

Surface Structure of Water and Ice

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ABSTRACT

The state of molecular orientation in a pure water surface is examined and it is concluded that the surface molecules are almost completely oriented with their negative vertices outward. Because of inter-molecular bonding this orientation decays approximately exponentially beneath the surface, the depth of orientation being about ten molecular layers. The driving energy for this orientation is supplied by the electrical asymmetry of the water molecule.

When the surface of ice is examined it is found that the free energy of the system can be lowered if the ice surface is covered by a thin liquid layer. Molecules in the liquid surface are oriented, and the orientation decays in the depth of the layer. Thermodynamic calculations based on a molecular model suggest that the equilibrium film thickness is finite above a temperature of about -30°C and that the film thickness increases greatly as the melting point is approached. Typical film thicknesses are of the order of tens of Angstroms.

§ 1. INTRODUCTION

As long ago as 1850 Faraday proposed that many of the peculiar mechanical properties of ice could be explained by the hypothesis that at temperatures not too far below the melting point its surface is covered with a thin film of water. Since that time many alternate explanations of these phenomena have been advanced including pressure melting (Thomson 1861), local frictional heating (Bowden and Tabor 1954) and polycrystalline creep (Glen 1955), and in any given case a combination of several of these effects may well be present.

Interest in Faraday's hypothesis has, however, continued and several more carefully controlled laboratory experiments have recently been interpreted in terms of it (Weyl 1951, Hosler *et al.* 1959, Jellinek 1959, Hosler and Hallgren 1960). Despite this continued interest no detailed investigation of the thermodynamic stability of such a film appears to have been made, though Weyl (1951) has advanced qualitative arguments for its existence.

It will be our purpose in the present paper to investigate the stability of this film, and, having established this, to discuss the variation of the film thickness with temperature.

The treatment cannot, in the present state of our knowledge of the structure of polar liquids, have any great claim to rigour, but it is felt that the results should have at least a semi-quantitative validity.

§ 2. STRUCTURE OF ICE AND WATER

The generally accepted structure of ordinary ice is a modification of that proposed by Bernal and Fowler (1933) in which the oxygen ions lie at the Zn and S sites of a wurtzite lattice. Each oxygen ion is linked to its four nearest neighbours by hydrogen bonds as shown in fig. 1, but instead of the protons being placed symmetrically on each O-H-O bond, they are nearer to one end than the other in such a way that each oxygen ion has two 'near' hydrogen ions. Pauling (1935) suggested that this is the only restriction placed upon the orientation of the bonds, so that a statistical structure with a large number of energetically equivalent configurations results. Owston (1958) has recently provided an experimental confirmation of this statistical structure by means of x-ray and neutron diffraction.

The structure of water is not known in any detail, though x-ray evidence (Bernal and Fowler 1933, Dorsch and Boyd 1951) as well as general considerations (Frenkel 1946, p. 112) suggest that in supercooled water the short-range order is very similar to that of ice. Water has, however, no long-range order, and this may be attributed to the cumulative effect of broken bonds within the structure, these amounting to about 13% of the total number of bonds. Finally it should be recognized that the structure is not static but fluctuates rapidly so that a given molecule is continually being included in the membership of different ice-like groups.

For our present purposes it will be sufficient to regard the water structure as an ice-like structure containing a considerable fraction of broken bonds. The entropy associated with the configuration of these broken bonds supplies an appreciable part, though not all, of the entropy of fusion. We shall not need to consider this in detail since the entropy of fusion is known from experiment.

§ 3. SURFACE STRUCTURE OF WATER

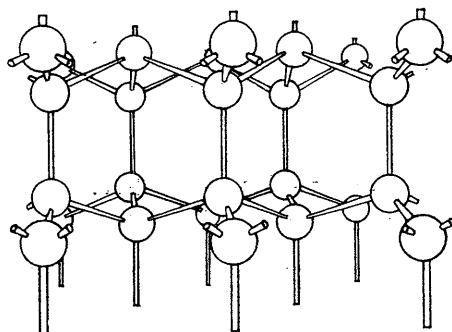
There is widespread evidence, which has been summarized by Henniker (1949), that below the surface of a liquid there is a transition zone which may extend through tens or even hundreds of molecular layers. In the case of liquids whose molecules are asymmetric this surface zone usually results from the preferential orientation of surface molecules with their most polar vertices directed into the liquid, as has been discussed in detail by Frenkel (1946, p. 356) and Harkins (1952, pp. 36-41).

Turning specifically to water we note that surface molecules are, on the average, only second nearest neighbours, and the energy of interaction between such neighbours is small, as evidenced by the close validity of Pauling's calculation of the residual entropy of the normal ice structure. We can therefore to a first approximation treat each surface molecule separately. Now a water molecule is not a symmetrical dipole, but possesses two positive vertices of low polarizability and two roughly tetrahedrally related negative vertices of high polarizability. It will thus be energetically favourable for surface molecules to be oriented with both

positive vertices directed towards the interior of the liquid. The energy gained by such orientation may be estimated in several ways, as indicated in Appendix A, and turns out to be of order 10^{-12} erg per molecule.

Now, as we shall see later, because of bonding requirements any preferential orientation of surface molecules extends for some distance below the surface. Thus, though surface orientation may reduce the total energy of a water surface below that of a random surface, the decrease which this occasions in the free energy of the system is offset to some extent by the decrease in configurational entropy of molecules near the surface. Both these effects must thus be taken into account when minimizing the total free energy to determine the equilibrium configuration of the surface. This we now proceed to do.

Fig. 1



The structure of ordinary ice. Only oxygen ions are shown, but there is one proton on each bond as discussed in the text.

Consider first a perfect ice structure as shown in fig. 1. Only the oxygen ions have been shown, but there is one proton on each bond, nearer to one end than the other as discussed above. The structure consists of crinkled layers parallel to (0001) planes, and if a layer contains $2N$ molecules, then it is linked by N bonds to the layer above and by N bonds to the layer below.

Take now the m th layer, and suppose that on the bonds directed towards the surface there are $(1 - \alpha_m)N$ protons contributed by molecules in the layer. Similarly on bonds directed away from the surface there will be $\alpha_{m+1}N$ protons contributed by molecules in the m th layer. Since each molecule has two protons, then the number of protons available for bonding within the layer is $(3 + \alpha_m - \alpha_{m+1})N$. In a perfect ice crystal the layer must contain $3N$ bonds, neglecting edge effects, and therefore $3N$ protons, so that

$$\alpha_{m+1} = \alpha_m \quad \dots \quad (1)$$

Turning now to a water structure, the same argument holds except that we must allow for the presence of defects, and particularly of broken bonds.

These defects may be assigned either a positive or negative sign according as they effectively add or subtract a proton from the layer in which they occur. Such defects are ordinarily generated in pairs of opposite sign, as for example the detached positive and negative vertices of a broken bond, and if their concentrations remain equal eqn. (1) still holds. If, however, the number of positive defects in the m th layer exceeds the number of negative defects by $\beta_m N$, then the number of protons in the layer must be $(3 + \beta_m N)$. In this case, instead of (1), we have

$$\alpha_{m+1} = \alpha_m - \beta_m. \quad \dots \dots \dots (2)$$

The total balance of defects is, of course, not disturbed, and the negative defects can be regarded as having migrated to the surface where they are exhibited as molecular orientations.

Equation (2) implies that the orientation α_m , which is greater than $\frac{1}{2}$ at the surface, will relax towards its equilibrium value of $\frac{1}{2}$ in the interior of the liquid.

Next we must consider the interaction between defects. In the absence of a detailed model this can only be done qualitatively, but fortunately this is all that is required. The interaction energy between two defects of like sign separated by a distance r can be expanded in a series

$$E = ar^{-1} + br^{-2} + cr^{-3} + \dots, \quad \dots \dots \dots (3)$$

whether the interaction be electrostatic or elastic, and we have neglected any angular dependence. The first term of this series would cause an infinite force upon the boundary of a semi-infinite slab, so cannot occur. The second term contributes a finite force on such a boundary and may be regarded as the origin of the volume change due to the defects. It will be completely compensated by intermolecular forces contributed by this volume change. The term with which we are concerned is the short-range term in r^{-3} . It may arise either from electric dipole-dipole interactions or from elastic effects as discussed in Appendix B.

The interaction energy with which we are concerned is thus as a first approximation proportional to the inverse cube of the distance between defects, and hence to β_m . Since the molecular fraction of defects is also β_m we can write the effective interaction energy per water molecule in the form

$$E = \delta \beta_m^2. \quad \dots \dots \dots (4)$$

The value of δ can only be evaluated on the basis of a specific model. That discussed in Appendix B suggests that δ should be of the order of 10^{-12} erg. We shall not require to use this value in our calculation, but it is helpful as a physical reference in our discussion.

We are now in a position to write a formal expression for the difference in free energy between a partially oriented and a completely random water surface. Let ϵ be the amount by which the enthalpy of a surface molecule with an outward directed proton exceeds that of a surface molecule with both protons directed inward. Then the enthalpy of a surface of orientation α_0 exceeds that of a random surface by $-(\alpha_0 - \frac{1}{2})\epsilon$ per surface molecule.

Suppose further that the average entropy of a molecule in a layer with orientation α is S^α . Then considering in addition the molecular layers beneath the surface, the average free energy per surface molecule of an oriented surface exceeds that of a random surface by an amount

$$\Delta G = -(\alpha_0 - \frac{1}{2})\epsilon + \sum_{m=0}^{\infty} \delta \beta_m^2 - T \sum_{m=0}^{\infty} (S^{\alpha m} - S^{1/2}). \quad (5)$$

The author has derived elsewhere (Fletcher 1959) an expression for the configurational entropy of an ice structure of orientation α . On the basis of our assumed water structure the entropy of supercooled water can to a good approximation be represented by the sum of an orientation-dependent term identical with that for ice, and another term, A , which is independent of α . Using this former result†, then

$$S^\alpha = k \log [3 \times 2^{-3/2} \alpha^{-\alpha/2} (1 - \alpha)^{-(1-\alpha)/2}] + A, \quad (6)$$

and the term represented by A does not appear in (5). The expression (6) has a broad maximum at $\alpha = \frac{1}{2}$ as would be expected.

From eqn. (6) and the relation (2) we can proceed to find the equilibrium configuration of the surface by minimizing ΔG , given by (5), with respect to α_0 and the form of the function β_m . To do this requires, however, a knowledge of the numerical values of ϵ and δ which we possess at best only in order of magnitude. The minimization can however be carried out formally in terms of ϵ and δ and the predicted configuration compared with available experimental data to determine ϵ and δ . It is this course which we shall now follow.

The first step in the minimization of ΔG is the choice of a suitable functional form for β_m . Clearly β_m is largest for $m=0$, and the fact that $\partial S^\alpha / \partial \alpha = 0$ when $\alpha = \frac{1}{2}$ suggests that β_m should tend asymptotically to zero as m approaches infinity. The simplest function satisfying these requirements is the exponential

$$\beta_m = \beta_0 \exp(-\gamma m), \quad (7)$$

where β_0 and γ are constants.

To simplify the solution it is convenient to replace the discrete variable m by a continuous variable so that the sums in (5) become integrals. From (2) and (7), together with the requirement that

$$\alpha(\infty) = \frac{1}{2}, \quad (8)$$

we then find that

$$\beta(m) = (\alpha_0 - \frac{1}{2}) \gamma \exp(-\gamma m) \quad (9)$$

and

$$\alpha(m) = \frac{1}{2} + (\alpha_0 - \frac{1}{2}) \exp(-\gamma m). \quad (10)$$

† As discussed in Fletcher (1959) the value given for S^α in (6) is strictly valid only for α fairly close to $\frac{1}{2}$. For α near 0 or 1 the factor $3 \times 2^{-3/2}$ in the argument of the logarithm should be replaced by $2^{1/6}$. We shall not consider this refinement here.

Furthermore the entropy integral in (5), as made explicit by (6) and (10), can be evaluated as a series in $(\alpha_0 - \frac{1}{2})$ of which the first term is

$$\int_0^\infty (S^\alpha - S^{1/2}) dm \approx -\frac{k}{2\gamma} (\alpha_0 - \frac{1}{2})^2, \quad \dots \quad (11)$$

so that (5) can be written to a first approximation as

$$\Delta G \approx -(\alpha_0 - \frac{1}{2})\epsilon + \delta\gamma(\alpha_0 - \frac{1}{2})^2 + kT(\alpha_0 - \frac{1}{2})^2/2\gamma. \quad \dots \quad (12)$$

This expression clearly has a minimum for a positive value of $(\alpha_0 - \frac{1}{2})$, and at the minimum $\Delta G < 0$, so that a partially oriented surface will be the stable state.

Minimizing (12) with respect to α_0 and γ we find

$$\gamma = (kT/2\delta)^{1/2}, \quad \dots \quad (13)$$

$$\alpha_0 = \frac{1}{2} + \epsilon(8\delta kT)^{-1/2}, \quad \dots \quad (14)$$

which represents a formal solution giving the configuration of the equilibrium surface. We can now compare these results with experimental data to determine the unknown constants ϵ and δ .

Good (1957) has made an extensive study of the variation of surface tension with temperature for many polar and non-polar liquids. From this information he has been able to deduce values for the surface entropies. The average molar surface entropy of non-polar liquids was found to be about 24.0 joule deg⁻¹, while for water the value is only 9.8 joule deg⁻¹. The entropy deficit of about 14 joule deg⁻¹ mole⁻¹, or about 1.7 k per molecule, he attributed to surface orientation of the type we have been discussing.

Comparing this value with the calculated value given by (11) we have

$$(\alpha_0 - \frac{1}{2})^2/2\gamma \approx 1.7 \quad \dots \quad (15)$$

and from (13) and (14) we have

$$(\alpha_0 - \frac{1}{2})/\gamma = \epsilon/2kT. \quad \dots \quad (16)$$

These two equations are not strictly sufficient to determine ϵ , α_0 and γ , but if we take account of the upper limit of unity for α_0 and the probable range of values of ϵ we find with reasonable confidence

$$\alpha_0 = 1; \quad \epsilon \approx 5 \times 10^{-13} \text{ erg.} \quad \dots \quad (17)$$

Using now (15) and (13) we have

$$\gamma \approx 0.074; \quad \delta \approx 3.4 \times 10^{-12} \text{ erg.} \quad \dots \quad (18)$$

It is reassuring that the value of ϵ lies quite close to that estimated from first principles in Appendix A, whilst δ is of the order indicated by the model of Appendix B.

We may sum up the results of this section with the statement that at temperatures near the freezing point the surface molecules of water are completely oriented with their negative vertices outwards. The orientation decays approximately exponentially with distance below the surface at

such a rate that about 13 molecular layers† (about 26 Å) are required to reduce the orientation by a factor 1/e. The electrostatic implications of this orientation are considered in Appendix C.

§ 4. SURFACE STRUCTURE OF ICE

Because the molecular fraction of defects in an ice crystal is very small the eqn. (1) is obeyed very closely and any orientation of surface molecules is transmitted through the entire crystal. Such a situation is energetically unfavourable because of the large loss of configurational entropy, so that no surface orientation can occur in ice.

There is however the possibility, discussed by Weyl (1951), that the surface free energy of ice may be lowered if the surface is covered by a thin water layer in which a transition from molecular orientation to the normal random ice surface can take place. We now examine the thermodynamic stability of such a layer on the basis of our discussion of orientation relaxation below a water surface.

Let us suppose that the ice surface is covered by d molecular layers of water in which the orientation varies from α_0 at the surface to α_d at the water-ice interface. Then considering surface enthalpies, which can be approximately evaluated by simple bond counting, we may write

$$\left. \begin{aligned} H_{\text{water-air}} &= -\epsilon_1(\alpha_0 - \frac{1}{2}) + h_1, \\ H_{\text{ice-water}} &= \epsilon_2(\alpha_d - \frac{1}{2}) + h_2, \\ H_{\text{ice-air}} &= h_3, \end{aligned} \right\} \dots \dots \dots (19)$$

where ϵ_1 is the enthalpy of reversal of a surface molecule, previously denoted simply by ϵ , and ϵ_2 is the enthalpy of rupture of a single hydrogen bond at the water-ice interface. The enthalpies h_i apply to surfaces without any orientation effects, and to a good approximation we expect

$$h_3 = h_1 + h_2. \dots \dots \dots (20)$$

From data on hydrogen bond enthalpies in ice (Pimentel and McClellan, 1960) and our previous discussion we have the approximate numerical values

$$\epsilon_1 \approx 5 \times 10^{-13} \text{ erg}; \quad \epsilon_2 \approx 4 \times 10^{-13} \text{ erg}. \dots \dots (21)$$

Turning to bulk effects, the free energy of water is higher than that of ice by ΔG_F , given by

$$\Delta G_F = \Delta S_F \Delta T, \dots \dots \dots (22)$$

where ΔT is the supercooling and ΔS_F the entropy of fusion which has the value

$$\Delta S_F = 3.7 \times 10^{-16} \text{ erg deg}^{-1} \text{ molecule}^{-1}. \dots \dots (23)$$

† In this context a single crinkled layer as in fig. 1 is regarded as consisting of two molecular layers, so that the effective thickness of a molecular layer is about 2 Å.

Assembling these contributions, including the effect of the entropy deficit in the partly oriented water and the interaction energy between defects, the free energy per surface molecule of the liquid-film structure exceeds that of a simple ice surface by an amount

$$\Delta G = \Delta S_F \Delta T d - T \sum_{m=0}^d (S^{\alpha m} - S^{1/2}) + \sum_{m=0}^d \delta \beta_m^2 - \epsilon_1(\alpha_0 - \frac{1}{2}) + h_1 + \epsilon_2(\alpha_d - \frac{1}{2}) + h_2 - h_3 \quad (24)$$

and the h_i cancel by virtue of (20).

We now follow the procedure used to treat the water surface, using again the expression (7) for β_m . The entropy integral can be evaluated to a first approximation to give

$$\int_0^d (S^\alpha - S^{1/2}) dm \approx - \frac{k}{2\gamma} (\alpha_0 - \frac{1}{2})^2 [1 - \exp(-2\gamma d)] \quad (25)$$

and for ΔG we obtain

$$\Delta G \approx \Delta S_F \Delta T d + \frac{kT}{2\gamma} (\alpha_0 - \frac{1}{2})^2 [1 - \exp(-2\gamma d)] + \delta\gamma(\alpha_0 - \frac{1}{2})^2 - (\alpha_0 - \frac{1}{2})[\epsilon_1 - \epsilon_2 \exp(-\gamma d)]. \quad (26)$$

This expression must now be minimized with respect to α_0 , d and γ , and if this is to represent the equilibrium situation it must be required in addition that $\Delta G < 0$.

The minimization of (26) is more difficult than was the corresponding problem for a simple water surface, and indeed to perform the process accurately numerical methods must be resorted to.

For our present purposes, however, considering the crudity of our model an approximate minimization will be sufficient. Such a result, valid for small ΔT , can be obtained by observing that when the liquid film is thick it must resemble the surface of water, so that the solution must transform to that for a water surface when $\Delta T = 0$. This means that we can use the relation (13) as a first approximation to γ , and after considerable manipulation we obtain the results

$$(\alpha_0 - \frac{1}{2}) \approx \frac{\epsilon_1}{(8\delta kT)^{1/2}} - \left(\frac{\delta}{2kT}\right)^{1/2} \frac{\Delta S_F \Delta T}{\epsilon_1} \quad (27)$$

and

$$d \approx \frac{1}{\gamma} \log \left(\frac{\epsilon_1 \epsilon_2}{4\delta \Delta S_F \Delta T} - \frac{\epsilon_2}{2\epsilon_1} \right) \quad (28)$$

The value of $(\alpha_0 - \frac{1}{2})$, as given by (27), is seen to approach the expression given by (14) as required.

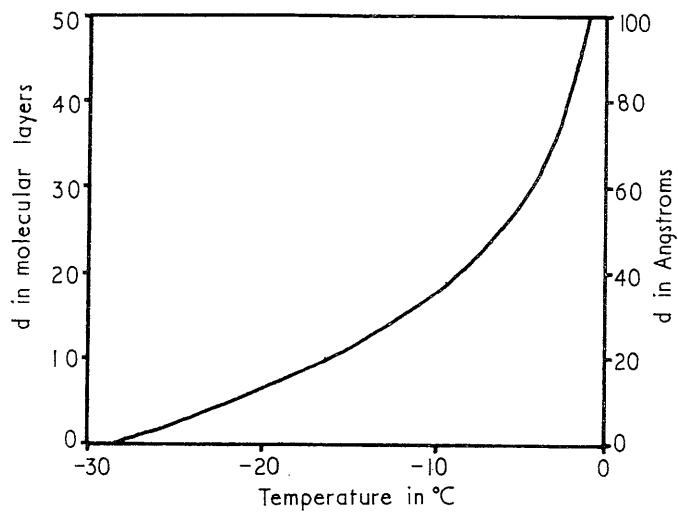
Inserting numerical values from (21), (23) and (18), and recalling that one molecular layer corresponds to approximately 2×10^{-8} cm film thickness, we find

$$\alpha_0 \approx 1.0 - 5 \times 10^{-3} \Delta T, \quad (29)$$

$$d \approx 2.8 \times 10^{-7} \log \left(\frac{40}{\Delta T} - 0.4 \right), \quad (30)$$

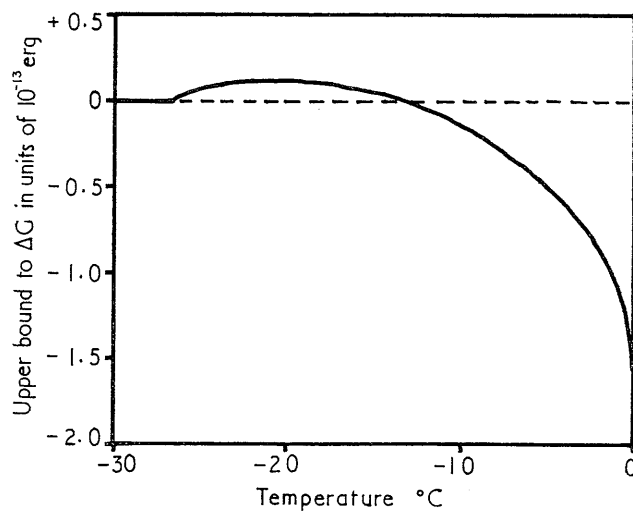
where ΔT is expressed in centigrade degrees and d in centimetres.

Fig. 2



The thickness d of the equilibrium liquid film on the surface of ice as a function of temperature.

Fig. 3



Upper bound to the amount ΔG by which the free energy of the equilibrium liquid film surface exceeds that of a solid crystalline ice surface. ΔG is given per surface molecule.

The variation of film thickness with temperature, as given by (30), is shown graphically in fig. 2. It can be seen that the film exists only at temperatures above about -30°C , and that its thickness is of the order of some tens of angstroms.

Before we can conclude that this surface structure is stable, we must verify that ΔG as given by (26) is negative. This is simply done by inserting the expressions (29) and (30) back into (26), and the result is shown in fig. 3. For temperatures above about -13°C we see that ΔG is unambiguously negative by an amount of the order of a few times 10^{-14} erg per molecule, which corresponds to about 10 erg cm^{-2} . In the region between -13°C and -30°C , ΔG is slightly positive, but it must be remembered that our approximate minimization gives only an upper limit to ΔG , and it is very probable that an accurate minimization not involving the approximation (13) for γ would yield a ΔG which was negative over the whole range from -30°C to the melting point.

We can thus state with some confidence that the liquid film is stable above about -13°C , and surmise that in fact this is also true down to temperatures of about -30°C , below which the film vanishes.

§ 5. DISCUSSION

Now that analysis of the stability and behaviour of the proposed liquid surface film has been completed, it is appropriate to re-examine briefly the method by which this has been done. The procedure has been primarily a variational one which has the advantage that since the trial functions used gave a stable film, a more accurate solution can only reinforce this stability. Furthermore the degree of stability found, as evidenced by the ΔG values of fig. 3, is so large that inaccuracies in the experimental data used, for example to evaluate ϵ_1 , or in the assumption of approximate relations like (20), can have little effect upon the final conclusion.

The major uncertainties lie then in the properties assumed for the quasi-liquid layer. We have considered this to have properties close to those of the surface layers of liquid water. This applies however principally to the thermodynamic quantities involved, and mechanical properties such as viscosity may well differ greatly from those of bulk water. It seems unlikely, however, that a more detailed consideration of this surface layer would greatly modify our conclusions.

Any attempt to explain experimental observations of the surface mechanical properties of ice in terms of this liquid layer structure must be treated with caution, since in most experimental situations it is likely that several of the phenomena mentioned in the Introduction may contribute to the observed behaviour. One or two experiments of special simplicity might however be mentioned briefly as giving indirect support to our conclusions.

Kingery (1960) placed small ice spheres in contact and observed microscopically the growth of an ice neck between them. He concluded that the growth was due to surface diffusion, but the observed diffusion rate was several orders of magnitude higher than expected, and the

temperature dependence of growth rate was very large. Both these effects can be explained in an obvious way in terms of the thickness and variation with temperature of the surface liquid layer. It may be remarked that over the range -2 to -24°C the behaviour of the film thickness is quite accurately represented by an expression of the form $A \exp(-Q/RT)$, where the apparent activation energy Q amounts to about 14 kcal/mole.

In a somewhat similar experiment Hosler *et al.* (1957) measured the force required to separate two ice spheres which had been placed in contact with a force less than 1 dyne. The force required for separation was of the order of 100 dynes and varied with temperature in almost exactly the manner followed by the film thickness d in fig. 3. If surface diffusion is neglected for the moment then this behaviour is exactly as would be expected from freezing of the surface film over the area of contact. Indeed the separation forces which would be predicted from this mechanism are only about a factor 6 less than the observed forces. This picture will be inevitably modified by the effects of surface diffusion, but this will be in such a direction as to bring the predictions more nearly into agreement with experiment.

Experiments of this type can only give indirect evidence of the existence of such a surface film, and it would be highly desirable to have some more direct method. Several possibilities suggest themselves such as proton spin resonance and infra-red absorption measurements. More directly still the film may show its existence through its effect on the ellipticity of light reflected from an ice surface, measured as a function of temperature. Again integration of dipole orientations through the surface layer, as discussed in Appendix C, suggests that ice should show a large and approximately linear variation of surface potential in the range 0 to -30°C , with a pronounced change in slope near -30°C . These experiments have yet to be carried out.

§ 6. CONCLUSIONS

The semi-quantitative treatment given above leads to the conclusion that the orientation of molecules in a water surface near 0°C extends in an exponentially decreasing manner for distances of the order of ten molecular layers below the surface.

When a similar analysis is made of the possibility of orientation effects at an ice surface it is found that such orientation is only possible if the surface is covered by a quasi-liquid film in which the orientation may relax. Such a liquid-film surface structure is found to give a total surface free energy considerably lower than that of a crystalline ice surface, and so is concluded to represent the actual state of the surface. The thickness of the liquid film is of the order of tens of angstroms, decreasing as the temperature is lowered, and vanishing below about -30°C .

The discussion has been limited to ice, and such a liquid surface is not a characteristic of crystals in general. However, molecular solids melting to form associated liquids, whose molecules are polar and strongly asymmetric and whose crystalline state does not have a polar structure, may exhibit similar effects.

APPENDIX A

The energy gained by orienting the surface dipoles in a water structure can be estimated in three independent ways. These are considered below.

(i) The energy gained when a proton, initially directed towards the vapour, is redirected inwards to the bulk of the liquid is approximately the energy of formation of a hydrogen bond. This leads to an estimate of 4×10^{-13} erg for ϵ (Pimentel and McClellan 1960.)

(ii) A similar estimate can be made from first principles. The energy of interaction of neighbouring surface molecules can be neglected as discussed in the text. Because of polarization effects if a molecule is oriented with its oxygen ion outwards then the electron cloud at the surface will be fairly smooth. On the other hand if a proton protrudes from the surface then it will appear as a small hill of positive charge elevated above a fairly flat area of negative charge contributed by the oxygen ion.

Since the O-H bond length in the water molecule is about 10^{-8} cm, one might estimate that the proton should protrude a distance of the order of 10^{-9} cm above the electron cloud. The average area occupied by a surface molecule is about 10^{-15} cm², and one can easily calculate the relative electrostatic energies of a flat surface and of a flat surface with a nearby positive charge. The energy of the latter is found to be higher by an amount of the order of 10^{-12} erg.

(iii) A thermodynamic argument based on measured quantities gives a completely independent estimate. Good (1957), as discussed in the text, found the surface entropy of water to be lower by an amount of $1.7k$ per molecule than the entropy of a randomly oriented surface. This entropy loss must be more than compensated by the enthalpy gained by surface orientation. In a random surface half the molecules are oriented inwards and half outwards, so that the enthalpy gained by complete orientation is $\epsilon/2$ per molecule. We must therefore have

$$\epsilon/2 > 1.7kT,$$

which, near 273°K, gives

$$\epsilon > 1.2 \times 10^{-13} \text{ erg.}$$

These three independent methods thus agree in predicting for ϵ a value of the order of 10^{-12} erg.

APPENDIX B

In this appendix we present a possible model for the interaction between defects in a water structure. It is emphasized that the validity of the theory as a whole is in no way dependent on the validity of this particular model.

A water structure may be regarded as an ice structure possessing a considerable molecular fraction of broken bonds. There is no long-range order and the whole structure is rapidly fluctuating. Consider two broken bonds separated by only a few molecular distances, then for an appreciable fraction ϕ of the time these two bonds will be members of a coherent group of molecules in an ice-like structure.

Consider for a moment this ice-like grouping as a static structure. Then because the broken bonds produce an appreciable overall volume change, they will be centres of elastic strain in the bonding structure. The long-range interactions between them have been taken up by the overall volume change, but short-range interactions remain due to the overlap of their elastic strain fields.

The interaction energy due to the overlap of these strain fields can be evaluated in order of magnitude by elastic continuum theory (Sokolnikoff 1956). The ice lattice is replaced by a medium of rigidity μ and the defects by spheres of radius a whose radius is then allowed to change by an amount Δa . If the separation between defects is r then the resulting energy can be calculated to be of order

$$E \sim 10^2 \mu a^4 (\Delta a)^2 r^{-3}.$$

Since in our water structure the defects spend only a fraction ϕ of their time linked in such a way, we may write

$$E \sim 10^2 \phi \mu a^4 (\Delta a)^2 r^{-3}.$$

To evaluate this expression we note that $a \approx 2 \times 10^{-8}$ cm, and from the fact that a concentration of about 0.13 of broken bonds causes a relative volume change of 0.1 on melting we deduce that $\Delta a \approx 5 \times 10^{-9}$ cm. Using the value of μ appropriate to ice ($\mu \approx 3.6 \times 10^{10}$ dyne cm⁻², Penny 1948) we then have

$$E \sim 10^{-35} \phi r^{-3}$$

for the interaction energy of a defect pair.

If there are n molecules per cm³ and the molecular fraction of defects is β , then considering interactions with about 10 nearest neighbours, the interaction energy per molecule is of order

$$10^{-34} \phi n \beta^2 = \delta \beta^2,$$

so that

$$\delta \sim 3 \times 10^{-12} \phi \text{ erg.}$$

Any estimate of ϕ must be very uncertain, but since the molecular fraction of defects is of order 10^{-1} , we may expect, for separations of only a few molecular diameters, that $\phi \sim 10^{-1}$ at least. This is borne out by the liquid distribution-function curve. Thus our estimate suggests

$$\delta \sim 10^{-12} \text{ erg.}$$

APPENDIX C

Because the surface layers of the water film we are considering consist of partially oriented molecular dipoles, we may expect to find an electrostatic potential jump across the surface zone. It is interesting to make an estimate of the magnitude of this potential change.

Neglecting polarization and other effects the potential jump is given by

$$\Delta V = 4\pi M,$$

where M is the electric dipole moment per unit area of surface. Now suppose

there are n molecules per unit area in a layer parallel to the surface and each has a dipole moment μ , these moments being directed, in an ice-like structure, at an angle of 55° to the normal to the layer. If then the layer concerned has an orientation α_m , its contribution to the surface dipole moment is

$$2n\mu(\alpha_m - \frac{1}{2}) \cos 55^\circ \approx 1.2n\mu(\alpha_m - \frac{1}{2}).$$

For a film of thickness d molecular layers, the surface moment is thus

$$M(d) \approx 1.2n\mu \int_0^d (\alpha_m - \frac{1}{2}) dm,$$

which, using eqn. (10), gives

$$M(d) \approx 1.2n\mu\gamma^{-1}(\alpha_0 - \frac{1}{2})[1 - \exp(-\gamma d)].$$

From our earlier results we have values for α_0 and γ and an expression for d as a function of temperature for ice, while for water $d = \infty$. The value of n appropriate to our method of counting molecular layers is $5 \times 10^{14} \text{ cm}^{-2}$, while $\mu \approx 1.8 \times 10^{-18} \text{ e.s.u.}$ Thus for a water surface this calculation gives

$$\Delta V = 30 \text{ volts,}$$

while for an ice surface ΔV varies approximately linearly from this value to zero as the temperature falls from 0°C to -30°C . This calculation however neglects two effects, the polarization of exposed oxygen ions at the surface, and the polarization of water molecules close to the ends of the dangling bonds within the bulk liquid. Both these effects tend to reduce the size of ΔV though it is difficult to estimate the magnitude of their contribution. Harkins (1952, p. 129) suggests on the basis of experimental comparisons that this simple method of calculation overestimates ΔV by a factor between 6 and 10. If we accept this, then ΔV is still of the order of a few volts and should produce measurable effects. It should be noted however that in any direct measurement the effects of a similar layer at the electrode-water interface may greatly decrease the measured potential jump.

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