will designate the position as an a-position, and in the other case, when the energy is negative, as a b-position. In ice, A and C must either both be in centric symmetric (cs) position to B, or one must be in centric symmetric

TABLE 3.

Electrostatic energies E_{AC} between two molecules (A and C) in ice, separated by one molecule (B), given in 10^{-12} erg.

A and C's position to B	a	b	A and C's position to B	a	b
$cs_1\ cs_1$..........	0.0267	— 0.0450	$cs_1\ ms_1$.........	0.0439	— 0.0151
$cs_1\ cs_2$..........	0.0611	— 0.0300	$cs_1\ ms_2$.........	0.0194	— 0.0451
$cs_1\ cs_3$..........	0.0300	— 0.0300	$cs_1\ ms_3$.........	0.0516	— 0.0451
$cs_2\ cs_1$..........	0.0611	— 0.0300	$cs_2\ ms_1$.........	0.0194	— 0.0516
$cs_3\ cs_1$..........	0.0300	— 0.0300	$cs_3\ ms_1$.........	0.0451	— 0.0516
$cs_2\ cs_2$..........	0.0267	— 0.0267	$cs_2\ ms_2$.........	0.0439	— 0.0439
$cs_2\ cs_3$..........	0.0300	— 0.0611	$cs_2\ ms_3$.........	0.0516	— 0.0194
$cs_3\ cs_2$..........	0.0300	— 0.0611	$cs_3\ ms_2$.........	0.0451	— 0.0194
$cs_3\ cs_3$..........	0.0450	— 0.0267	$cs_3\ ms_3$.........	0.0151	— 0.0439

and the other in mirror symmetric (*ms*) position to B. Of the 6 AC pairs around a B molecule, 3 are *cs-cs* and 3 *cs-ms*. Finally, both for *cs-* and *ms*-positions there are 3 possibilities: an inverse position (cs_1 and ms_1) and two oblique positions (cs_2 and cs_3, ms_2 and ms_3). The symbol $b\,cs_1\,ms_2$ denotes a position, in which A and C present similarly charged corners to B, and A is in inverse centric symmetric position to B, while C is in oblique mirror symmetric position to B. Since the two oblique positions in the asymmetric ABC-system are no longer necessarily energetically alike, we must now differentiate between them.

This is done in the following way. When a molecule (A), as seen from an other molecule (B), must be turned through 120° *clockwise* in order to obtain an inverse position to it, we will denote the position as a 2-position (cs_2, ms_2). When the same effect is obtained by turning it 120° *counterclockwise*, we will call the position a 3-position (cs_3, ms_3). For *a*-positions it is furthermore necessary to clear that the charges of the B molecule must be placed so that by turning the B molecule 120° clockwise, seen from A (or C) around an axis through the A (or C) molecule, the corner towards C (or A) is brought over to a corner with the same sign. Let us denote the other possibility as an a'-position. On mirroring and subsequent inversion of an ABC-system, 2-positions are changed to 3-positions, 3-positions to 2-positions and *a*-positions to a'-positions. Since mirroring and inversion do not change the energy, we need not consider a'-positions especially. A *b*-position on inversion becomes a *b*-position again.

A control of the correctness of the calculations is obtained in

the following way. It can be shown that the following rule is valid: the E_{AC}-value for an a-position is numerically equal to the E_{AC}-value for a b-position, if the indices are calculated for the a-positions according to the following rule: $1 \rightarrow 2$, $2 \rightarrow 3$, $3 \rightarrow 1$.

7. The electrostatic lattice energy of ice crystals calculated with consideration of the energies between non-adjacent molecules.

Six molecules are connected with a pair AB of adjacent molecules. We consider the E_{AC}-values of these 6 C-molecules correctly if we add half of their 6 E_{AC}-values to the E_{AB}-value in question. When calculating the lattice energy of the whole crystal from E_{AB}-values, each E_{AC}-value will be accounted for by two adjacent molecular pairs (AB and BC). The calculation of such corrected E_{AB}-values is made difficult by the fact that the ratio between inverse and oblique positions depends on the temperature. In the following section, the calculation is performed for the two limiting cases, corresponding to high temperature and to low temperature. By high temperature we understand here a temperature at which the inverse and oblique positions, in spite of their different energies, are equally probable, not only within whole ice crystals, but also within the different types of positions (a and b, cs and ms). (This state, however, is far from being reached at the melting point of ice). By low temperature we understand a state in which inverse positions are quite predominant among ms-positions, and oblique positions are quite predominant among cs-positions (comp. table 6).

Around a mirror symmetric molecular pair in an ordinary hexagonal ice crystal, all AC-positions will be of the type cs-ms, and $^2/_3$ of them will be a-positions, and $^1/_3$, b-positions. Around a centric symmetric molecular pair 4 positions will be of cs-cs type and two of cs-ms type. Of the 6 positions, $^2/_3$ will be of the a-type, and $^1/_3$ of the b-type, and we will assume that this is also true within the cs-cs group and the cs-ms group.

If this assumption should not be justified, it will only serve to increase the inaccuracy of the assumption that all $(^3/_2)^N$ configurations of an ice crystal are equally probable.

By using the E_{AC}-values in table 3 and the E_{AB}-values in table 1, the corrected E_{AB}-values (E_{AB} cor.) presented in table 4 are obtained.

If these corrected E_{AB}-values are used in place of those previously used, the electrostatic energies between molecules, which are separated by a single molecule, are taken into consideration in the correct way.

TABLE 4.

Electrostatic energies between two adjacent molecules in ice, corrected for the E_{AC}-values of the adjacent 6 molecules. The values are given in 10^{-12} erg.

A. Ordinary *hexagonal* ice crystal.

	E_{AB}	$6/2\ E_{AC}$	E_{AB} cor.
1. At *low temperature*.			
AB mirror sym. inverse (ms_1)	0.5067	0.0129	0.5196
AB — — oblique (ms_2, ms_3)	0.4319	0.0462	0.4781
AB centric sym. inverse (cs_1)	0.4117	0.0415	0.4532
AB — — oblique (cs_2, cs_3)	0.4792	0.0351	0.5143
2. At *high temperature*.			
AB mirror sym. inverse (ms_1)	0.5067	0.0328	0.5395
AB — — oblique (ms_2, ms_3)	0.4319	0.0394	0.4713
AB centric sym. inverse (cs_1)	0.4117	0.0430	0.4547
AB — — oblique (cs_2, cs_3)	0.4792	0.0351	0.5143

B. Hypothetical ice crystal with diamond structure.

	E_{AB}	$6/2\ E_{AC}$	E_{AB} cor.
1. At *low temperature*.			
AB centric sym. inverse (cs_1)	0.4117	0.0611	0.4728
AB — — oblique (cs_2, cs_3)	0.4792	0.0220	0.5012
2. At *high temperature*.			
AB centric sym. inverse (cs_1)	0.4117	0.0435	0.4552
AB — — oblique (cs_2, cs_3)	0.4792	0.0351	0.5143

The results of similar calculations for a hypothetical ice crystal with diamond structure are also given in table 4. At low temperature it is assumed that the majority of positions is oblique

2*

(cs_2 and cs_3) and at high temperature that the positions cs_1, cs_2 and cs_3 are equally frequent.

Calculations on the energies between molecules, which are separated from each other by two or more molecules, would be almost impossible to perform. The energies E_{AD} between molecules A and D, which are separated by the two molecules B and C, will, however, only contribute a very small effect, and the effect will tend to make the differences between the 4 "corrected" E_{AB} slightly larger. This can be estimated by considering systems of 4 consecutive molecules A, B, C, D, the outermost molecules of which are simplified to real dipoles by coalescence of the three outermost charges in the tetrahedral models to a single charge at the centre of the triangle formed by the corners at which they are placed. It is permissible to make this approximation when it may be assumed that the three ways in which the three charges can be placed are equally probable. Molecules, separated from each other by more than three molecules, will be so randomly orientated with respect to each other that their mutual internal energy can be considered as being, on the average, insignificant.

With the corrected E_{AB} from table 4, the following differences between the energies for inverse and oblique positions are obtained, (the figures expressed in 10^{-12} erg):

	With corrected E_{AB}-values		Previous calculation with uncorrected E_{AB}-values
	Low temp.	High temp.	
$E_{AB}ms_1$—$E_{AB}ms_2$	0.0415	0.0682	0.0748
$E_{AB}cs_2$—$E_{AB}cs_1$	0.0611	0.0594	0.0675

It will be seen that consideration of the E_{AC}-values has made the differences less. It is, however, only the difference between the two types of ms-bonds, which has become appreciably less, and only at low temperature. The differences are still larger than kT at $0°C$ (0.0374×10^{-12} erg). Our previous considerations on the predominance of inverse positions among ms-positions and oblique positions among cs-positions, are therefore still valid.

If the electrostatic lattice energy is calculated (by the method given on p. 14) from the corrected E_{AB}, the figures given in table 5 are obtained.

<div align="center">

TABLE 5.

The electrostatic lattice energy of ice crystals, calculated from the corrected E_{AB}-values given in table 4.

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	Ordinary hexagonal ice crystal	Hypothetical ice crystal with diamond structure
At low temperature	14.93 kcal/g mol	14.51 kcal/g mol
At high temperature	14.32 —	14.32 —

These electrostatic lattice energies are about 1 kcal higher than those calculated in table 2. At high temperature the difference between the lattice energies for hexagonal and for cubic ice is, as in the previous calculations, extremely small, but at low temperature the lattice energy for hexagonal ice is 0.42 kcal higher than for cubic ice. According to the previous calculation it was only 0.16 kcal higher. The new higher value makes it easier to understand the reason why ice crystallizes hexagonally and not cubically. Even at the melting point of ice, as we shall see later, ms_1- and cs_2- and cs_3-positions are so predominant that the lattice energy must be assumed to lie nearer to that calculated for low temperature than to that calculated for high temperature.

8. Quantitative calculation of the percentage of inverse and oblique positions.

Difficulties are encountered in exact calculation of the amount of inverse and oblique positions in ice. As an approximation, we will try to express the probability of the different positions by a BOLTZMANN e-function:

$$W = e^{-E/kT}$$

where E is the energy of the position. If no correlation existed between positions of pairs close to one another, it can be shown that this formula is correct. There is, however, a considerable correlation; this appears from the fact that, without correlation, the number of configurations of an ice crystal should be 3^{2N}, while it is actually only $(3/2)^N$. We may hope that, nothwithstanding this, the formula will be a useful approx-

imation. Using the corrected E_{AB}-values* from table 4, we have calculated the percentages of the 4 different positions at four different temperatures. The results are given in table 6.

TABLE 6.

Calculated percentages of inverse and oblique positions in ice.

	273° K	136.5° K	90° K	68.25° K
Inverse ms-positions	68.4 %	90.4 %	97.7 %	99.44 %
Oblique ms-positions	31.6 -	9.6 -	2.3 -	0.56 -
Inverse cs-positions	9.1 -	2.0 -	0.38 -	0.08 -
Oblique cs-positions	90.9 -	98.0 -	99.62 -	99.92 -

The figures in table 6 show that, even at the highest possible temperature, the melting point, the ratio between inverse and oblique positions is still far from being the statistical ratio $1:2$. At the boiling point of liquid air (90° K) only about 1 per cent of the oblique mirror symmetric and inverse central symmetric positions remain.

When the figures in table 6 are used, it must not be forgotten that they are rather uncertain; partly because they rest on the assumption of a rough molecular model, and partly because the forces between molecules, which are not adjacent molecules, are only considered incompletely, and finally because the use of BOLTZMANN's equation is only an approximation. On the whole, however, the figures are to be considered as a useful approximation.

9. The effect of temperature on the rate at which the equilibrium between inverse and oblique positions is reached.

The equilibrium between the energetically different inverse and oblique positions must be reached very rapidly at the melting point of ice. This can be concluded from the fact that the heat of fusion of ice has a very well defined size (1.4357 ± 0.0009

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* It is preferred to use the mean of the values corresponding to high temperature and to low temperature. The corrections for the E_{AD} values have such a sign that it seems reasonable to use mean values in place of values nearer to the low temperature values.

kcal/gmol. Cf. also the use of the ice calorimeter). If only 0.1 per cent of the positions are changed from inverse to oblique, this would change the heat of fusion by 0.0012 kcal/gmol, hence more than the indicated uncertainty of the determination.

If the temperature is lowered, a temperature range will finally be reached, at which the equilibrium between the positions of the molecules freezes in. MURPHY[11]) has given some observations on how cooling of an electrically polarized ice crystal to the temperature of liquid air ($90° K$) freezes a permanent dipole moment into it. This shows that at this temperature the molecules in ice have ceased to change their orientation. GIAUQUE and STOUT[5]), who have carried out very accurate measurements on the heat capacity of ice down to very low temperatures, write: "At temperatures between 85 and $100° K$ the attainment of thermal equilibrium in the solid was very much less rapid than at other temperatures. For this reason the heat capacity measurements in this region are somewhat less accurate than the others." This slow attainment of equilibrium is, according to them, presumably due to the initial stages of excitation of some new degrees of freedom. They suspect that these new degrees of freedom are associated with the dipole orientation mechanism. It is tempting to explain slow attainment of equilibrium as due to fixation by freezing of the equilibrium between inverse and oblique positions. According to table 6, in this temperature range the energetically preferred positions are already so predominant (they constitute about $99\ ^o/_o$) that it might seem reasonable to suppose that differences in the fixation of the configuration by cooling have had a perceptible, but only slight influence. In order to investigate this, a theoretical calculation of the specific heat of ice is given and is compared with experimental data in the following chapter.

10. The heat capacity of ice.

In ice the H_2O molecules can be considered as rigid systems, vibrating and oscillating without undergoing changes themselves (the slowest atomic oscillation in a H_2O molecule ($1590\ cm^{-1}$) contributes, even at the melting point, only 0.03 to the heat capacity

(C_v in cal/mol/degree) according to EINSTEIN's function). Thus the ice molecules only contain heat energy in the form of "hindered translations" and "hindered rotations", we will call these movements *vibrations* and *oscillations*, respectively.

From the RAMAN spectrum of ice [8]) we know that the wave number of the vibrations is 210 ± 2 cm^{-1} and that of the oscillations 700—900 cm^{-1}. The observed frequency 210 ± 2 must be due to vibrations, as it changes in the ratio $\sqrt{18/20}$ from light to heavy ice, and the frequency 700—900, to oscillations as it changes in the ratio $\sqrt{1/2}$ from light to heavy ice. The spectroscopic vibration frequency is in good agreement with the frequencies calculated from the volume compressibility of ice. For the most rapid vibration in the direction of the main axis we have calculated 223 cm^{-1}, for vibrations perpendicular to the main axis and to the line between two adjacent molecules, 218 cm^{-1}, and for the vibrations perpendicular to the two former, 203 cm^{-1}. The calculations are carried out on the assumption that the forces between the molecules are pure central forces, not influenced by valency angle forces, and that the compressibility is the same in all directions.

A heat capacity of ice (C_v(Debye)) is calculated from the spectroscopic frequencies as the sum of three DEBYE functions [13]) corresponding to 210 cm^{-1} (C_v(210)) and three others corresponding to 800 cm^{1-} (C_v(800)). Table 7 contains the results.

TABLE 7.

Heat capacity of ice, determined spectroscopically.

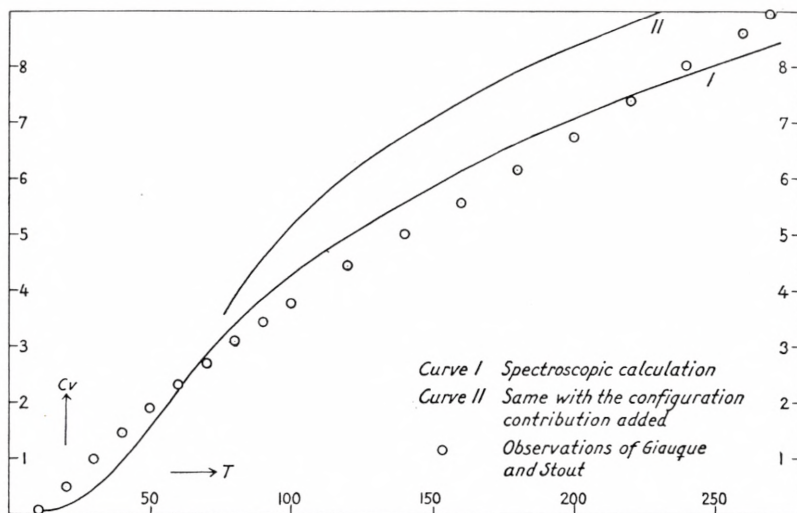| $T°K$	C_v (210)	C_v (800)	C_v (Debye)
10.0	0.017	0	0.017
15.05....................	0.058	0.001	0.059
20.1	0.137	0.002	0.139
30.1	0.452	0.008	0.460
37.6	0.823	0.016	0.839
50.2	1.582	0.039	1.621
60.2	2.197	0.067	2.264
75.2	2.996	0.131	3.127
100.3	3.947	0.309	4.256
150.5	4.918	0.933	5.851
200.7	5.337	1.741	7.078
273	5.609	2.822	8.431

Fig. 5. Heat capacity of ice (C_v). Curve I: spectroscopic calculation. Curve II: Same with the configuration contribution added. ⊙: Determinations of GIAUQUE and STOUT.

In fig. 5 curve I represents the spectroscopically calculated values (C_v(Debye), and GIAUQUE and STOUT's[5]) experimental values for C_p (which do not deviate appreciably from C_v) are introduced as small circles. It can be seen that the general trend is not badly reproduced.

We will now calculate the contribution to C_v of the change in configuration in ice. Let α_{ms} be the fraction of mirror symmetric positions, which are oblique, Q_{ms} the difference in energy between inverse and oblique mirror symmetric positions and $C_v(ms)$ the contribution to C_v of the change of mirror symmetric positions from inverse to oblique. Using BOLTZMANN's e function as an approximation we obtain:

$$\frac{\alpha_{ms}}{1-\alpha_{ms}} = \frac{e^{-Q_{ms}/RT}}{2}, \qquad \frac{d\alpha_{ms}}{dT} = \frac{Q_{ms}}{RT^2} \cdot \frac{2\,e^{Q_{ms}/RT}}{(e^{Q_{ms}/RT}+2)^2},$$

$$C_v(ms) = \left(\frac{Q}{RT}\right)^2 \frac{Re^{Q_{ms}/RT}}{(e^{Q_{ms}/RT}+2)^2},$$

and similarly for centre symmetric positions (α_{cs} fraction of inverse positions):

$$\frac{\alpha_{cs}}{1-\alpha_{cs}} = 2\,e^{-Q_{cs}/RT}, \qquad \frac{d\,\alpha_{cs}}{dT} = \frac{Q_{cs}}{RT^2} \cdot \frac{2\,e^{Q_{cs}/RT}}{(2\,e^{Q_{cs}/RT}+1)^2},$$

$$C_v(cs) = \left(\frac{Q_{cs}}{RT}\right)^2 \frac{3\,Re^{Q_{cs}/RT}}{(2\,e^{Q_{cs}/RT}+1)^2}.$$

By introducing 0.793 and 0.871 kcal/gmol as values for Q_{ms} and Q_{cs} respectively, (mean of values for high and low temperatures) these equations lead to the contributions to the heat capacity given in table 8.

TABLE 8.

Contributions ($C_v(ms)$ and $C_v(cs)$) to the heat capacity of ice from the change of configuration with temperature. $Q_{ms} = 0.793$ and $Q_{cs} = 0.871$ kcal/gmol.

T	90° K	136.5° K	273° K
$C_v(ms)$	0.442	0.743	0.470
$C_v(cs)$	0.269	0.596	0.636
$C_v(ms) + C_v(cs)$	0.711	1.339	1.106

These contributions, when added to the spectroscopic C_v values, give a curve for the heat capacity (curve II in fig. 5) which deviates more from the experimental values than does the spectroscopical curve itself. This is not a serious objection against our calculated Q-values, as the spectroscopic calculation of the heat capacity of solids by means of DEBYE functions for substances with polyatomic molecules generally is only a poor approximation. A more serious objection is the high value (0.711) of the contribution to the heat capacity at the temperature (90° K), at which GIAUQUE and STOUT observed their small thermal irregularities. The contribution in this temperature range should have been considerably less than 0.1 in order to be in agreement with GIAUQUE and STOUT's observations. Small changes in Q cannot remove this disagreement. The contribution ($C_v(ms) + C_v(cs)$) has a maximum in the neighbourhood of $T = Q/2R$ and with our Q-values the maximum lies at about 200° K. If the Q-values had been twice as high the maximum would have been removed to about 400° K and the contribution would have been:

at $90°K$ 0.030,   at $136.5°K$ 0.276,   at $273°K$ 1.339

Also with lower Q-values acceptable values for the contribution can be obtained, but the lowering must be very great. If the Q-values had been 10 times as small, the contributions would have been:

at $90°K$ 0.172,   at $136.5°K$ 0.067,   at $273°K$ 0.021,

and first with Q-values twenty times lower acceptable values would have been reached:

at $90°K$ 0.047,   at $136.5°K$ 0.021,   at $273°K$ 0.005.

We must conclude that acceptable values for the contribution to the heat capacity of ice from changes in the configuration equilibrium cannot be obtained with our formulas and with Q-values in reasonable agreement with our calculations based on the tetrahedron model.

It is most probable that the use of the BOLTZMANN function has been an unsatisfactory approximation, and that the α-values are much smaller than those in table 6 ($\sim 0.1 \, ^0/_0$ instead of $1 \, ^0/_0$ at $90° K$). When the number of configurations is lowered from 3^{2N} to 1.5^N on account of correlations (see p. 21) it does not seems improbable that the energy differences between the configurations have a strongly increased effect on the configuration equilibrium.

11. The zero-point entropy of ice.

The views on the structure of ice, presented here, are presumably correct in the main lines, even if the calculated figures must be treated with some caution. If, however, they are correct in the main lines, then PAULING's explanation of the zero-point entropy of ice can not be used. It requires that the energetic difference between the possible orientations of the molecules in ice must be so small that they are all almost equally probable, even at the low temperature at which they are fixed by freezing, and this seems to be very far from the case.

As a possible explanation for the zero-point entropy of ice, GIAUQUE and ASHLEY[5]) have proposed the existence of ortho-

and para-states in the H_2O molecule. Against this view, however, is the fact that a similar zero-point entropy (0.77 kcal/gmol, LANG and KEMP[12])) has been found for heavy water. According to GIAUQUE and STOUT[5], the ortho-para-hypothesis should give a considerably smaller zero-point entropy for heavy water than for light.

The question of the cause for the zero-point entropy of ice, therefore, for the present, remains open.

Summary.

1. A crystal in which every atom has 4 neighbours in regular tetrahedral arrangement is either cubic or hexagonal. In a cubic crystal the arrangement around two neighbours is always centre symmetric (see fig. 2), but in a hexagonal crystal the arrangement around two neighbour atoms is in some cases (maximally in a fourth of the cases) mirror symmetric and only in the rest centre symmetric. The fact that ice crystallises hexagonally and that in ice a fourth of the bonds are mirror symmetric suggests that the bond energy between two H_2O molecules in mirror symmetric position is greater than that between H_2O molecules in centre symmetric position. Earlier measurements by H. D. MEGAW show, in agreement with this suggestion, that the mirror symmetric bond in ice is actually $1/2$ % shorter than the centre symmetric.

2. Using a tetrahedron with positive charges on two corners and negative charges on the other two as a model of a H_2O molecule (fig. 3), the suggestion given above can be supported. For the ordinary hexagonal ice crystal the electrostatic lattice-energy is calculated to 14.91 kcal/gmol and for a hypothetical cubic ice crystal to 14.51 kcal/gmol. These values are valid for low temperatures. For reasons given in the following, the values increase with temperature and approach each other somewhat.

3. An ice crystal can posses a large number of different configurations (1.5^N, where N is the number of molecules). The reason is that both centre symmetric and mirror symmetric positions can be either inverse or oblique (see fig. 4). It has been assumed that all these configurations have nearly the same lattice energy (PAULING). Using the tetrahedral model described above it is found, however, that the electrostatic bond energy is con-

siderably greater for the *inverse* mirror symmetric and for the *oblique* centre symmetric than for the two other positions (see table 4).

4. In an ice crystal the number of the two bond types with the highest bond energy must increase with decreasing temperature at the cost of the two other types. By means of BOLTZMANN's e-function, approximate values are calculated for the ratio between inverse and oblique positions at several temperatures (table 6). Even at the melting point the ratio is far from the statistical one, corresponding to equal bond energy.

5. At the melting point the configuration of ice changes very rapidly, but at the temperature of liquid air ($90°\,K$) the configuration freezes in. At this temperature, according to BOLTZMANN's e-function, about 99 % of the positions are the most stable inverse mirror and oblique centre symmetric positions (see table 6). Consequently it could seem reasonable that the irregularities in the thermal behaviour of ice in this temperature range, found by GIAUQUE and STOUT, were rather insignificant.

A calculation, however, revealed that even the small proportion of about 1 % oblique mirror and inverse centre symmetric positions should create irregularities much greater than those observed by GIAUQUE and STOUT. It is suggested that the application of BOLTZMANN's e-function here represents a poor approximation, and that at $90°\,K$ the most stable positions predominate to a proportion of perhaps 99.9 %.

6. If the 1.5^N configurations of an ice crystal are not all equally probable at the temperature when the configuration freezes in, then the zero-point entropy of ice must be smaller than PAULING's value $R\,ln\,1.5 = 0.806$ kcal/gmol/degree. The values in table 6 suggest that the value of the zero point entropy should be only about a hundredth of this value. It is not yet possible to give another explanation for the experimentally found value 0.82 ± 0.15.

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II.

CHANGE IN CONFIGURATION AND MOLECULAR TURNS

1. Information, gained from the dielectric properties of ice.

It is mentioned in part I of this series that ice changes configuration very frequently at the melting point, and that its configuration is first frozen in near the temperature of liquid air (ca. $90°\,K$).

Investigations on the dielectric properties of ice have yielded more accurate information about the power of ice to change configuration. P. DEBYE[1]) has shown that it is possible to explain the dielectric properties of ice by assuming that its dipole molecules, under the influence of thermal movements, frequently turn. In the absence of external electrical forces, the molecules are orientated so that their dipole moments are mutually neutralized, but under the influence of an external electrical force the molecules become arranged so that the ice has a dipole moment in the direction of the force. DEBYE writes that under the influence of a field strength of 1 volt/cm it is only necessary for one molecule in 5 million to turn in order to produce the dipole moment which the ice obtains under the effect of this field strength. The rate at which the orientation of the molecules takes place can be investigated by subjecting ice to an alternating current field. At low frequencies the molecules have time to adjust themselves to the field, and a dielectric constant equal to the static is found; but if the frequency is increased, a frequency range can be reached, at which the molecules of ice do not have time to adjust themselves, and at sufficiently high frequencies ice possesses a dielectric constant, corresponding only to the electron- and atom-polarization of the molecules.

SMYTH and HITCHCOCK[2]) have performed measurements of this type. From their measurements DORSEY[3]) has calculated, by means of DEBYE's equations, values for τ, the relaxation time for the molecular turns in ice. Table 1 gives these values for a few temperatures. Values for $n = 1/\tau$, the rate of turns performed by a molecule, are also given in the table.

TABLE 1.

Relaxation time (τ) and rate ($n = 1/\tau$) of molecular turns, determined dielectrically.

t° C	0°	-30°	-70°
$\tau \times 10^6$ sec.............	1.205	25.3	1467
$n \times 10^{-6}$ sec^{-1}..........	0.831	0.0395	0.00068

No great accuracy must be ascribed to these calculations of τ and n. DEBYE's equation does not reproduce SMYTH and HITCHCOCK's measurements quite exactly, especially not at temperatures of below -30°. According to W. KAUZMANN's[4]) opinion, the LORENTZ correction used for the internal field is probably too large. This correction makes the n values ca. 16 times higher. It is not improbable that all the n values are e. g. 5 times too high.

From the decrease of n in the interval 0° to -30°, an energy of activation E for the dipole turns of 13.4 kcal/gmol is calculated by means of the expression $E = R\, dln\, n/d\, (1/\tau)$. Since DORSEY has smoothed the figures of SMYTH and HITCHCOCK rather strongly, I have carried out a new calculation of n and E from SMYTH and HITCHCOCK's unsmoothed figures. This led to almost the same E value (13.5 kcal/gmol). From the same experimental material KAUZMANN has calculated 12.2 kcal/gmol. He has presumably arrived at the lower value by also considering the more uncertain measurements at temperatures below -30°. From the measurements of WINTSCH[5]) and E. J. MURPHY[6]), KAUZMANN calculates 9.3 and 14.6 respectively (here and in the future the energies of activation are always stated in kcal/gmol). Finally HØJENDAHL[7]) by calculations from the size of the dielectric loss in SMYTH and HITCHCOCK's measurements, obtained the value of 10.8. The equation presented by HØJENDAHL for the loss angle,

however, only fits after the introduction of an empirical coefficient in place of the theoretical. Everything considered, a value for the energy of activation of ca. 13 seems to be most probable.

2. Energies of activation for turns of ice molecules, calculated from molecular models.

It is not possible by turning a single molecule to transform an ideal ice crystal of the type described in part I into a new stable configuration. A consequence of this is that even at the melting point changes in configurations can be rare: The thermal movements of the molecules will cause the disappearance of the forces which are responsible for the crystal structure, before the molecules can turn into a new configuration to any great extent.

If a new stable configuration is to be obtained, a ring of molecules must turn simultaneously. Such a ring contains at least 6 molecules. The ring must fulfill the condition that the order of positive and negative corners is the same throughout the whole ring. This condition is only fulfilled by a small fraction of all existing rings. Turns of molecular rings, which fulfill this condition, will certainly change the configuration of the crystal, but not its dipole moment, and hence the large dielectric constant of ice can not be caused by such turns. Turns of molecular rings must be rare, because a coordinated turning of many molecules simultaneously is statistically not very probable and also and especially because a ring during its turning must pass a high energy threshold. If, as molecules, we use the tetrahedral model described in the previous paper, and only consider the electrostatic forces, we obtain for the critical energy threshold (the energy of activation) a value of at least 21.6 kcal/gmol (for a six membered ring).

Details of the calculation. In a ring of the type described above, it is possible, by simultaneously turning all molecules through 120° round one of their tetrahedral axes, to reach a new stable configuration. The axis of rotation must be one of the two tetrahedral axes which do not lie in the ring itself. During the turning a critical energy threshold is passed when the molecules have turned through 60°. In order to reach this threshold position, work must be performed against the electrostatic attraction between the molecules of the ring and the surrounding molecules and also between the molecules of the

ring themselves. If we only pay attention to the forces between adjacent molecules and disregard the small forces, which are active between two adjacent molecules, when the one molecule rotates around their common axis, we shall, for each of the molecules in the ring, only consider the forces from a single molecule outside the ring. Hence the problem is to bring two molecules (A and B) into the positions shown in fig. 1 a. Since, however, the calculations can only be made approximately and are easier to carry
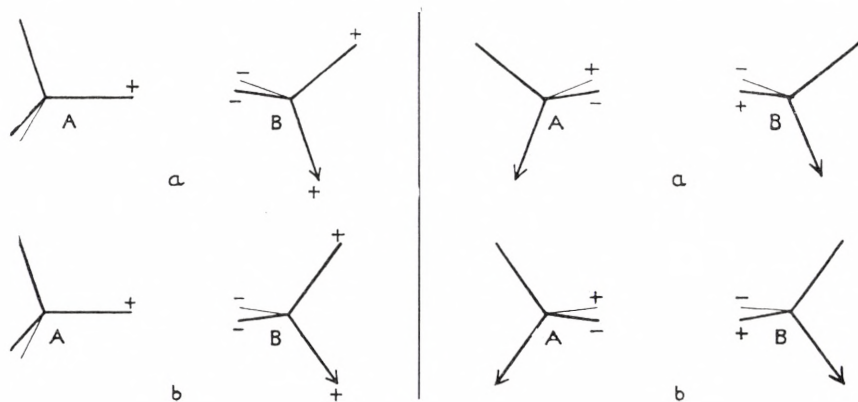

Fig. 1.   Fig. 2.

Fig. 1. Threshold position between a ring molecule and a molecule outside the ring. a correct. b modified. Rotation axes marked with an arrow.

Fig. 2. Threshold position between two ring molecules. a correct. b modified. Rotation axes marked with an arrow.

through for the modified position shown in fig. 1 b, the calculations, are performed for the latter. The modification consists of a rotation of the B molecule ca. $12^3/_4°$ around an axis perpendicular to the plane of the drawing. This modification will only change the energy of activation slightly and will generally make it a little lower. The energy necessary for bringing the molecules to the threshold position is somewhat dependent on the position of the negative and positive charges on those corners of the A molecule, which are furthest away from the B molecule, and on whether the initial position has been centric symmetric or mirror symmetric (the modified threshold position is the same in both cases). The calculation shows that 2.3 to 3.6, mean ca. 3 kcal/gmol, is necessary. If there are 6 molecules in the ring the consideration of the surrounding molecules alone thus causes an energy of activation of *at least* $6 \times 2.3 = 13.8$.

The energy necessary in order to bring two adjacent molecules in a ring into the critical threshold position depends on the mutual positions of the molecules (mirror symmetric or centric symmetric, inverse or oblique) and of the position of the axes of rotation in the molecules. The lowest transfer of energy is required, when the molecules are in

mirror symmetric position and the axes of rotation lie in the same plane (fig. 2a). The modified position 2b, in which the mutual position of the molecules is more symmetric, is used in the calculations and can be expected to give a slightly lower energy of activation. The amount of energy necessary depends somewhat on the position of the charges on the corners of the molecules which in 2b are furthest apart. A mean value of at least 1.3 kcal/gmol must be considered. Since there are at least six molecules in the ring, the contribution to the energy of activation from the electrostatic forces between the molecules in the ring must be at least $6 \times 1.3 = 7.8$. Hence the total energy of activation will be at least $13.8 + 7.8 = 21.6$.

While turns of molecular rings do not change the dipole moment of an ice crystal, turns of a molecular row between two surface points will change the dipole moment. If the ice crystal, however, is not ultramiscropically small such turns of molecular rows can not be of much importance. Impurities in the ice will produce internal surfaces in it, but it is not probable that turns of molecular rows, beginning and ending in impurities in the crystal, will be decisive for the rate of dipole turns responsible for the dielectric properties of ice. In contrast to the many molecules in the interior, the few molecules which lie in the surfaces, both external and internal, of the crystal will be able to turn and thus alter the dipole moment of the ice crystal, but it is not probable that such turns of surface molecules can play any important role. Even in an ideal, pure ice crystal, however, lattice faults occur and at these fault sites single molecules will be able to turn and their dipole axes to change direction. We must here turn our attention to the lattice faults which are caused by the thermal movements of the molecules and which occur at a concentration determined by the temperature. There are two types of such fault sites: some, which are due to the incorrect mutual *orientation* of two neighbour molecules, there being either two protons or no protons between them, and others, which are due to *ionization*, the presence of H_3O^+ and HO^- ions in the lattice. We will in this paper examine the orientation fault sites.

3. Orientation fault sites as cause of molecular turns in ice.

If an ice molecule, on account of especially strong thermal movements, has turned around such a large angle that two protons

3*

have come between its oxygen atom and the oxygen atom of an adjacent molecule and no proton between its oxygen atom and the oxygen atom of another neighbouring molecule (fig. 3b) the chance that it will turn back is very great; but it may happen that one of the neighbours has turned before it can turn back. In such a case the two sites with two or no protons respectively have been separated (fig. 3c). Continued molecular turns can
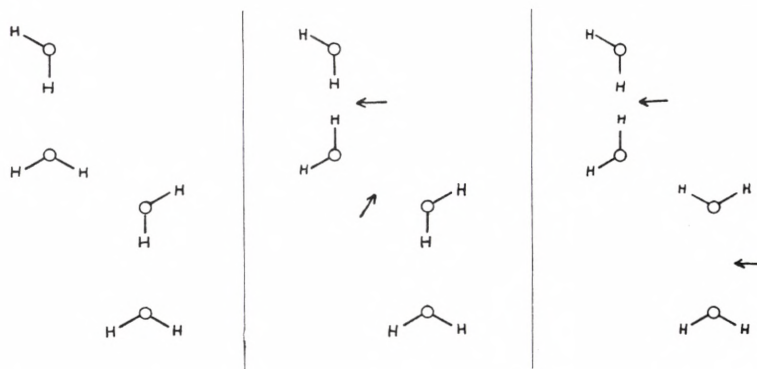

a. Normal   b. Orientation faults in adjacent linkages   c. Orientation faults separated

Fig. 3. Formation of orientation fault sites.

separate the two sites completely and cause the appearance of two independent fault sites of opposite types: sites with two protons and sites with no protons between the oxygen atoms. These fault sites will migrate through the crystal until they meet a fault site of the opposite type with which they will recombine. Under the influence of formation and recombination of such fault sites, an equilibrium will be reached in the ice crystal with equally high concentration of these two types of orientation fault sites.

Two molecules, between which there is an orientation fault site, can easily turn, and every time a molecule turns the fault site will move over to an adjacent site and the dipole moment of the molecule will be turned through 90°. The fault sites will thus act as a kind of catalyst for the promotion of dipole turns.

If the tetrahedral model, previously described in part I, is used, the formation of such fault sites is estimated to require a accumulation of energy E of between 10.2 and 13.6 kcal/gmol, and the critical energy threshold for turns of the molecules

between which the fault site lies, can be estimated to be 2.5 kcal/gmol. Consequently the concentration (c) of the fault sites will change with temperature according to the expression $dln\ c/dT = E/RT^2$, where E is a figure between 10.2 and 13.6, and the rate of turns (n') per fault site will change according to the equation $dln\ n'/dT = 2.5/RT^2$. The rate of turns per H_2O molecule ($n = c \times n'$) will therefore change according to the equation $dln\ n/dT = (E + 2.5)/RT^2$. The apparent energy of activation for the number of turns must therefore lie between 12.7 and 16.1. The energy of activation for dipole moments estimated from the dielectric properties of ice was 13. The calculation shows that it is permissible to assume that the dipole turns which are required by DEBYE's theory are the turns made by the molecules at the orientation fault sites. On the basis of this assumption and assuming a threshold value of 2.5, the energy content of the orientation fault sites can be estimated to be 10.5.

The accumulation of energy necessary for the formation of an orientation fault site is calculated in the following way. In a gram molecule of ice, the electrostatic lattice energy originates chiefly as the result of the attraction between the $2N$ adjacent molecular pairs. The total lattice energy, according to table 2 in the first part of this paper, is about 13.6 kcal/gmol and the bond energy between a single molecular pair is consequently $13.6/2N$. At an orientation fault site the two adjacent molecules possess a bond energy numerically equal to the normal energy, but with the opposite sign. Hence every such fault site will diminish the lattice energy by $13.6/N$ and the formation of a gram molecule of fault sites will require 13.6 kcal. This value must be considered as a maximum value. For in the calculations it is assumed that the two similarly charged tetrahedral corners are in the normal position to one another, and that both lie on the connecting line between the centres of the tetrahedra. When the corners are differently charged the existence of this position is due to electrostatic attractions between the charges in the corners. The repulsion between two similarly charged corners must cause the corners to be forced away from the connecting line between the centres in opposite directions. If they are removed in this way 0.3 Å from the connecting line (the radius of the tetrahedron is 0.99 Å), the distance between the corners increases ca. 30 %, and if the distances between the differently charged tetrahedral corners at the other places of the lattice are assumed not to be altered appreciably from the normal value 0.78 Å, the total lattice energy will not be decreased by $13.6/N$ on account of a fault site, but only by $10.2/N$. We will assume that the formation of a gram molecule of fault sites must require between 10.2 and 13.6 kcal.

The critical threshold energy for molecular turns at a fault site can be calculated in the following way. Fig. 4 shows the initial, the threshold and the final positions during turning of a molecule (A). Before turning the fault site lies between molecules A and B and after turning between A and C. In the initial position the contribution made by the molecular pairs AB, AC and AD to the lattice energy amounts to $2 \times 6.8/N - 6.8/N = 6.8/N$, and

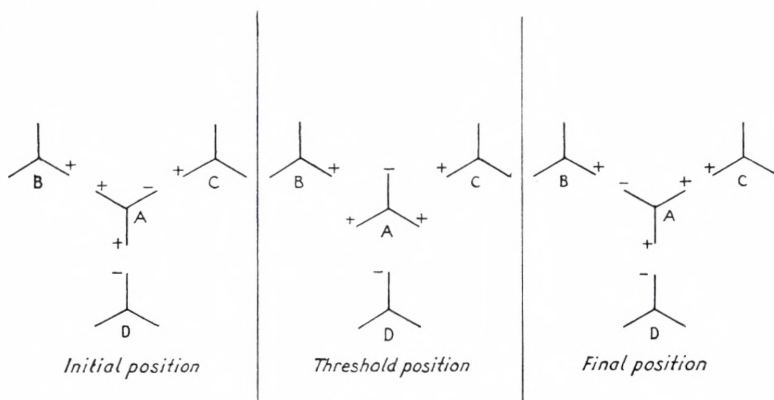Initial position   Threshold position   Final position

Fig. 4. Positions during moving of an orientation fault site.

the same contribution is given by the three pairs in the final position. In the threshold position the contributions of AB and AC are both zero. The contribution of AD (using the same approximations as on p. 34) can be calculated to $3.8/N$. In order to reach the threshold value an energy accumulation of $(6.8 - 3.8)/N$ is consequently required, corresponding to 3.0 kcal/gmol. This accumulation of energy will also be decreased on account of the deformation of the lattice at the fault site. In the following we will assume this value to be 2.5.

The rate of turns (n) per H_2O molecule is the product of the number (c) of fault sites per molecule and the rate of turns (n') per fault site ($n = c \times n'$). It is not possible to carry out the separation of n into these two factors with certainty; but in order to obtain a plausible value of c we have tried to carry out a reasonable separation, paying attention to the energy content of the fault sites (10.5) and to the critical energy threshold for turns at a fault site (2.5). From the RAMAN spectrum of ice it is known that the frequency (ν) of the hindered rotation of the ice mole-

cules is ca. 2.4×10^{13}. Since turning of a molecule to a new equilibrium position requires that an energy threshold of 2.5 must be passed, we will assume that the rate of such turns per fault site is $n' = \nu \times 2 \times e^{-2.5/RT}$ (the factor of 2 is due to the fact that at each fault site there are two molecules that can turn). From this expression the value of n' at $0°$ C is calculated to 4.8×10^{11}. The rate of dipole turns (n) per molecule is according to table 1 0.83×10^6 at $0°$. If the dipole turns are due to fault sites, the number of these fault sites per molecule must be $c = n/n' = 1.7 \times 10^{-6}$ at $0°$ and hence about 10^{-6} of each of the two types. This number is rather too large for a state with an energy content of 10.5 kcal/gmol. According to BOLTZMANN's e-function the number should lie somewhere near $e^{-10.5/RT} = 0.36 \times 10^{-8}$. It must be remembered, however, that BOLTZMANN's function here represents only an approximation. If the uncertain LORENTZ correction for the internal field is omitted in the calculation of n from the dielectric properties of ice, the number of fault sites per molecule decreases to 1.1×10^{-7}. Even with this modification the number of orientation fault sites, necessary to explain the dielectric properties of ice, is 30 times higher than expected from the BOLTZMANN calculation. This is, however, no sufficient reason to discard this explanation.

Summary.

1. DEBYE has explained the dielectric properties of ice by the existence in ice of dipoles which can turn. From the dielectric properties of ice the rate of dipole turns is calculated to ca. 0.83×10^6 per second per molecule at $0°$ and the energy of activation to ca. 13 kcal/gmol. If the LORENTZ correction used for the internal field is too large or even may be perhaps completely omitted, the rate of dipole turns may be up to ca. 16 times less.

2. The configuration of an ideal ice crystal can not change by turning of a single molecule, but only by the simultaneous turning of a closed ring of molecules. Such turns of molecular rings do not alter the dipole moment of the crystal and therefore can not represent the dipole turns required by DEBYE's theory. If the tetrahedral model with electric charges on the corners,

described in part I of this series, is used as a model of a water molecule, the energy of activation for a turning of a ring of six molecules is calculated to at least 21.6 kcal/gmol.

3. In an ice crystal fault sites are present where two or no protons are found between two oxygen atoms instead of the one normally present. These two types of fault sites occur in equal amounts. Molecules, between which such orientation fault sites are present, can easily turn and thereby rotate their dipole moments 90°. The apparent energy of activation for such turns is calculated from the above mentioned molecular model to between 12.7 and 16.1 kcal/gmol. The energy of activation thus has a size similar to that required for dipole turns in DEBYE's theory (ca. 13 kcal/gmol). It may therefore be assumed that the molecular turns at orientation fault sites represent the dipole turns required by DEBYE's theory.

4. The rate of molecular turns at an orientation fault site is estimated to be ca. 4.8×10^{11} per second at $0°$, and the concentration of each of the two types of fault sites to be ca. 1 in each 10^6 ice molecules. If the rate of dipole turns in ice should be less than $0.83 \times 10^6 \sec^{-1}$ per molecule the concentration of fault sites will be correspondingly higher.

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III.

IONISATION OF ICE AND MOLECULAR TURNS PRODUCED BY THE IONS. THE PROTON JUMP CONDUCTIVITY OF ICE (AND WATER)

1. Ions as producers of molecular turns.

In addition to orientation fault sites, there exist in ice fault sites, which are due to the presence of ions. If a proton jumps from an H_2O molecule to a neighbouring molecule, an H_3O^+ and an HO^- ion are formed. The chance that the proton will jump back again is great; but before there is time for this to happen, a proton may have jumped over from the H_3O^+ ion to a third H_2O molecule (or from another H_2O molecule to the HO^- ion). Hereby two spacially separated ions have appeared (see fig. 1). By new proton jumps of the types $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$ and $H_2O + HO^- \rightarrow HO^- + H_2O$ the ions may be separated further from each other and migrate freely in the crystal lattice and cause the ice to become electrically conducting. As is well known, it is usual to explain the exceptionally high conductivity of the H_3O^+ ion in water in a similar way by assuming that this ion can move its charge, not only in the same way as normal ions, by moving as a unit through the medium of the solution, but also by the jumping of one of its protons over to an adjacent H_2O molecule, and similarly, the abnormally high conductivity of the HO^- ion is explained by the jumping of a proton from an adjacent H_2O molecule over to the HO^- ion[1]). In ice, the H_3O^+ and HO^- ions formed will continue to migrate until an H_3O^+ and an HO^- ion meet and thus have the possibility of recombination. Formation and recombination of the ions will lead to a state of equilibrium with definite ion concentrations.

The ion concentrations in ice must be of a similar order of magnitude to those in water, since the conductivities of ice and water do not differ considerably. J. H. L. JOHNSTONE[2]) gives the following values for the static conductivity of ice $(\varkappa)$:

Temp.	$-1°$	$-4°$	$-10°$	$-19°$
$\varkappa \times 10^8$	2.8	0.23	0.11	0.026

His determination at $-1°$ appears improbably high. According to the other determinations, a rise in temperature of ca. 5° causes

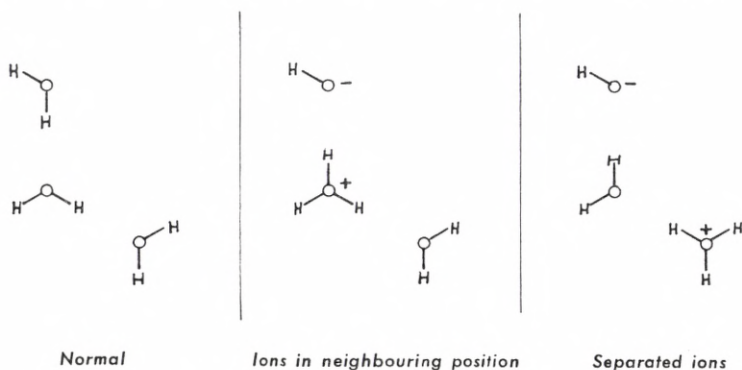Normal   Ions in neighbouring position   Separated ions

Fig. 1. Formation of ions by proton jumps.

a doubling of the conductivity, hence it is not natural that a rise from $-4°$ to $-1°$ should make the conductivity 12 times higher. A value of 0.35×10^{-8} at $-1°$ (and 0.4×10^{-8} at $0°$) would be more reasonable. Perhaps the high value at $-1°$ is due to the presence of impurities in the ice, which have contributed to the conductivity, because they were ·still present in the form of aqueous solution between the ice crystals.

The conductivity of water at $0°$ is calculated from the ionisation constant of water (0.119×10^{-14}) and the molecular conductivity of the ions (345) to $\varkappa = 1.2 \times 10^{-8}$. This value is 2.3 times lower than the conductivity given by JOHNSTONE for ice at $-1°$, and 3 times higher than the value obtained for ice at $0°$ by extrapolation from the determinations by JOHNSTONE at lower temperatures.

A calculation of the ion concentration in ice can be performed as follows. We will assume that the conductivity of ice is due

exclusively to its content of H_3O^+ and HO^- ions, and that these ions move exclusively by means of proton jumps. It is improbable that these ions as a unit can migrate through the crystal lattice of the ice at rates which are of significance in this connection or that other ions can do it.

In passing, it should be mentioned that, on account of these considerations, impurities do not have the same large effect on the conductivity of ice as they have on that of water. It is therefore easier to determine éxperimentally the conductivity of pure ice than that of pure water.

Only a fraction of the conductivity of pure water $(1.2 \times 10^{-8}$ at $0°$ C) is due to proton jumps. Of the molecular conductivity of H_3O^+ ions at $0°$, $\mu = 240$, only 200 is due to proton jumps, and of the molecular conductivity of HO^- ions at $0°$, $\mu = 105$, only 64 is due to proton jumps (see section 6 for further details). Hence the proton jump conductivity of pure water at $0°$ is $1.2 \times 10^{-8} \times 264/345 = 0.92 \times 10^{-8}$. We will now make the assumption that proton jumps between ions and H_2O molecules in ice are just as frequent as they are in water at the same temperature between ions and H_2O molecules in the right positions (hydrogen bond positions) to each other. According to conceptions developed later, the rate of proton jumps in water is reduced, on account of the more random orientation of the H_2O molecules to the ions, at $0°$ in the ratio 0.93 for H_3O^+ ions and 0.77 for HO^- ions. When this reduction is taken into consideration, the molecular conductivities of the ions in ice amounts to: for H_3O^+ ions, $200/0.93 = 215$ and for HO^- ions, $64/0.77 = 83$, total 298. If the specific conductivity of ice is taken to be 0.4×10^{-8} at $0°$, the molecular concentrations of the H_3O^+ and the HO^- ions are calculated to 1.34×10^{-8}, corresponding to the transformation of 0.27×10^{-9} parts of the H_2O molecules to H_3O^+ ions and of the same amount of H_2O molecules to HO^- ions.

2. Rates of proton jumps in ice.

From the specific conductivity of ice it is possible to calculate how frequently proton jumps of the types $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$ and $H_2O + HO^- \rightarrow HO^- + H_2O$ take place. The cal-

culation can be performed by the use of EINSTEIN's theory for
BROWNIAN movements.

EINSTEIN[3]) has developed the following equation:

$$D = \overline{\Delta^2}/(6\tau)$$

where D is the coefficient of diffusion of a particle and $\overline{\Delta^2}$ the
mean value of the square of the displacement of the particle in
space in the time τ. The coefficient of diffusion for a monovalent
ion can be calculated from its molecular conductivity by means
of the following equation:

$$D = \mu \times RT/F^2 \times 10^7 = \mu \times 0.244 \times 10^{-6} \text{ at } 0° \text{ C.}$$

If the molecular conductivity of an ion is known, it is possible,
from EINSTEIN's equation, to calculate an expression for the time
τ taken by the ion to be displaced a certain distance. To give
an exact result, EINSTEIN's equation requires that the displace-
ments of the particle are changed by collisions many times within
the time τ. We will, however, use the equation for the approximate
determination of the mean time (τ_0), in which the ion is displaced
2.76 Å, corresponding to a proton jump. The rate of proton jump
displacements of an ion will then be

$$n' = \frac{1}{\tau_0} = \frac{6D}{(2.76 \times 10^{-8})^2} = \mu \times 0.193 \times 10^{10} \text{ sec}^{-1}.$$

If the values of μ for H_3O^+ (215) and for HO^- (83) are sub-
stituted in this equation, we obtain for the rate of proton jumps
at an H_3O^+ ion, 41.5×10^{10} and at an HO^- ion, 16.0×10^{10}, all
per second. For the rate of proton jumps per H_2O molecule we
finally obtain (c is the molar ion concentration and 50.9 the
number of gram moles in 1000 cm^3 of ice):

$$n = n' \times c/50.9 = c \times \mu \times 3.79 \times 10^7 = \varkappa \times 3.79 \times 10^{10}.$$

If the specific conductivity of ice at $0°$ is taken as 0.4×10^{-8},
the rate of proton jumps per H_2O molecule in ice is calculated
by means of this equation to 152 per second. Even at the melting
point, where the proton jumps must be most frequent, an H_2O
molecule only turns ca. 150 times in a second owing to the
presence of the H_3O^+ and HO^- ions in the ice.

3. Ionisation and proton jumps at the ions cannot explain the dielectric properties of ice.

The idea that proton jumps and ionisation may be of significance for the occurrence of the frequent dipole turns, required by DEBYE's theory for the dielectric properties of ice, has been advanced from several quarters.

M. L. HUGGINS[4]), who was perhaps the first to put forward this view, was doubtful of the idea as it leads to the existence of H_3O^+ and HO^- ions in ice. He therefore considered proton displacements in rings of H_2O molecules as the explanation for the high dielectric constants of ice and water. He does not appear to have noticed that proton displacements in rings do not change the dipole moment.

W. M. LATIMER[5]) has put forward the idea that the configuration changes in ice are connected with the processes during which the ions H_3O^+ and HO^{--} appear and disappear in ice. Since the rate at which these processes occur may be high, even if the concentration of the ions is low, LATIMER thinks that there is a possibility of explaining the rapid configuration changes in ice in this way. Quantitatively viewed, this is, however, not possible. Formation and recombination of the ions must be a far more infrequent process than molecular turns during migration of the ions.

W. KAUZMANN[6]) has expanded HUGGINS' idea in an interesting way. He has put forward the proposition that the changes in the configuration of ice could be due to the proton jumps, which accompany migration of the ions in ice. An H_2O molecule which, during migration of the ions, has momentarily been an ion, is left in a new position, if the proton does not jump back to the same H_2O molecule from which it came. I myself have worked with this proposition, without knowing KAUZMANN's work. There is no doubt that migrations of the ions must produce molecular turns, during which the dipole moments of the ions are turned through 90°. These turns, however, are far from sufficiently frequent to explain the dielectric properties of ice (ca. 150 per sec. per ice molecule, whereas ca. 10^6 are required). An even more important objection is the following. The dipole moment produced by these molecular turns is in the opposite direction

to that which is required. This can be shown in the following way. The dipole moment produced by migration of the ions in an isolated ice block is the vector sum of a series of proton jumps, each of 0.78 Å. The dipole moment produced can also be considered as the sum of the dipole changes, caused by displacements of the ions, and the dipole changes, caused by turns of the H_2O molecules. The change of the dipole moment, due to displacements of the ions, is 2.76/0.78 times larger than the dipole moment corresponding to the proton jumps (the displacement of the ion is 2.76 Å, when the proton jumps 0.78 Å). Consequently the dipole moment due to turns of molecules must be in the opposite direction and numerically 1.98/0.78 times larger than the dipole moment corresponding to the proton jumps (1.98/2.76 parts of the dipole moment produced by displacements of the ions).

Hence it is not possible to use the molecular turns connected with the migration of the ions as an explanation for the dielectric properties of ice. Only the molecular turns produced at orientation fault sites, which are described in part II of this paper, can be used.

4. The proton jump conductivity of ice (and water).

In the previous section an account is given of how the ions H_3O^+ and HO^- move in ice by means of proton jumps and how these movements are connected with molecular turns, which produce dipole moments in the direction opposite to the movements and amounting to 1.98/2.76 parts of the dipole moment produced by the ion displacements. If an electric current is passed through a block of ice, avoiding polarization (electric charges) at the two ends, where the current is lead in and out, the ion movements in themselves will not give the block a dipole moment. On the contrary, it might be expected that the turns of the molecules would produce a gradually increasing dipole moment in the opposite direction to that of the electric force. The molecules are, however, also able to turn at orientation fault sites, and since the turns at orientation fault sites are ca. 10^4 times as frequent as the turns at the ions, they are not only able to prevent the appearance of this dipole moment, but in addition

to produce the dipole moment required by Debye's theory in the direction of the force.

For the hypothesis of the proton jump conductivity of ice it is thus of vital importance that the molecular turns produced at orientation fault sites are far more frequent than the molecular turns produced at ions.

In water the molecular turns at orientation fault sites are even more frequent than in ice (according to the dielectric properties ca. 10^5 to 10^6 times more frequent). There is therefore very good reason to consider the abnormally high conducivity of the H_3O^+ and HO^- ions in water as a result of the ability of these ions to move, not only as a unit, but also by means of proton jumps.

5. Ion concentration and proton jumps in ice at lower temperatures. Energies of activation.

The specific conductivity of ice ($\varkappa$) decreases on cooling. From Johnstone's determination at $-4°$ and $-19°$ an apparent energy of activation $E = 19.6$ kcal/gmol is calculated by means of the expression $E = -R\,d\ln\varkappa/d\,(1/T)$. Let us try to calculate theoretically a value for this energy of activation.

Assuming that the total conductivity is due to proton jumps, the conductivity must decrease in the same ratio as the rate of proton jumps. The rate of proton jumps decreases partly because of the decrease in the ion concentration and partly because proton jumps require a certain energy of activation. *The decrease in the ionisation* depends on the heat production during the process of "neutralization" $H_3O^+ + HO^- \rightarrow 2\,H_2O$. In water this process is accompanied by an evolution of heat of 13.7 kcal/gmol. This heat production (disregarding the difference between production of heat and of energy) can be separated into two parts: the energy, liberated during the actual proton jump, and the energy, liberated on account of the electrostatic attraction between the ions when they approach each other. The latter part can be calculated from the expression $e^2/\varepsilon a$ to 1.4 kcal/gmol, when the dielectric constant (ε) in water at $0°$ is taken as 88, and the distance (a) between the ions when they touch as 2.76 Å. The energy which is released during the proton jump itself from

H_3O^+ to HO^- is therefore $13.7 - 1.4 = 12.3$ and hence forms the greater part. In ice we will assume that the production of energy during the proton jump itself is the same as it is in water and since the static dielectric constant in ice is of a similar size to that in water, we will for the present assume that also that part of the energy production, which is due to the electrostatic attraction between the ions, has the same size in both ice and water. Hence the formation of the ions in ice requires the same amount of energy as in water (13.7) and the ion concentration in ice should therefore decrease with temperature according to the expression:

$$-R \, d \ln c / d \, (1/T) = 13.7/2 = 6.85. \qquad (1)$$

The energy of activation (E_p) *for proton jumps* between the ions and the H_2O molecules can be calculated from the temperature coefficient for that part of the conductivity of the ions in water, which is due to proton jumps. As will be shown later, the following energies of activation are thus obtained:

For H_3O^+ $E_p = 2.5$ and   for HO^- $E_p = 4.7$.

The fact that the energy of activation is lower for H_3O^+ than for HO^- is of course in agreement with the higher proton jump conductivity of H_3O^+.

Let the number of proton jumps per H_2O molecule be n, per. H_3O^+ ion n' and per HO^- ion n'', and let c be the molecular concentration of the ions H_3O^+ and HO^- (these concentrations must be equal, assuming that the ice lattice contains no other ions), then:

$$n = c \, (n' + n'')/50.9$$

(50.9 is the number of H_2O molecules in 1000 cm^3 of ice).

For the change of c with temperature (1) is valid and for changes of n' and n'':

$$-R \, d \ln n' / d \, (1/T) = 2.5 \quad \text{and} \quad -R \, d \ln n'' / d \, (1/T) = 4.7.$$

For the variation of n with temperature we obtain:

$$-R \, d \ln n / d \, (1/T) = 6.85 + E,$$

where $E = 2.5 \times n'/(n' + n'') + 4.7 \times n''/(n' + n'')$.

At $0°$ C according to the statement on p. 43 the proton jump conductivity in ice of H_3O^+ is 215 and of HO^- 83. n' and n'' are proportional to these figures. Hence we obtain $E = 3.1$ at $0°$ C. At lower temperatures the ratio n'/n'' will increase and E will decrease gradually towards 2.5.

The apparent energy of activation, corresponding to the temperature coefficient of the conductivity of ice, should hence be $6.85 + 3.1 = 9.95$ near the melting point. This is only half of the value calculated from JOHNSTONE's determinations of the conductivity of ice. The reason may be that JOHNSTONE's determinations are not sufficiently accurate to be used for determination of temperature coefficient. It is, however, more probable that in the calculation of the energy required for separation of the ions it has not been permissible to use the high static dielectric constant of water (88). If we had used a value 15 times lower (5.9, this is the size of the dielectric constant of ice in an alternating field, which changes ca. 40,000 times in a second) a release of 21.0 and not 1.4 kcal/gmol would have been found when the ions approached contact. The evolution of heat by the process of "neutralization" would have in this case been calculated to $12.3 + 21.0 = 33.3$ and the apparent energy of activation to $33.3/2 + 3.1 = 19.75$ and thus have been in agreement with JOHN-STONE's conductivity determinations.

On the other hand, it must not be forgotten that the ion concentrations in water and ice are of about the same size, and that this is an indication that the heat of "neutralization" in ice and water should also be expected to be approximately the same.

The use of the *static* dielectric constant has been shown to be permissible in calculations of the forces between the ions in water. This is apparent e. g. from DEBYE and HÜCKEL's work on the coefficients of ion activity[7]) and from BJERRUM's calculations on the relation between the dissociation constants of poly-acidic acids[8]).

The molecules in ice, however, turn ca. 10^6 times less frequently than they do in water. Therefore it appears reasonable that in ice, not the static dielectric constant, but a dielectric constant corresponding to an alternating field of high frequency, has to be used.

6. Calculation of the energies of activation for the reactions $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$ and $H_2O + HO^- \rightarrow HO^- + H_2O$ from temperature coefficients of proton jump conductivities of the ions H_3O^+ and HO^- in water.

In table 2 the electrical conductivities at infinite dilution (μ_∞) are given for the ions H_3O^+, K^+, HO^- and Cl^- at temperatures from $0°$ to $100°$ according to J. JOHNSTONE[9]).

If it is assumed that the H_3O^+ ion, in the absence of proton jumps, would have the same conductivity as the potassium ion, and the HO^- ion the same conductivity as the chloride ion, the figures given in table 3 are obtained for that part of the conductivity (μ_p) which is due to proton jumps. From these proton jump conductivities energies of activation are calculated by means of the usual equation:

$$E = -R \, d \ln \mu / d \, (1/T).$$

These energies of activation are presented in table 4. (In the calculation, in place of differentials, differences have been used).

TABLE 2.

Molar conductivities at infinite dilution (μ_∞) in water.

t	$0°$	$25°$	$50°$	$75°$	$100°$
H_3O^+	240	350	465	565	644
K^+	40.4	74.5	115	159	206
HO^-	105	192	279*	360	439
Cl^-	41.1	75.5	116	160	207

* JOHNSTONE gives 284. An interpolation between the value at the four other temperatures makes 279 more probable.

TABLE 3.

Molar conductivities due to proton jumps (μ_p).

t	$0°$	$25°$	$50°$	$75°$	$100°$
H_3O^+	199.6	275.5	350	406	438
HO^-	63.9	116.5	163	200	232

TABLE 4.

Energies of activation (E) expressed in kcal/gmol, calculated from the proton jump conductivities of the ions in water.

$t°$ C	0–25	25–50	50–75	75–100
H_3O^+	2.07	1.83	1.33	0.78
HO^-	3.85	2.58	1.83	1.53

In the range $0°$ to $25°$ the energies of activation for H_3O^+ are ca. 2 and for HO^- ca. 4. These values ought not, however, to be considered, without reservations, as the energies of activation E_p for the proton transitions $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$ and $HO^- + H_2O \rightarrow H_2O + HO^-$. The energies of activation in the table decrease steeply with rising temperature. This fall can be explained in the following way: In order that the proton jump can take place, an H_2O molecule must be orientated towards the ion in a so-called hydrogen bond position, i. e. so that a positive proton-containing corner in the H_3O^+ ion is turned towards a negative proton-free corner in an H_2O molecule, and a negative proton-free corner in the HO^- ion turned towards a positive proton-containing corner in an H_2O molecule. This condition is always fulfilled for the ions in ice, but on the contrary not always in water. With rising temperature the number of favourable positions in water will decrease. This will reduce the rise in μ_p with temperature and thus make the calculated E values, given in table 4, lower than the true energies of activation E_p for proton jumps in a hydrogen bond position.

This effect can be corrected for as follows: Let α be the fraction of the protons in the H_3O^+ ions, which are associated with an H_2O molecule in hydrogen bond position. The following equation can be used for the variation of α with temperature:

$$ln \frac{\alpha}{1-\alpha} = \frac{Q}{RT} - A = \frac{Q}{R\theta}\left(\frac{\theta}{T} - 1\right) \qquad (2)$$

Q is here the evolution of heat on association of an H_2O molecule with the ion in hydrogen bond position, and A is a constant, which can be calculated when the value of α is known at one temperature, e. g. if we know the temperature θ at which

4*

α is equal to 0.5. This temperature θ is substituted for A in equation (2). Equation (2) is correct if the value of Q is the same whether other H_2O molecules are already associated with the ion or not, and if the tendency of the ion to associate with an H_2O molecule is also independent of this.

The rate h of proton jumps $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$ per H_3O^+ ion may be equated to $3\alpha\beta$, where α is the fraction of associated protons defined above and β is the rate of proton jumps per hydrogen bond $H_3O^+ - H_2O$. Hence we obtain:

$$E = -R\frac{d \ln h}{d(1/T)} = -R\frac{d \ln \alpha}{d(1/T)} - R\frac{d \ln \beta}{d(1/T)} = -R\frac{d \ln \alpha}{d(1/T)} + E_p \quad (3)$$

From (2) it can be deduced that $R\, d \ln \alpha / d(1/T) = Q(1-\alpha)$. If we use this equation we obtain from (3):

$$E_p = E + Q(1-\alpha). \quad (4)$$

By means of (2) and (4) E_p for H_3O^+ is calculated for a series of different pairs of values for Q and θ. Table 5 gives the

TABLE 5.

E_p values for H_3O^+, calculated from E values for a series of sets of values of Q and θ.

Q	θ	0°–25°	25°–50°	50°–75°	75°–100°	mean of E_p (H_3O^+)
3	200	4.84	4.64	4.20	3.68	. .
3	273	3.75	3.81	3.54	3.16	. .
3	320	3.16	3.23	2.99	2.67	. .
3	400	2.66	2.69	2.30	1.97	. .
4	273	4.39	4.47	4.52	4.21	. .
4	300	3.74	4.06	4.01	3.76	. .
4	320	3.34	3.64	3.62	3.47	. .
4	400	2.54	2.63	2.43	2.24	. .
4.5	273	4.71	5.13	5.13	4.76	. .
4.5	320	3.41	3.84	3.95	3.88	. .
4.5	360	2.79	3.04	3.07	3.17	. .
4.5	400	2.49	2.55	2.46	2.36	2.46
5	273	5.06	5.59	5.56	5.30	. .
5	320	3.47	4.04	4.28	4.32	. .
5	400	2.44	2.53	2.47	2.46	. .

results of these calculations. Similar calculations are performed for HO^- and the results are presented in table 6.

TABLE 6.

E_p values for HO^-, calculated from E values for a series of sets of values of Q and θ.

Q	θ	0°–25°	25°–50°	50°–75°	75°–100°	mean of E_p (HO^-)
3	200	6.62	5.39	4.70	4.43	..
3	273	5.53	4.56	4.04	3.91	..
3	320	4.94	3.98	3.49	3.42	..
3	400	4.44	3.44	2.80	2.72	..
4	273	6.17	5.22	5.02	4.96	..
4	300	5.52	4.81	4.51	4.51	..
4	320	5.12	4.39	4.12	4.22	..
4	400	4.32	3.38	2.93	2.99	..
4.5	273	6.49	5.88	5.63	5.51	..
4.5	320	5.19	4.59	4.45	4.63	..
4.5	360	4.57	3.79	3.57	3.92	..
4.5	400	4.27	3.30	2.96	3.11	..
5	273	6.84	6.34	6.06	6.05	..
5	320	5.25	4.79	4.78	5.07	4.97
5	400	4.22	3.28	2.97	3.21	..

It is not possible, solely by the use of the figures in table 5, to find the set of Q and θ which make the calculated E_p values for H_3O^+ independent of the temperature, or to solve the corresponding problem for HO^-. The conductivities, on which these calculations are based, are too inaccurate for this purpose and this is especially true for HO^-. We know, however, that the energy of the hydrogen bond $H_2O - H_2O$ in water generally is considered to be ca. 4.5 [10]), and we will therefore use Q values near this figure. Considering this and also that the E_p values of course should be as uniform as possible in all temperature ranges, it appears reasonable to choose

for H_3O^+ Q = 4.5   and   θ = 400° K.
for HO^- Q = 5   and   θ = 320° K.

This choice leads to the following E_p values:

for H_3O^+ $E_p = 2.5$;   for HO^- $E_p = 4.7$.

For H_3O^+ in water, α (the fraction of the protons of the ion which have an H_2O molecule in hydrogen bond position) is 0.95 at $0°$ C and 0.61 at $100°$ C. For HO^-, α (the fraction of the proton-free corners of the ion which have an H_2O molecule in hydrogen bond position) is 0.77 at $0°$ C and 0.44 at $100°$ C. For comparison it should be stated that BERNAL and FOWLER[11]) have roughly estimated, from the heat of fusion of ice and from the heat capacity of water, that in water at $0°$ 0.88 of the hydrogen bonds between the H_2O molecules are intact and at $100°$, 0.75.

Summary.

1. Ice contains in its lattice H_3O^+ and HO^- ions in equal concentrations. They are formed, without displacements of oxygen atoms, by proton jumps between two adjacent H_2O molecules: $H_2O + H_2O \rightarrow H_3O^+ + HO^-$, and they are separated similarly, without displacements of oxygen atoms, by proton jumps between the ions and H_2O molecules: $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$ and $H_2O + HO^- \rightarrow HO^- + H_2O$. The ions migrate in the ice by means of proton jumps, until oppositely charged ions meet again and have the possibility of recombining.

2. The conductivity of ice may be assumed to be due exclusively to migration of H_3O^+ and HO^- ions by means of proton jumps. The molecular conductivity of these ions in ice can be calculated from the proton jump conductivity of the ions in water to be: 215 for H_3O^+ and 83 for HO^- at $0°$ C. The molecular concentration of the ions in ice is calculated from the specific conductivity of ice to 1.34×10^{-8}, corresponding to the transformation of 0.27×10^{-9} parts of the molecules to H_3O^+ ions, and of an equal fraction of the molecules to HO^- ions.

3. The rate of proton jumps in ice can be calculated, by means of EINSTEIN's equation for BROWNIAN movements, to be:

per H_2O molecule..............................152
per H_3O^+ ion (type $H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$) . 4.15×10^{11}
per HO^- ion (type $H_2O + HO^- \rightarrow HO^- + H_2O$) .....$1.6 \times 10^{11}$

all per second at $0°$ C.

4. The energies of activation for the proton jumps at the ions are calculated, from the temperature coefficient for the proton jump conductivity of the ions in water to be:

for H_3O^+ 2.5 kcal/gmol,   for HO^- 4.7 kcal/gmol.

Using these values it is possible to calculate the temperature coefficient for the rate of proton jumps at the ions. The temperature coefficient for the molecular conductivity of the ions is the same as for the rate of proton jumps.

The fall in the ion concentration with temperature is dependent on the evolution of heat by the process of neutralization $H_3O^+ + HO^- \rightarrow 2\ H_2O$. This must be of a similar size in ice and in water (13.7), if it is permissible to use the static dielectric constant for the electrostatic forces between the ions in ice. A heat of neutralization of this order seems probable, as the ionization in ice is not very different from that in water. If, on account of the lower mobility of the dipoles in ice, a lower dielectric constant has to be used, the heat of neutralization in ice will be higher than that in water. If, e. g., a dielectric constant of 5.9 is assumed (corresponding to an alternating field frequency of 40 kc) the value is calculated to 33.3 kcal/gmol.

From JOHNSTONE's not very reliable determinations of the conductivity of ice, an apparent energy of activation of 19.6 kcal/gmol is calculated. The same energy of activation is calculated from the energies of activation for the proton jumps and from the heat of neutralization to only 9.95, when the heat of neutralization is taken as 13.7. On the other hand, a heat of neutralization of 33.3 gives an energy of activation of 19.75, which is in agreement with JOHNSTONE's figure.

5. The migration of the ions in ice is connected with turns of the H_2O molecules. If the ions migrate under the influence of an electric force, these turns will produce a dipole moment in the opposite direction to that of the force. The molecular turns produced by migration of the ions can not therefore be those required by DEBYE's theory for the dielectric properties of ice. They are also too infrequent to account for these properties.

6. For the justification of assuming the conductivity of ice to be the result of proton jumps in ice, it is of decisive importance that the molecular turns at orientation fault sites are between

10^3 and 10^4 times as frequent as molecular turns at the ions. This means that they are able to neutralize the dipole moment produced by the migration of the ions in an electrical field.

7. For the justification of assuming the abnormally high conductivity of the H_3O^+ and HO^- ions in water to be the result of proton jumps between the ions and the water molecules, it is of decisive importance that the molecular turns, connected with these proton jumps, only amount to a very small fraction of all the molecular turns in water.

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