

Entropy Effect in Ice Crystal Nucleation

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The effect of bond orientation in ice, which leads to its residual entropy, is also found to be important in its heterogeneous nucleation. Any substrate which orients ice dipoles at its surface parallel to one another is a poor nucleating agent, because it reduces the entropy and hence raises the free energy of any small embryos growing upon it. Critical temperatures are calculated for surfaces of this type, and it is shown that for crystals like AgI or PbI_2 the basal faces are poor ice crystal nuclei, and activity is mostly confined to the prism faces. This result leads to improved agreement between observed and theoretical nucleation thresholds and gives an explanation of some of the phenomena observed in nucleation by monocrystalline substrates.

INTRODUCTION

THE nucleation of ice crystals from a supercooled fog by foreign particles is a subject of great interest in the field of cloud physics. Because of this interest a very large amount of experimental information is available, and the field is a useful testing ground for theories of the nucleation process.

Ice is, however, an unusual substance in many ways, and most nucleation theories do not take account of some of its special properties. In this paper we shall pursue the consequences of the fact that ice has a finite entropy at absolute zero. At first sight this seems irrelevant to the nucleation process, but we shall see that in fact it imposes strict conditions upon the types of crystalline substances which can be efficient ice-forming nuclei.

In this discussion we shall neglect many features of the nucleation process which have been treated elsewhere, and concentrate for the most part on nucleation by perfect plane crystallographic surfaces.

THE STRUCTURE OF ICE

The generally accepted structure of ordinary ice is a modification of that proposed by Bernal and Fowler,¹ in which the oxygen atoms lie at the Zn and S sites of a wurtzite lattice. Each oxygen is linked to its four nearest neighbors by hydrogen bonds, but instead of the hydrogen being symmetrically placed on each O—H—O bond, it is nearer to one end than the other, in such a way that each oxygen has two "near" hydrogens. Pauling² suggested that this was the only restriction placed upon the orientation of the bonds, so that a statistical structure with a large number of equivalent configurations results. Owston³ has recently provided an experimental confirmation of this statistical structure by means of x-ray and neutron diffraction.

Pauling² has shown that the large number of possible configurations of this structure leads to a residual entropy of $k \ln (3/2)$ per molecule at absolute zero.

¹ J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).

² L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).

³ P. G. Owston, *Advances in Physics* (Taylor and Francis, Ltd., London, 1958), Vol. 7, p. 171.

This value is in good agreement with that found experimentally.⁴

Pauling's model is now fairly generally accepted, though there has been some criticism of his method of evaluating the number of possible configurations, and Meijering⁵ concludes that Pauling's value for the residual entropy should be increased by about 5%. The experimental results are not sufficiently precise for this to affect the observed agreement.

We shall now discuss a partially "polar" or preferentially oriented form of ice and evaluate its residual entropy. This is not proposed as an equilibrium structure but, as we shall see later, as one imposed by surface constraints. This entropy calculation will then form the basis of our subsequent discussion.

In Fig. 1 we show part of two basal (0001) layers of ice. Only oxygens are indicated, but there is a hydrogen at one of two positions along each bond as discussed above. There are clearly two classes of molecules in each layer—those with a bond pointing upward to link with the layer above, and those with a bond pointing downward to the layer below. Let us suppose that there is some large number n of oxygens of each class in one puckered layer.

Of the n bonds directed downward, exactly $n/2$ would have hydrogens associated with this layer in normal ice. We shall consider a polar form of ice in which a fraction α of the n bonds have hydrogens associated with this layer. We shall first show briefly that this partial polarization extends through all subsequent layers, and then evaluate the residual entropy of the structure.

In the puckered layer itself there are just $3n$ bonds which must contain $3n$ hydrogens since the density of ionized molecules is negligible. The n molecules with downward-directed bonds contribute $(2-\alpha)n$ hydrogens to the layer. The n molecules with upward-directed bonds therefore must contribute $(1+\alpha)n$ hydrogens, which leaves $(1-\alpha)n$ hydrogens on the upward-directed bonds. The next layer thus must have a fraction α of hydrogens on downward-directed bonds, so that

⁴ W. F. Giaque and J. W. Stout, *J. Am. Chem. Soc.* **58**, 1144 (1936).

⁵ J. L. Meijering, *Philips Research Repts.* **12**, 333 (1957).

the polarization is constant throughout the lattice. Similar arguments apply to polarization along other crystallographic directions.

We should remark that this discussion has neglected edge effects, and so only applies to crystals of moderately large lateral extent. In very small crystals the orientation will revert to its normal random state at some distance from the constrained layer. We shall not treat this effect explicitly, but merely note that in some situations involving very small embryos it must be taken into account.

Evaluation of the residual entropy of this partly ordered structure is rather more complicated than for either a normal or a completely polar structure. Since even in these simpler cases an exact result has not yet been obtained,⁵ we shall be content with a moderately good approximation. To find this we shall first calculate the entropy of polar ice and then evaluate the number of additional configurations available when orientation is not complete.

Consider a puckered layer containing n molecules. In completely polar ice, one set of $n/2$ molecules has one hydrogen each in the layer, and the remaining set has two hydrogens. Each of these $3n/2$ hydrogens has two available positions on its bond giving $2^{3n/2}$ configurations, but only $3/8$ of these give the correct number of hydrogens at a particular molecule. The number of possible configurations is thus $(3/8)^n 2^{3n/2}$ or $(3 \times 2^{-3/2})^n$. For m layers or nm molecules the number of configurations is $(3 \times 2^{-3/2})^{nm}$.

This result is known to be inaccurate,^{5,6} as will be discussed in the following; for the present we shall accept it for the sake of later consistency.

Now consider an ice structure in which the orientation factor is α as defined above. In a single puckered layer there are $\alpha n/2$ bonds which can be distributed in any way over the bottom of the layer, and $(1-\alpha)n/2$ bonds which can be distributed over the top of the layer. These represent the bonds in opposition to the prevailing orientation. However the upward-directed bonds of one layer fix the configuration of downward-directed bonds of the next layer, so that each layer only has additional configurations to number ${}^{n/2}C_{\alpha n/2}$ or $(n/2)! / (\alpha n/2)! [(1-\alpha)n/2]!$. This expression is, of course, symmetrical between α and $(1-\alpha)$.

Since n is large we use Stirling's approximation to expand the factorials, and, retaining only logarithmically important factors, we find that the number of additional configurations is

$$\alpha^{-\alpha n/2} (1-\alpha)^{-(1-\alpha)n/2}.$$

If now there are m layers and we write N for nm , the total number of configurations is

$$[3.2^{-3/2} \alpha^{-\alpha/2} (1-\alpha)^{-(1-\alpha)/2}]^N$$

⁶ W. N. Lipscomb, *J. Chem. Phys.* **22**, 344 (1954).

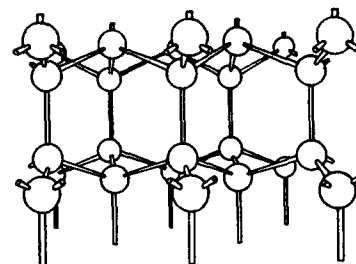


FIG. 1. An expanded view of the normal ice lattice. Only oxygens are shown, but there is one hydrogen on each bond (as discussed in the text).

and the configurational entropy per molecule is

$$S^{\alpha} = k \ln [3.2^{-3/2} \alpha^{-\alpha/2} (1-\alpha)^{-(1-\alpha)/2}]. \quad (1)$$

This value reduces to the simple oriented ice value for $\alpha=0$ or 1 , and to the Pauling value $k \ln(3/2)$ when $\alpha=1/2$ and the orientation vanishes.

As we remarked above, however, the value $k \ln(3.2^{-3/2})$ is not a very good approximation to the entropy of oriented ice, and the correct value is more nearly⁶ $k \ln 2^{1/6}$. In addition we have assumed complete independence of bond distributions on either side of a puckered layer, which is not exactly valid. These two counting errors compensate each other to some extent, so that the result (1) is reasonably accurate for values of α near 0.5 . For α values near 0 or 1 it is a better approximation to write

$$S^{\alpha} = k \ln [2^{1/6} \alpha^{-\alpha/2} (1-\alpha)^{-(1-\alpha)/2}]. \quad (2)$$

By interpolation between these two forms, a reasonably accurate result can be obtained for all α .

Since the expressions (1) and (2) are symmetrical between α and $(1-\alpha)$, we shall for convenience discuss in the following only values of α lying between 0 and 0.5 .

NUCLEATION ON CRYSTAL FACES

When an ice crystal is nucleated and grows upon the face of a crystal of predominantly ionic structure, the binding between the two faces in contact is caused largely⁷ by the interaction of one of the OH dipoles of each H_2O molecule with the electric field at the surface of the nucleating crystal. The energy of the interface will be lowest when each dipole is oriented parallel to the field in its neighborhood, but this configuration may cause lower entropy, and hence higher free energy, in the bulk material away from the interface. The manner in which this relation between interfacial energy and bulk entropy influences the nucleation behavior of the surface will be the subject of our discussion.

Consider the situation shown in Fig. 2. We have a crystalline substrate 3, upon which is growing an embryo of ice 2, from a parent phase 1, which may either be supersaturated vapor (sublimation) or supercooled water (freezing). We have drawn the ice embryo as a hexagonal prism, corresponding to nucleation upon

⁷ J. H. De Boer, *Advances in Colloid Sci.* **3**, 1 (1950).

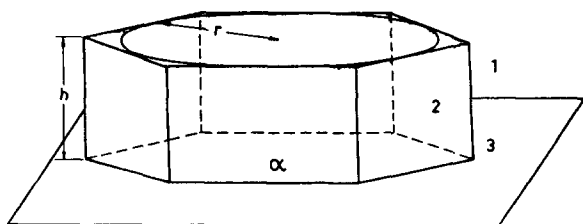


FIG. 2. A prismatic ice embryo 2 growing upon a crystalline substrate 3 from a parent phase 1. Dimensions of the embryo are as shown, and α represents the equilibrium orientation factor for growth of an embryo of this size upon the particular substrate.

the basal plane of a substrate with hexagonal symmetry, because we shall see later that this is the case of particular interest. There is some uncertainty as to whether subcritical crystalline embryos will show crystalline habit, or whether they may be better approximated by spherical caps. We shall show later that it matters little to the final result which assumption is made.

We shall denote volumes by V and surfaces by Ω with appropriate subscripts, while surface free energies will be denoted by σ . If we write ΔG_v for the difference in free energy, per unit volume of ice, between ice and parent phases of infinite extent, then the free energy of formation of the embryo of Fig. 2, neglecting orientation effects, is

$$\Delta G = \Delta G_v V_2 + \sigma_{12} \Omega_{12} - (\sigma_{13} - \sigma_{23}) \Omega_{23}. \quad (3)$$

We have for simplicity neglected here any difference in surface free energy from one crystal face to another, which seems to be a reasonable approximation in the case of ice.⁸

For a prismatic embryo of height h whose base is a regular polygon with inscribed circle of radius r as shown, we have

$$\left. \begin{aligned} V_2 &= \xi \pi r^2 h \\ \Omega_{12} &= \xi \pi r^2 + 2 \xi \pi r h \\ \Omega_{23} &= \xi \pi r^2 \end{aligned} \right\}, \quad (4)$$

where $\xi \geq 1$ and depends upon the number of sides. For a regular hexagon, $\xi = 1.1$. Equation (3) then becomes

$$\Delta G = \xi \pi r^2 h \Delta G_v + \xi \pi r^2 (\sigma_{12} + \sigma_{23} - \sigma_{13}) + 2 \xi \pi r h \sigma_{12}. \quad (5)$$

A critical embryo is one for which

$$\partial \Delta G / \partial r = 0, \quad \partial \Delta G / \partial h = 0. \quad (6)$$

An embryo of this size will develop into a macroscopic crystal, whilst a smaller embryo will tend to disappear. Applying the conditions (6) to (5) we find the relations

$$h = [(\sigma_{12} + \sigma_{23} - \sigma_{13}) / \sigma_{12}] r = \gamma r \quad (7)$$

and

$$r^* = -2 \sigma_{12} / \Delta G_v. \quad (8)$$

⁸ A. V. S. de Reuck, *Nature* **179**, 1119 (1957).

The constant γ defines the habit of the critical embryo and r^* defines its size. The critical free energy is, from (5), (7), and (8),

$$\Delta G^* = 4 \pi \xi \gamma \sigma_{12}^3 / \Delta G_v^2. \quad (9)$$

The nucleation rate is now given by the Volmer theory⁹ as

$$J = A \exp(-\Delta G^* / kT) \quad (10)$$

where A is a kinetic constant which is typically of the order of $10^{25} \text{ cm}^{-2} \text{ sec}^{-1}$.

Without introducing any further complications, we can see that substances differ in nucleating ability because of differences in the constant γ . Good nucleating substances have very small γ values, while completely inactive substances have $\gamma > 2$, and homogeneous nucleation predominates.

We shall now introduce the effects of entropy as discussed above, and make a more realistic treatment of some actual crystal faces.

BASAL FACES

Hexagonal crystals with lattice dimensions similar to those of ice form an important class of nucleating compounds, and in this discussion we shall confine our attention to such substances. Typical members of this class are silver iodide and lead iodide.

For simplicity we shall first neglect the small differences between the lattice dimensions of these substances and those of ice, and assume the primitive lattices to be identical. This means that certain atoms are in one-to-one correspondence with a subset of the oxygen atoms of the ice lattice. We shall first consider the nucleation behavior of the basal $\{0001\}$ faces of these materials.

In Fig. 3 we have shown, approximately to scale, the oxygen atoms of the ice lattice. In Figs. 4 and 5 are shown two views of the lattice of β -AgI, drawn to the same scale.¹⁰ The positions of the silver atoms are actually not well defined at room temperature and

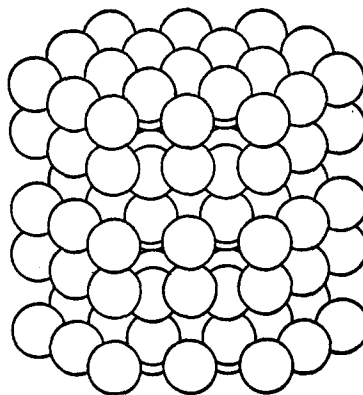


FIG. 3. The ice lattice drawn approximately to scale. Hydrogen atoms are not shown, but are located on bonds as shown in Fig. 1.

⁹ M. Volmer, *Kinetik der Phasenbildung* (T. Steinkopf, Dresden and Leipzig, 1939).

¹⁰ From data given by R. W. G. Wyckoff, *The Structure of Crystals* (Chemical Catalog Company, New York, 1931).

they tend to be statistically distributed over positions differing slightly from those of the ideal lattice.¹¹ It will be seen that the lattice is polar, so that there are two classes of {0001} face. In Fig. 6, again to the same scale,¹⁰ is shown the lattice of PbI₂.

Looking now at the hexagonal basal faces shown in these figures, we see that the oxygens of ice are in complete one-to-one correspondence with the iodines of the other lattice faces (or alternately with the silvers on one of the AgI faces). Since these crystals are at least partially ionic,¹² this means that if ice grows on a basal face of one of these crystals, the oxygens will be directly above ions which all have the same sign. For lowest interfacial energy then, the OH dipoles of the ice molecules at the interface must all be parallel, giving an α value of 0. To say that this is the surface of minimum free energy involves neglecting an entropy term, but we shall return to this later.

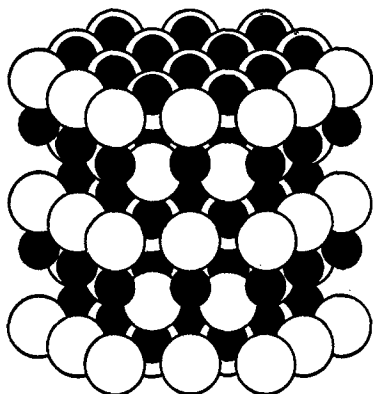


FIG. 4. The silver iodide lattice drawn to the same scale as Fig. 3. White spheres represent iodide and black spheres silver ions. Note the similarity of exposed faces to those of ice.

As an embryo builds up on the surface, however, (as shown in Fig. 2), the state of minimum total free energy will have a finite α value, as discussed previously. We shall now calculate the value of ΔG^* associated with growth of a critical embryo upon this surface.

Let us suppose that α has an arbitrary value in the situation shown in Fig. 2. Using the notation of the previous section, with a superscript for the α value, the interfacial free energy becomes

$$\sigma_{23}^\alpha = \sigma_{23}^0 + \alpha\nu\epsilon - \nu T\Delta S^\alpha, \quad (11)$$

where there are ν molecules per unit area and ϵ is the increase in energy caused by reversing one of the dipoles. Here, since $\epsilon \gg kT$, the entropy term can be neglected, and we can write to a good approximation

$$\sigma_{23}^\alpha \approx \sigma_{23}^0 + \alpha\nu\epsilon. \quad (12)$$

Similarly, neglecting entropy terms,

$$\sigma_{12}^\alpha \approx \sigma_{12}^0, \quad (13)$$

¹¹ L. Helmholtz, *J. Chem. Phys.* **3**, 740 (1953).
¹² Linus Pauling, in *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1944), second edition, p. 73, estimates the bonding of AgI to be 46% covalent and 54% ionic. The bonding of PbI₂ is probably similar.

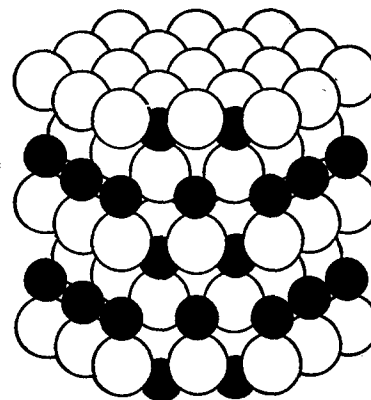


FIG. 5. An inverted view of the silver iodide lattice shown in Fig. 4. Note that this basal face exposes no silver ions.

and of course σ_{13} does not involve α . The bulk free energy becomes

$$\Delta G_v^\alpha = \Delta G_v^0 - nT\Delta S^\alpha, \quad (14)$$

where n is the number of molecules per unit volume. It should be noted that ΔG_v^0 refers to polar ice, and the value for ordinary ice is ΔG_v^\ddagger .

From the definition (7) of α , we find

$$\gamma^\alpha \approx \gamma^0 + \alpha\nu\epsilon/\sigma_{12}, \quad (15)$$

and instead of (9) we have

$$\Delta G^* \approx \frac{4\pi\xi\sigma_{12}^3(\gamma^0 + \alpha\nu\epsilon/\sigma_{12})}{(\Delta G_v^0 - nT\Delta S^\alpha)^2}. \quad (16)$$

This expression can be immediately generalized by the methods of Turnbull and Vonnegut¹³ to include the effects of lattice misfit. We shall discuss only the simple case for the moment, however.

The value of α producing a minimum in ΔG^* depends upon ΔG_v^0 and hence upon the temperature, as well as on the other constants of the system. It is necessary to make some simplifying assumptions in order to calculate a typical case.

For a good nucleating agent, γ must be close to zero

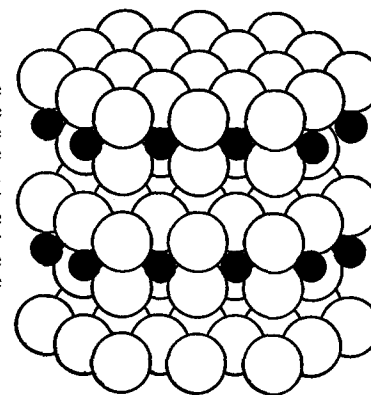


FIG. 6. The lead iodide lattice drawn to the same scale as Fig. 3. White spheres represent iodide and black spheres lead ions. Note the similarity of the basal face to those of ice (Fig. 3) and silver iodide (Fig. 5) but the difference between the prism faces.

¹³ D. Turnbull and B. Vonnegut, *Ind. Eng. Chem.* **44**, 1292 (1952).

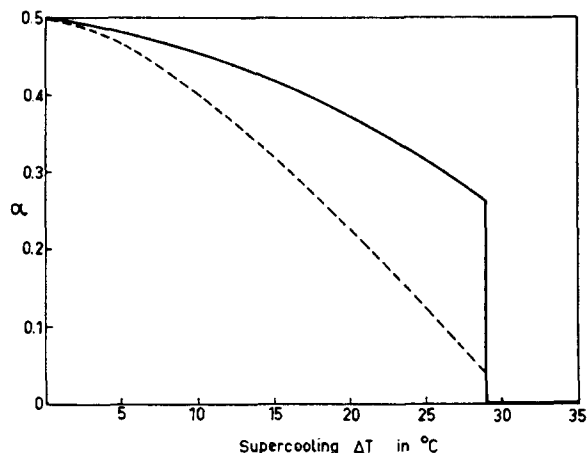


FIG. 7. Orientation factor α giving minimum free energy for a critical embryo formed on an orienting substrate with supercooling ΔT . The full curve is based on the assumption of an embryo with prismatic habit, and the broken curve on an embryo having the form of a spherical cap.

on the active surfaces. For simplicity,¹⁴ we shall assume therefore $\gamma^0=0$. The binding of water molecules on ionic surfaces is caused principally by the energy of the dipole in the ionic field.⁷ Even for the slightly covalent bonding of the crystals we are considering,¹² this will remain substantially true. If, therefore, we were to reverse the orientation of half the dipoles at the interface, the cohesion would be virtually destroyed, implying

$$\gamma^{\frac{1}{2}} \approx 2. \quad (17)$$

Substituting this result in (15) then gives

$$\nu\epsilon/\sigma_{12} \approx 4. \quad (18)$$

For any other reasonable assumption about the relative importance of polar and nonpolar forces at the surface this quantity will almost certainly lie between 2 and 4, and, as we shall see later, an uncertainty of this order has little effect upon our final result.

By (14) we also have

$$\Delta G_v^0 = \Delta G_v^{\frac{1}{2}} + nT\Delta S^{\frac{1}{2}} \quad (19)$$

so that (16) becomes

$$\Delta G^* \approx \frac{16\pi\xi\sigma_{12}^3\alpha}{(\Delta G_v^{\frac{1}{2}} + nT\Delta S^{\frac{1}{2}} - nT\Delta S^\alpha)^2} \quad (20)$$

This expression, together with (1) or (2) for ΔS^α , allows us to calculate the value of α which minimizes ΔG^* at various temperatures and in various situations. From this minimum ΔG^* and the rate equation (10), the nucleation rate can be determined under the given conditions.

¹⁴ If the surface forces are such that $\gamma^0 < 0$, then an adsorbed monolayer will be produced even in a slightly unsaturated environment. This monolayer will transmit the polarization and on it γ^0 cannot be less than zero.

The most important case in practice is nucleation by sublimation from a supercooled fog, in which case the environment is at water saturation. This also corresponds, except for the value of σ_{12} , to the case of freezing of water in contact with the surface.

Under these conditions it is a good approximation to write

$$\Delta G_v^{\frac{1}{2}} = -nkT \ln Z \approx -nkT \times 10^{-2} \Delta T, \quad (21)$$

where Z is the saturation ratio over ice, and ΔT is the supercooling, in $^{\circ}\text{C}$ below 0°C . Substituting (21) and (1) into (20) we get

$$\Delta G^* \approx \frac{16\pi\sigma_{12}^3}{n^2k^2T^2} \frac{\xi\alpha}{\{10^{-2}\Delta T + \ln[2^{-\frac{1}{2}}\alpha^{-\alpha/2}(1-\alpha)^{-(1-\alpha)/2}]\}^2} \quad (22)$$

with the restriction that the term in curly brackets, as written, must be positive. This merely expresses the condition that the free energy of formation of bulk material must be negative, and ensures that the process can take place.

When the α value giving minimum ΔG^* is very small, it is a better approximation to use (2) instead of (1); this leads to an expression like (22) but with the logarithm term in the denominator replaced by

$$\ln[2^{7/6}3^{-1}\alpha^{-\alpha/2}(1-\alpha)^{-(1-\alpha)/2}]. \quad (23)$$

At a given temperature, and hence for a given ΔT , the expression (22), or the alternate form using (23), can be minimized with respect to α . This is most simply done graphically. The resulting variation of α with temperature is shown in Fig. 7, which is an interpolation between the values given by the two approximate expressions (22) and (23). The discontinuity in the curve at -29°C corresponds to the freezing point of completely oriented ice. Below this temperature the surface is "wet" by ice, while above it the critical embryo behaves as though on a surface of finite "contact angle" (if we may apply these terms qualitatively to solids). It must be borne in mind that the polarization factor α of Fig. 7 refers only to an embryo of critical size. Once a crystal has nucleated and begins to grow, the volume free energy becomes dominant and α approaches its normal value of 0.5.

We may now apply these results to the determination of freezing and sublimation thresholds for a perfect basal face in an environment at water saturation. Again we note that we are supposing this face to have exactly the lattice dimensions of ice.

If we take an appreciable nucleation rate to be $1 \text{ cm}^{-2} \text{ sec}^{-1}$, then from Eq. (10) nucleation occurs if ΔG^* is less than about $60kT$. We choose approximate values of σ_{12} for sublimation and freezing to be

$$\sigma_{12} \approx 100 \text{ erg cm}^{-2} \text{ (ice-vapor)}$$

$$\sigma_{12} \approx 20 \text{ erg cm}^{-2} \text{ (ice-water)}$$

and find graphically the following approximate temperatures

$$T \approx -29^\circ\text{C for sublimation}$$

$$T \approx -24^\circ\text{C for freezing.}$$

Since in the absence of an entropy effect our assumptions would have led to a threshold almost equal to 0°C , the polarization effect is clearly very important.

A similar calculation can be carried out on the initial assumption that the ice embryo has the form of a spherical cap. The only differences are details of geometry which give for the critical free energy, instead of the expression (16), the result

$$\Delta G^* \approx \frac{4\pi\sigma_{12}^3(2+m^0-\alpha\nu\epsilon/\sigma_{12})(1-m^0+\alpha\nu\epsilon/\sigma_{12})^2}{3(\Delta G_v^0-nT\Delta S^\alpha)^2}, \quad (24)$$

where

$$m = (\sigma_{13}-\sigma_{23})/\sigma_{12} = 1-\gamma. \quad (25)$$

Minimizing with respect to α under our simplifying assumptions we find the curve shown in Fig. 7, which gives nucleation thresholds of -29°C for sublimation and -20°C for freezing.

Since we have made a somewhat arbitrary assumption as to the value of the quantity $\nu\epsilon/\sigma_{12}$ of Eq. (18), it is interesting to see to what extent the results are affected by variations in this quantity. Taking the rather extreme value of 2 for $\nu\epsilon/\sigma_{12}$, we calculate a freezing threshold of about -12°C for a spherical cap. The sublimation threshold remains unchanged at -29°C .

As we mentioned when introducing the polarization effect, our analysis is not accurate for very small embryos, because edge effects allow the orientation factor α to tend toward 0.5 away from the constraining surface. Critical embryos in the sublimation process are large enough for this effect to be of no importance, but the embryos in freezing are much smaller and it must be considered. The end result is that the severity of the entropy effect is reduced and the nucleation temperature raised. A rough estimate suggests that the nucleation temperature may be raised to the extent of a few degrees by this effect.

Summarizing these calculations, we see that the sublimation threshold lies near -29°C and the freezing threshold probably between -15 and -24°C .

PRISM FACES

If we compare the prism $\{10\bar{1}0\}$ faces of ice (Fig. 3) with those of silver iodide (Fig. 4) we see that once again the surface atoms are in one-to-one correspondence. Now, however, instead of having ions of only one sign exposed, equal numbers of both Ag^+ and I^- ions appear at the interface. The interface of lowest energy thus has $\alpha=0.5$, and though the configurational entropy of this first ice layer is small, the entropy of the second layer has its normal value. There is thus no

entropy effect on these prism faces and in the absence of misfit and for $\gamma=0$, freezing and sublimation can take place essentially at 0°C .

Looking now at the surface of a crystal such as lead iodide (Fig. 6), we find that there is no longer a one-to-one correspondence with the surface of ice. There is, however, a correspondence between the I^- ions and half of the oxygens in the ice surface, while the remaining oxygens are at least approximate to the Pb^{++} ions. This should thus again lead to $\alpha=0.5$ and no entropy effect. In this case, however, we should not expect $\gamma=0$ because of the nonideal pairing of dipoles between the two surfaces.

REAL CRYSTALS

So far in our discussion we have assumed plane crystal faces of infinite extent, with $\gamma=0$ and lattice dimensions identical with those of ice. None of these conditions are likely to be realized in practice and we must show how small deviations from the ideal can be taken into account. A treatment of lattice misfit has been given by Turnbull and Vonnegut,¹³ and the effects of finite size and "contact angle" have been treated in a recent paper by the present author.¹⁵ From these discussions the point emerges that to a first approximation all these effects act independently, so that we can write

$$\Delta T \approx \Delta T_1 + \Delta T_2 + \Delta T_3 + \Delta T_4, \quad (26)$$

where ΔT is the total supercooling necessary for nucleation by freezing or sublimation, ΔT_1 is contributed by the entropy effect discussed above, ΔT_2 is due to lattice misfit, ΔT_3 to finite γ value ("contact angle"), and ΔT_4 to finite size.

Our foregoing discussion has shown that ΔT_1 is large for basal faces and zero for prism faces in crystals like AgI or PbI_2 . The observed nucleation threshold on large crystals must thus be caused by these prism faces. Since the generally observed thresholds¹⁶ are about -4°C for AgI and -6°C for PbI_2 when not too finely divided, we attribute these values to the sum of ΔT_2 and ΔT_3 for prism faces. Estimating $\Delta T_2 + \Delta T_3 = 4^\circ\text{C}$ for basal faces of AgI and 3°C for basal faces of PbI_2 , we can summarize the results of our previous discussion as applied to these materials as shown in Table I. In compiling this table we have taken no account of solubility, and since PbI_2 is appreciably soluble in water its activity as a freezing nucleus may be much less than suggested by the table.

Finally we should point out that we have been considering perfect surfaces. Real surfaces have many imperfections, the most important from our present viewpoint being steps. If these steps are large enough (~ 100 A) they will act as areas of the other surface

¹⁵ N. H. Fletcher, *J. Chem. Phys.* **29**, 572 (1958).

¹⁶ B. J. Mason, *The Physics of Clouds* (Oxford University Press, London, 1957), p. 164.

TABLE I. Supercooling thresholds in °C below 0°C.

	Freezing	Sublimation
AgI { Prism	4	4
Basal	19 to 28	33
PbI ₂ { Prism	6	6
Basal	18 to 27	35

which they expose. Large steps on basal faces expose prism faces, and are thus good ice nucleation sites. Large steps on prism faces, however, usually expose basal faces which are of much lower activity. Such steps are therefore not particularly good ice nucleation sites, though all steps favor the condensation of water in the liquid form.

COMPARISON WITH EXPERIMENT

Our discussion and calculation enables us to explain several hitherto puzzling experimental results which we will now deal with in order.

From Figs. 5 and 6 the basal faces of AgI and PbI₂ are almost identical in structure. AgI has a basal misfit against ice of 1.4% while PbI₂ has a misfit of only 0.6%. We should thus expect PbI₂ to be a better nucleating agent than AgI which is not borne out by experiment. Our discussion shows, however, that it is the prism rather than the basal faces which are active as nuclei. The misfit for AgI on this face is 1.6% and for PbI₂, 3.6%, which explains the observed inferiority of PbI₂. In a similar manner if hexagonal substances of comparable structure are ordered by prism face rather than basal face misfits, agreement with experimental nucleating efficiencies is greatly improved.

We now turn to two experiments in which the behavior of nucleating substrates has been examined microscopically. Schaefer¹⁷ grew large near-perfect hexagonal plate-like crystals of PbI₂ and observed them in a fog at -20°C. He found that droplets of water which collided with the crystal either bounced off, or else evaporated without freezing. This was tentatively explained by Turnbull as due to the absence of disloca-

tion sites on the exposed face. We can go further and say that it is the natural behavior of such a face, and that nucleation will not occur at temperatures warmer than this without a step of sufficient height to expose effectively an area of prism face.

In a somewhat similar experiment, Montmory and Jaffray¹⁸ observed that drops condensed onto a basal plane of AgI froze at -5 to -7°C. We attribute this to condensation on large step sites followed by freezing onto the exposed prism faces. They further observed that at temperatures below -32°C large numbers of ice crystals were produced upon the substrate without visible condensation. This is in strikingly good agreement with our predicted sublimation threshold near -33°C.

What experimental evidence there is thus lends considerable support to our theory. It is unfortunately difficult to carry out definitive experiments, particularly in the present case where perfect crystal faces are postulated.

CONCLUSION

We have shown that ice is a special substance in that the dipoles of the H₂O molecules which make it up normally have a random arrangement. If these dipoles are oriented parallel to one another by coming into contact with a polar surface of uniform sign, then the entropy of the resulting ice structure is reduced, and a large supercooling is required for nucleation upon the surface.

These considerations predict that the basal planes of substances like AgI and PbI₂ will be poor ice crystal nuclei despite their close similarity to ice in structure and dimensions. On the other hand, the prism faces should be good nucleating surfaces, and it is upon these that growth should occur.

This modification of the usual nucleation theory leads to a better agreement with experiment for nucleation thresholds, and gives a semiquantitative understanding of some of the phenomena observed in the growth of small ice crystals upon crystalline substrates.

¹⁷ V. J. Schaefer, *J. Meteorol.* **11**, 417 (1954).

¹⁸ R. Montmory and J. Jaffray, *Compt. rend.* **245**, 2221 (1957).