ICE CRYSTAL NUCLEATION BY AEROSOL PARTICLES

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The action of insoluble particles as ice crystal nuclei is discussed from a molecular viewpoint, and it is concluded that though some important issues are becoming more clearly understood, the theory is not yet sufficiently developed for practical application. A non-molecular approximate theory is then developed which gives adequate treatment of the nucleation activity of aerosols and particularly of the effects of particle-size distribution. The decay of nucleation activity caused by ultra-violet irradiation is also discussed. The results are illustrated with special reference to aerosols of silver iodide.

1. Introduction

The nucleation of ice crystals by aerosol particles is a subject which is at present exciting considerable interest because of its importance in the natural and artificially-stimulated precipitation of rain clouds. Interest has mainly been experimental and has concentrated on two lines of research—the nature, origin and properties of naturally occurring ice-forming nuclei, and the production and properties of aerosols of efficient nuclei of simple substances like silver iodide. The first topic belongs most properly to the fields of meteorology and cloud physics, and it is with some physical-chemical aspects of the properties of simple nuclei that we shall here be concerned.

Most studies of the nucleation behaviour of aerosols have been experimental and because of the lack of a coherent body of theory their results have often been hard to interpret. It is the aim of this paper to put forward theoretical results, some rather speculative and some more soundly based, which bring a measure of order to the experimental findings, and which, it is hoped, point to some aspects worthy of further investigation.

2. Classical Theory

Classical nucleation theory [1] leads to an expression for J, the rate of formation of freely growing embryos of the new phase, of the form,

$$J = K \exp\left(-\Delta G^*/kT\right), \tag{2.1}$$

where ΔG^* is the height of the free energy barrier which must be surmounted to form such an embryo, and K is a kinetic constant typically of order 10^{25} cm^{-2} sec^{-1} for the cases which we shall consider. In the classical theory, free use is made of macroscopic concepts like surface free energy, though their validity when applied to aggregates of a few hundred molecules is uncertain. Despite this fact the theory generally gives excellent agreement with experiment in cases to which it has been applied.[2, 3]

Progress in extending the theory should ultimately lead to an expression for ΔG^* in molecular terms, abandoning macroscopic quantities, but little progress has been yet made in this direction. Nevertheless, a recognition of the detailed molecular nature of the embryo has helped to clarify some aspects of nucleation behaviour. Postponing this molecular treatment it has been found possible, using strictly classical ideas, to extend the theory to cover a variety or more complex and practically important situations in a way which we shall discuss.

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3. MOLECULAR ASPECTS

In the classical theory of heterogeneous nucleation the important parameter is θ, the angle of contact between the material of the embryo (ice, in our case) and the nucleating substrate. This enters the theory in terms of its cosine which is related to properties of embryo and substrate by

$$m \equiv \cos \theta = (\gamma_n - \gamma_i)/\gamma, \qquad (3.1)$$

where γ_n, γ and γ_i are respectively the surface free energy per unit area of the nucleating substrate, the embryo phase and the interface between them. As $m \to 1$, the nucleating surface becomes " perfect " and $\Delta G^* \to 0$. This requires in general a close similarity between the nucleus and the embryo phase as we shall see below.

From (3.1) the criterion for an efficient nucleus is that the interfacial free energy γ_i be as small as possible. This quantity can conveniently be divided into two parts, one chemical, involving binding energies, and one mechanical, representing dislocations and elastic strains at the interface. Binding of water molecules to a foreign surface is largely due to their dipole moments and this suggests that a good nucleating surface should have strong electric fields in its vicinity, a condition satisfied by a dipolar or ionic crystal structure.

The interfacial energy is in general increased by the presence of dislocations or elastic strains,[4] so that these should be minimized in an efficient nucleus. This occurs most simply if the surface structure of the nucleus is geometrically the same as that of some low index plane of ice, though the approximate coincidence of a moderate fraction of atoms of the two structures is actually sufficient.

Good nucleating agents like AgI, PbI_2 and CuS are found to satisfy these conditions, though for PbI_2 and CuS only a fraction of the atom sites correspond to atom sites on possible surface planes of an ice crystal. In all cases the relative misfit against the ice structure is only a few percent so that elastic contributions to γ_i are small, and the degree of ionization of the component atoms is sufficient to ensure large electric fields at the surface.

An effect has been suggested by the present author[5] which may further limit the types of surfaces which are efficient in ice nucleation. It is well known that the ice structure has a residual entropy at absolute zero which is associated with the distribution of hydrogen ions on the bonds connecting the oxygen ions. Expressing this in another way, the orientation of molecular dipoles in an ice crystal is normally random, subject only to certain limitations on the orientations of neighbouring dipoles.

If, then, an ice crystal is nucleated upon a substrate for which the lowest interfacial free energy corresponds to a parallel orientation of interfacial dipoles, then the entropy of the ice structure will be reduced and its free energy increased. This results in an overall increase in ΔG^* and a very marked decrease in nucleating efficiency. On the other hand, if the nucleating surface contains equal numbers of positive and negative ions, the orientation of the ice dipoles is random after the first monolayer has been deposited and the effect does not occur.

Applied to actual crystals this suggests that basal (0001) planes of AgI or PbI_2 should not nucleate ice efficiently despite their close structural resemblance to it, since all the exposed ions are of one sign. On the other hand, prism faces such as $(10\bar{1}0)$ which have equal numbers of ions of both signs exposed should nucleate efficiently. These conclusions are consistent with the experimental evidence,[6] but as yet no precise experimental tests of the theory have been devised.

4. SURFACE IMPERFECTIONS

In the theory of crystal growth at low supersaturations, surface imperfections, and particularly screw dislocations, play a very important part. It is natural to enquire whether such imperfections are equally important in heterogeneous nucleation.

Considering first the screw dislocation, its chief importance is due to the fact that it obviates the necessity for surface nucleation in crystal growth. For the nucleation problem we must balance against this the fact that a small embryo containing a screw dislocation is in a state of considerable elastic strain and hence its bulk free energy is raised. A consideration of both these effects [6] suggests that, in the case of ice, screw dislocations do not act as favoured nucleation sites.

Other important imperfections are growth steps and re-entrant corners having depths greater than the dimensions of the embryo concerned. For a simple cubic crystal and substrate, particularly simple results can be obtained,[6] If ΔG_o^* is the free energy barrier to homogeneous nucleation then the barrier to nucleation involving n perpendicular intersecting planes, each of surface parameter m is

$$\Delta G_n^* = \Delta G_o^* \left[(1-m)/2 \right]^n, \qquad (4.1)$$

where $n = 0, 1, 2$ or 3 corresponds to nucleation in space, on a plane, in a step or in a corner. The results for hexagonal crystals such as ice are more complicated [6] but show the same general features. Since $-1 \leqslant m \leqslant 1$ corners and steps will always be favoured nucleation sites.

Whilst these considerations throw some light on molecular mechanisms of the nucleation process, it must be admitted that the position is still far from satisfactory. In particular, since screw dislocations are apparently not good nucleation sites, the problem of the energy barrier imposed by two-dimensional nucleation remains. It is possible that this barrier is lowered by the effects of the vapour molecules adsorbed on the substrate surface, but no theory of this effect has yet been proposed. In what follows we shall ignore this complication and derive a theory based on an entirely " classical " model. The justification for this procedure is found in the value of the results derived which appear to give an adequate description of many nucleation phenomena.

5. SIZE EFFECT

The theory of heterogeneous nucleation as developed by Volmer and others treated only nucleation upon a plane foreign surface. Such results have little direct application to the behaviour of aerosol particles of which the average surface curvature may be very large. It has proved possible, however, to solve the nucleation equations for a spherical cap embryo nucleating upon a perfect spherical particle.[7] This geometrically idealized situation is actually not a bad approximation to many cases of practical interest, though it is hoped to complete calculations for a more " crystalline " geometry soon.

If ΔG_o^* is the free energy barrier to homogeneous nucleation in a given situation, then it can be shown that the free-energy barrier to nucleation on a spherical particle of radius R and surface parameter m is

$$\Delta G^* = \Delta G_o^* f(m, x), \qquad (5.1)$$

where

$$x = R/r^*, \qquad (5.2)$$

r^* being the radius of curvature of the surface of a critical embryo in this situation. The form of the function $f(m, x)$ is shown in fig. 1 from which it can be seen that values of m close to unity and values of x greater than unity are required for efficient nucleation.

This theory can be applied to many interesting nucleation processes, but for our present purposes we shall consider only the nucleation of ice crystals by particles suspended in an atmosphere at water saturation and at a temperature below 0°C. If we restrict ourselves to particles which are insoluble and which have a finite contact angle for liquid water. then ice nucleation can only proceed by a process of sublimation. There is reason to believe that this is the case for an aerosol of silver iodide particles.[8]

Making the plausible assumption that the surface-free energy of ice is about 100 erg cm^{-2} and using eqn. (5.1) and fig. 1 we can then derive the activity curves shown in fig. 2. For a given surface parameter m these show the temperature at which a spherical particle of radius R will on the average, nucleate an ice crystal from the environment in about one second. The broken curve given for silver iodide is derived not from any precise knowledge of the appropriate value for m, but rather from the experimental fact that large particles of silver iodide are active as ice-forming nuclei at a temperature of about $-4°C$. There is some measure of experimental verification of this curve.[8]
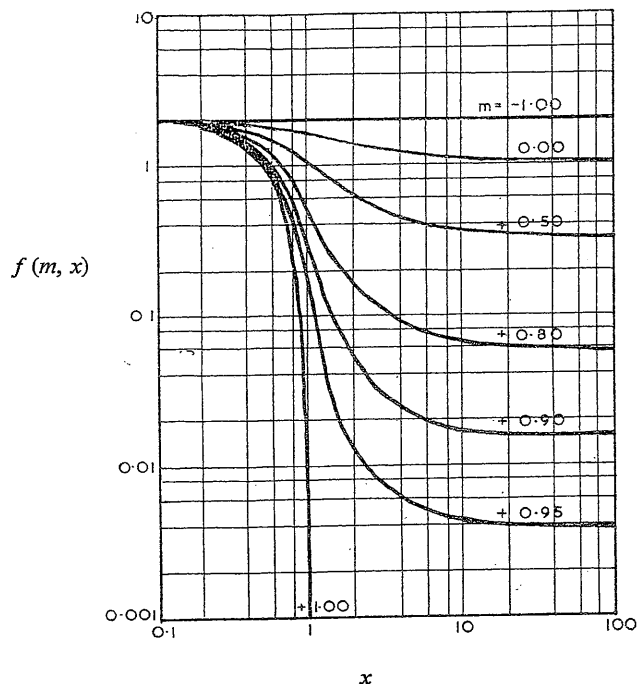

FIG. 1.—The geometrical factor $f(m, x)$ in terms of the ratio $x = R/r^*$. m is shown as a parameter.[7]

6. ACTIVITY OF AEROSOLS

Curves such as those shown in fig. 2 can now be used to derive the activity spectrum of an aerosol once its composition and size distribution are known. We shall illustrate this for silver iodide.

A convenient measure of the activity of an aerosol is the number of nuclei, per gram of suspended material, which are active in producing ice crystals above a certain temperature. A plot of this quantity as a function of temperature then characterizes the behaviour of the aerosol.

At a given temperature the activity will be greatest if the aerosol is mono-disperse and has a particle size which is just active at the temperature considered. This maximum possible activity at a given temperature can easily be derived for silver iodide from the characteristic curve of fig. 2, and is displayed in fig. 3. The activity spectrum of a polydisperse AgI aerosol must at all points lie below this curve, and its detailed shape will be determined by its size distribution.

The size distribution of a silver iodide aerosol is typically log-normal with most probable particle radius near 100Å, though, of course, there may be wide

variations in this parameter. In fig. 3 the broken curve gives the computed activity spectrum for an AgI aerosol having median particle radius 100 Å and with radii distributed log-normally with standard deviation of a factor 2·5. This curve agrees very well both in general shape and also in numerical magnitude with
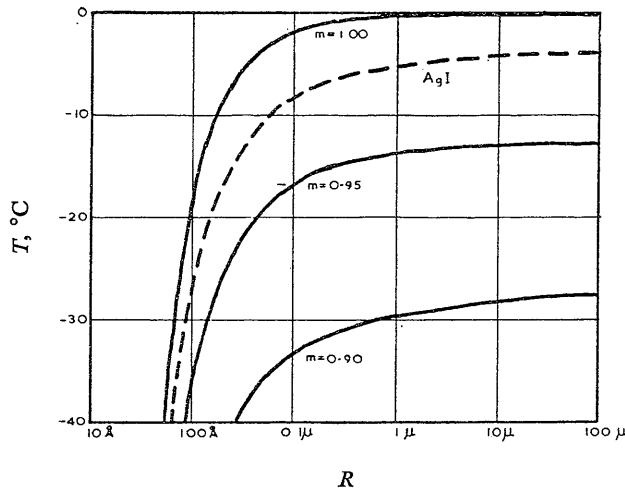

FIG. 2.—Temperature T at which sublimation occurs in one second on a spherical particle of radius R in an environment at water saturation.[7] Parameter is $m = \cos \theta$. Broken curve is for silver iodide.
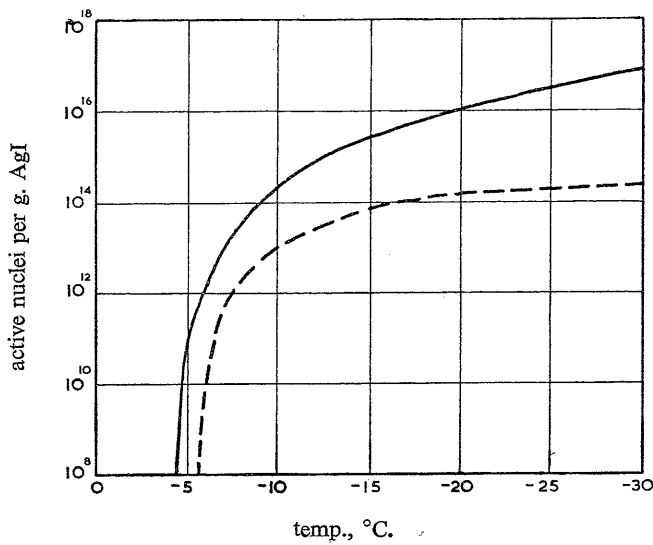

FIG. 3.—Full curve shows maximum number of nuclei active at a given temperature that can be produced from 1 g of AgI. Broken curve shows theoretical activity spectrum for the aerosol described in the text.

activity curves measured on the smoke produced from practical burners.[9] The behaviour of these smokes may be complicated by the presence of materials like NaI, but the agreement of their behaviour with theoretical expectations provides gratifying support for the approximate validity of the theory.

7. PHOTO-DECAY

Since the nucleation behaviour of a particle depends critically upon the structure of its surface it may be expected that any agent which tends to modify the state of the surface will have an important effect upon nucleation activity. Vapours which are adsorbed on the crystal surface and gases which react chemically with it are examples of this effect. At the present time, however, experimental evidence bearing on these processes is meagre and little purpose is served by a theoretical analysis.

One form of surface modification exists, however, for which there are abundant experimental results. This is the progressive modification produced by photolysis of the crystal material by ultra-violet light. For silver iodide it has been found that irradiation in the fundamental absorption band decreases the activity of the aerosol, though widely diverging figures have been quoted for the de-activation rate, ranging from a decrease of a factor 2 during 1 h irradiation to a decrease of a factor 10^9 in the same time, the intensity involved being that of sunlight.

With the aid of a few simple assumptions and the theory of the size effect discussed above, it is possible to treat the de-activation process equantitatively and to explain the origin of the different observed decay rates.[10]

The absorption of ultra-violet light by silver iodide particles depends critically upon their size, since the absorption coefficient in the fundamental absorption band is $\sim 10^5$ cm^{-1} while the radius of the particles with which we are dealing is $\sim 10^{-5}$ cm. The approximate rate of energy absorption per particle can, however, be easily evaluated. If a quantum efficiency α for the production of photolytic silver atoms by absorbed quanta is assumed, then the rate of production of these atoms can be found.

The distribution of photolytic silver within the particle will depend upon the distribution of trapping centres for the photo-electrons produced by the incident radiation. If there are special surface traps associated with the outer layers of the particle, then the ratio of their concentration to that of traps in the bulk of the crystal is important, otherwise the trap density appears only through its effect on the quantum efficiency α.

Only silver atoms produced at the surface of the nucleating particle have any effect on its properties, and their effect is to increase approximately linearly the value of the interfacial free energy γ_i. This in turn decreases the surface parameter m linearly with time and decreases the nucleation activity.

Discussion of the de-activation of an aerosol as a whole involves consideration of this process for an appropriate distribution of particle sizes.[10] We shall not go into this in detail here but simply summarize the general results obtained.

(i) The decay is only roughly exponential, the decay rate varying with time.

(ii) Typical decay rates in sunlight are of the order of a factor 10^2 per hour, but decay rates ranging from a factor   to a factor 10^4 per hour can be expected depending upon details of   size distribution in the aerosol.

(iii) In general the activity of small part'cles decays at a faster rate than does that of large particles.

Whilst these results have been applied specifically to an aerosol of silver iodide, the general approach can be used to treat the photo decay of aerosols of other materials if the relevant parameters are available.

8. CONCLUSION

The behaviour of aerosols in the nucleation of ice crystals from a supercooled vapour is fairly well described by the theory which has been outlined above. It is recognized, however, that the theory itself can only be a first approximation in its present state, and further progress should come from a more detailed consideration of the molecular processes involved.

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