

# HOMOGENEOUS NUCLEATION OF SUPERCOOLED WATER DROPS

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## ABSTRACT

The experimentally observed crystallization of supercooled water near  $-40^{\circ}\text{C}$  is examined in terms of the theory of homogeneous nucleation. The thermodynamic and molecular-kinetic nature of the nucleation process is outlined to show why supercooling in natural clouds can occur so frequently. Past efforts to explain the  $-40^{\circ}\text{C}$  transition are examined critically, and are found to contain a number of significant errors. Because the theoretical nucleation rates are extremely sensitive to the numerical value of the specific surface free energy of a water-ice interface, particular attention is devoted to the refinement of previous estimates of this parameter. It is shown that both Krastanow's and Mason's estimates were inaccurate, and that in the latter's approach, neglect of the distortion energy of the surface layer of ice led to a marked underestimate of the nucleation efficiency which was concealed by the effects of several counteracting errors. Difficulties lying in the way of a direct calculation of the distortion energy for ice are examined and found to be very serious. A crude correction for distortion effects leads to a theoretically predicted temperature of  $-26^{\circ}\text{C}$  for the threshold of spontaneous nucleation of drops of cloud-particle size. It is concluded that although this result lies well above the experimentally observed range of transition temperatures, it is close enough to that range (considering the inherent difficulty of assessing the effect of distortion), to strengthen the belief that the  $-40^{\circ}\text{C}$  transition is due to homogeneous nucleation.

## 1. Introduction

Although a number of years have elapsed since the first clear recognition (Cwilong, 1945; Schaefer, 1946) that there exists a temperature near  $-40^{\circ}\text{C}$  at which ice crystals seem to form abundantly and spontaneously in a cloud of supercooled water drops, the exact physical nature of the transition has not yet been ascertained. Its importance to the subjects of cloud physics and aircraft icing makes it desirable to investigate all possible mechanisms which might account for the phenomenon. The principal division of present opinion seems to hinge upon the question of whether the observed formation of ice crystals near  $-40^{\circ}\text{C}$  occurs as a result of direct sublimation from the vapor phase (Cwilong, 1947; Bradley, 1951; Schaefer, 1952) or as a result of spontaneous freezing of supercooled water drops (Fisher, Hollomon, and Turnbull, 1949; Lafargue, 1950; Mason, 1952).

The sublimational hypothesis encounters serious difficulties on both theoretical and experimental grounds. First, Krastanow (1941) has shown thermodynamically that water vapor at temperatures below  $0^{\circ}\text{C}$  will condense to the supercooled liquid state in an energetically easier manner than it will sublime to the solid state, since the liquid-vapor interfacial energy is certainly smaller than the solid-vapor interfacial energy in the temperature range of meteorological interest. Second, it has been found experimentally

(*e.g.*, Schaefer, 1952) that the ice phase does not make its appearance in vapor saturated just with respect to ice, but rather in vapor saturated with respect to liquid water, which implies that formation of ice crystals in the atmosphere proceeds by some intermediate process involving supercooled liquid drops (assuming no foreign nuclei to be present). A very complete and critical summary of past studies of this problem has been given by Mason and Ludlam (1951), so the background of the problem need not be elaborated here.

When one next inquires as to how a supercooled drop of water might freeze, two distinct classes of processes must be considered. If the crystallization takes place in entirely pure water, it is said to depend upon "homogeneous nucleation." If the crystallization instead depends critically upon the presence of trace quantities of some foreign solid substances, it is said to involve "heterogeneous nucleation." It has been clearly demonstrated within the past few years that a large number of inorganic salts will promote heterogeneous nucleation when added to suitably supercooled clouds, and much effort has been directed towards gaining an understanding of the exact mechanisms involved. In contrast to these experiments, the experiments on the  $-40^{\circ}\text{C}$  transition<sup>3</sup> seem to indicate that heterogeneous nucleation is not involved in this phenomenon; so it becomes very desirable to exploit all available experimental and theoretical methods for gaining insight into the problem of homo-

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<sup>3</sup> Different investigators have observed the transition in question at slightly different temperatures lying within the range from about  $-38^{\circ}\text{C}$  to about  $-41^{\circ}\text{C}$ . Here, for brevity, it will be referred to simply as the " $-40^{\circ}\text{C}$  transition."

geneous nucleation of supercooled water. The present paper summarizes a theoretical study of this latter phenomenon.

It may be noted at the start that the theoretical expression describing the rate of homogeneous nucleation is of such mathematical form as to be extremely sensitive to the numerical values assigned to certain parameters entering into it. Consequently a major objective of the present study has been the careful examination of all quantities affecting the nucleation rate, particular effort being devoted to refining such numerical estimates of these quantities as have been made in the past. In addition, several thermodynamic aspects of the nucleation problem have been investigated and shown to be in need of revision. After all recognized refinements have been discussed here, calculations of the nucleation rate will be made on the basis of three independent and disparate estimates of the critically important surface free energy for a water-ice interface.

## 2. Theory of homogeneous nucleation

One of the principal benefits to be derived from even a qualitative study of the theory of homogeneous nucleation of supercooled liquids is an appreciation of the fact that as the temperature of a pure liquid substance is lowered to and then below the melting point of that substance's solid phase, a certain degree of supercooling is not only possible, but is in fact difficult to avoid. Thus the well-known and meteorologically important phenomenon of supercooling of cloud drops ought not be regarded by meteorologists as a paradox demanding some special explanation. Viewed in the light of the theory of homogeneous nucleation, this phenomenon is seen to be thermodynamically and kinetically inevitable in pure water drops. That it would really be the opposite case of "well-behaved" freezing at 0°C which would demand special explanation if invariably observed in the atmosphere does not appear to be widely appreciated, if one is to judge from comments on the phenomenon of supercooling to be found in many meteorology texts. Therefore it may be in order here to discuss briefly the qualitative nature of this problem before turning to a quantitative examination.

The supercooling of a pure liquid is quite closely analogous to the supersaturation of a pure vapor. Since the latter is of conceptual interest in cloud physics, but particularly since certain quantitative aspects of the latter are likely to be better known to most readers, the basic physical nature of homogeneous nucleation will be described first in terms of processes occurring in a supersaturated vapor.

In this latter case, one observes that a vapor which contains no intermixed foreign particles and which is not in contact with a liquid water surface of any kind may be cooled far below its nominal dew point without

any appearance of water drops. The fundamental reason for this possibility of supersaturation of pure vapor is that the only way in which liquid drops can be formed under such homogeneous conditions is for a chance succession of collisions to build up embryonic water droplets one molecule at a time. But this mode of formation of drops is inherently improbable, even at temperatures well below the nominal dew point of the vapor because (to describe it in simplified terms) the total binding force exerted by very small aggregates of molecules upon one of their surface members is too low to overcome the disgregative action of thermal motions of the individual members.<sup>4</sup> Only by cooling the system far below its nominal dew point can one suppress this thermal disgregating effect on randomly forming embryos sufficiently to permit the embryos to gain member molecules faster by bombardment from the vapor phase than the embryos lose them to the vapor phase by evaporation. Even from as crude a model as this, one can sense that for any given temperature below the nominal dew point there ought to exist a critical embryo radius below which an embryo is unstable and will tend to evaporate, but above which it will tend to grow rapidly. Furthermore, the same model suggests the important relation that the magnitude of this critical radius must surely decrease with decreasing temperature. Both of these conclusions can be given firm support and, still better, quantitative expression by means of the corresponding thermodynamic arguments.

One of the main results of the thermodynamic argument is a quite familiar relation, Kelvin's equation. However, the form into which this equation is almost invariably put in meteorological applications, and the way in which it is then interpreted, tend to conceal its interesting implications as an equation from the theory of homogeneous nucleation. Kelvin's equation, as conventionally written, relates the vapor tension  $e_r$  of a pure water drop of radius  $r$  and temperature  $T$  to the vapor tension  $e$  of a plane surface of pure water of density  $\rho_l$ , specific surface free energy (surface tension)  $\sigma_l$ , and temperature  $T$ , according to

$$\ln (e_r/e) = 2\sigma_l/\rho_l R'Tr, \quad (1)$$

where  $R'$  is the gas constant per gram for water vapor. It is usually, and correctly, stated that Kelvin's equa-

<sup>4</sup> For aggregates containing, say, only a half dozen molecules, the binding force for any given member molecule may be understood in terms of the small *total* number of other molecules available to attract the given molecule. For larger aggregates, the total number of members ceases to be the significant parameter, since it is well established that the range of intermolecular forces is so small as to become generally negligible over distances of the order of two or three molecular diameters. Instead, the deficiency in binding energy for a surface molecule in an aggregate of, say, a few hundred molecules depends almost entirely on a purely geometric effect due to the large surface curvature of such tiny aggregates. The curving surface of the embryo falls away so rapidly on all sides of a given surface molecule that there exists a slight deficit of near-neighbors whose radially inward components of attraction go to make up a portion of the total binding force in a perfectly plane liquid surface.

tion shows how much larger the vapor tension of a tiny drop is than that of a plane surface of the same liquid at the same temperature. What is too frequently ignored in meteorological discussions, is that the same equation is equally appropriately regarded as an equation giving the critical embryo radius as a function of the degree of supersaturation and hence of the degree of undercooling below the nominal dewpoint. To bring out the latter interpretation, one may substitute for  $\ln(e_r/e)$  from the integrated form of Clapeyron's equation to get, on expressing it as an equation to determine  $r$ ,

$$r = 2\sigma_l T_0 / \rho_l L_v (T_0 - T), \quad (2)$$

where  $L_v$  is the latent heat of vaporization of the liquid and  $T_0$  is the temperature (greater than  $T$ ) at which  $e_r$  corresponds to the saturation vapor pressure; *i.e.*,  $T_0$  is simply the nominal dew point of the given sample of supersaturated vapor which is in equilibrium with drops of radius  $r$ . Equation (2), though still essentially Kelvin's equation, tells rather more than (1), for it defines the radius  $r$  that an embryo must just attain to grow rather than to evaporate in the presence of water vapor which has been undercooled isobarically from its nominal dew point  $T_0$  to its actual temperature  $T$ . Kelvin's familiar but amazing derivation of (1) from consideration of a capillary column (Humphreys, 1940) completely conceals this physical interpretation. A more straightforward thermodynamic derivation brings it out clearly, since  $r$  in (1) or (2) is then seen to represent the radius for which the net free energy change due to addition of molecules to an embryo attains a maximum. For embryos smaller than this critical size, the free energy *increase* due to increase of surface area accompanying the addition of more molecules more than cancels the free energy *decrease* accompanying the phase change. Hence in this  $r$ -range, further growth does not tend to occur "spontaneously" in the thermodynamic sense, *i.e.*, the process does not involve a net decrease of free energy. For embryos greater than the critical size, the  $r^2$  dependence of the surface term is overpowered by the  $r^3$  dependence of the bulk term and rapid growth ensues spontaneously. Viewed in this light, the critical radius given by (2) is that for which the free energy has a stationary value.

To gain a firmer understanding for the homogeneous nucleation process as it operates in the case of supersaturated vapor, one may use (2) to compute the actual size of these critical embryos in a particular case. Thus, a sample of water vapor which has a vapor pressure of 17 mb is known to be nominally saturated at 15C. If cooled isobarically to 5C in the absence of condensation nuclei and free water surfaces, it attains a relative humidity of about 200 per cent, and (2) reveals that homogeneous nucleation cannot then occur unless chance collisions build up embryos with

radii of about 17 Angstrom units. Since this radius is of the order of ten times the molecular radius of water, it follows that spontaneous condensation will not begin unless aggregates of some  $10^3$  water molecules are built up. This turns out to be so very improbable at the vapor density and temperature in question that the chance of even one such critical embryo appearing in a volume of many liters of vapor in a time of many minutes is negligible.

The preceding discussion of homogeneous nucleation in a supersaturated vapor raises the question of how one predicts the average rate at which embryos of the critical size may form by random molecular processes at a given degree of undercooling. This question is of equal significance in the problem under discussion in this paper, namely nucleation of a supercooled *liquid*; so, with the basic features of a typical homogeneous nucleation process outlined, attention will now be returned to this problem which is of primary interest here. Just as was true for the case of nucleation of vapor, one can only expect to find embryos (now crystalline embryos) forming in a supercooled liquid as a result of random collision processes; and, again, survival of these is prejudiced by chance until they can grow to such size that the surface molecules in the embryonic crystal lattice are bound with energies rather greater than the average thermal vibrational energy corresponding to the temperature of the liquid. An equation very similar to (2), namely (5) below, specifies the critical crystallite radius for any given degree of supercooling, and the problem is to find a theoretical expression for the rate of formation of these critical embryos per unit volume of supercooled liquid as a function of the degree of supercooling.

This problem has been solved through the successive efforts of Becker and Döring (1935), Turnbull and Fisher (1949), and others. An extensive discussion of the nucleation rate problem (exclusive of the recent contribution of Turnbull and Fisher) may be found in Frenkel (1946); and a more recent summary has been given by Bradley (1951). In a liquid supercooled below its nominal freezing point  $T_0$  to an actual temperature  $T$ , the rate of formation of nuclei (critical embryos) per unit volume per unit time is given by Turnbull and Fisher as

$$J \approx (nkT/h) \exp [(A + F_c)/kT], \quad (3)$$

where  $J$  is the specified nucleation rate,  $n$  is the number of molecules per unit volume in the liquid phase,  $k$  is Boltzmann's constant,  $h$  is Planck's constant,  $A$  is the free energy of activation for self-diffusion of the liquid molecules, and  $F_c$  is the free energy of formation of a nucleus. The contribution to this theoretical equation made by Turnbull and Fisher was the approximate evaluation of the prefactor of the exponential in (3) based on the quantum statistical theory of absolute reaction rates (Glasstone, Laidler, and

Eyring, 1941). It is to be noted that  $nkT/h$  is *not* simply the collision frequency, as was once thought to be true. Very loosely, (3) may be said to give  $J$  as the product of a fundamental molecular (or atomic) rate constant,  $nkT/h$ , multiplied by two fractional probability factors rather similar to Boltzmann factors. The first,  $\exp[-A/kT]$ , cuts down the fundamental rate by a fraction measuring the rather low probability that any given liquid molecule will possess, at any given instant, sufficient energy to permit it to "break loose" from the liquid structure and reach an energy state in which it is free to diffuse from the liquid region onto and into the embryonic lattice (see section 9 below). The second factor,  $\exp[-F_c/kT]$ , further reduces  $J$  by a factor which measures the generally very small probability that random processes can succeed in amassing an embryo of critical size in the face of the associated free energy increase of the system. Clearly, homogeneous nucleation should be thought of as an intrinsically improbable event, as has been stressed above in pointing out that the common occurrence of supercooled cloud drops is not really paradoxical at all.

The activation energy for self-diffusion  $A$  cannot readily be expressed as a thermodynamic function of more elementary parameters, so its evaluation will be reserved for section 9. On the other hand, the free energy increase  $F_c$  associated with the formation of an embryo of critical radius  $r_c$  (or of characteristic length  $r_c$  if one visualizes formation of some other geometric shape than a sphere), is found from thermodynamic considerations (see, for example, Frenkel, 1946) to be

$$F_c = \sigma_s gr_c^2/3, \quad (4)$$

where  $\sigma_s$  is the specific surface free energy of the solid-liquid interface and  $g$  is a geometric factor such that  $gr_c^2$  is the total surface area of the critical embryo. An expression of the form of (4) holds so long as edge energies may be ignored. The critical radius  $r_c$  is given by an equation analogous to the Kelvin equation [written above as (2)] for the corresponding case of vapor-liquid nucleation. The form of the  $r_c$ -equation given by Frenkel (1946) is

$$r_c = 2\sigma_s T_0 / \rho_s L_f (T_0 - T), \quad (5)$$

where  $\rho_s$  is the density of the solid phase and  $L_f$  is the latent heat of fusion of the substance in question. It has been argued qualitatively in the discussion of vapor nucleation above that the rate of formation of nuclei (critical embryos) increases with increasing degree of supercooling. Superficial inspection of (3) might seem to yield a contradiction to this, for the  $nkT/h$  prefactor as well as the factor  $kT$  in the exponent both tend to lower the nucleation rate as the temperature of the supercooled liquid falls. It is, however, in spite of these factors and because of the sensitive dependence of  $F_c$  on  $T$ , as given by (4) and

(5), that  $J$  increases rapidly with decreasing temperature. Hence spontaneous crystallization does tend to become more probable the greater the degree of supercooling. The problem of cloud physical interest is: Does this probability pass through some sort of threshold value near  $-40^\circ\text{C}$  such that freezing of drops becomes nearly inevitable within periods of time characteristic of cloud processes? Some past efforts to answer this question will be examined next.

### 3. Previous cloud physical applications of nucleation theory

The present position of the theoretical investigation of homogeneous nucleation of supercooled water will be summarized in this section by reviewing the salient features of the principal past studies of this problem. In the course of the present study, significant errors have been found in each of them. Perhaps the major contribution of the present investigation has been the detection of and at least partial correction for these errors.

Krastanow (1941) sought to apply the theoretical work of Becker and Döring (1935) and of Volmer (1939) to the meteorological problems of homogeneous and heterogeneous nucleation of both supersaturated vapor and supercooled water. Although he reached conclusions (*i.e.*, energetically greater probability of condensation than sublimation in vapor below  $0^\circ\text{C}$ ) whose significances have not always received the attention they seem to deserve, he could make no definitive calculations because at the time of his writing the rate factor appearing in (3) had not yet been adequately evaluated. Krastanow made certain estimates of  $A$  and of  $\sigma_s$  which will be discussed below. It appears not to have been previously noticed that Krastanow failed to take account of the appreciable temperature variation of the latent heat of fusion of water (see section 5 below) in his calculations of  $\sigma_s$ .

Fisher, Hollomon and Turnbull (1949), recognizing that it is very difficult to determine  $\sigma_s$  by experiment or theoretical calculation, used nucleation theory to work backwards from the observed  $-40^\circ\text{C}$  transition temperature to *compute*  $\sigma_s$  on the assumption that  $-40^\circ\text{C}$  is in fact the temperature for which  $J$  becomes of the order of unity. For unstated reasons, they omitted  $A$  in the nucleation equation which, as will be pointed out below (section 9), is neither qualitatively nor quantitatively permissible. Secondly, they, like Krastanow, ignored the substantial decrease of  $L_f$  with decreasing temperature. Finally, although they did not state explicitly what mass of supercooled water they were considering, one can determine this by solving for their  $N$  (the  $n$  of the present paper multiplied by the volume considered) after putting their computed value of  $\sigma_s$ ,  $32.8 \text{ erg cm}^{-2}$ , back into their equation along with all other numerical values they

specify. One then finds that they were tacitly considering the  $-40^{\circ}\text{C}$  ( $-38^{\circ}\text{C}$  according to them) transition as occurring when one nucleus formed each second somewhere within a sample of one *gram* of supercooled water. This was a quite fallacious basis for the calculation since the temperature at which homogeneous nucleation occurs will clearly vary with the mass of liquid involved, and experimental observations yielding the  $-40^{\circ}\text{C}$  effect concern individual water drops whose masses are only of the order of  $10^{-9}$  g. Because of these several errors, no significance can be attributed to their estimate of  $\sigma_s$ . A corrected calculation of the same type will be made below at the end of section 10.

Lafargue (1950) made a rather curious calculation whose results he presented as proof that the  $-40^{\circ}\text{C}$  transition is due to homogeneous nucleation of supercooled drops. He began by pointing out that x-ray diffraction studies of the structure of liquid water have revealed that each oxygen atom is immediately surrounded tetrahedrally by four other oxygen atoms at 2.76 Angstroms, and that the second-nearest neighbors, twelve in number, lie at a radial distance of 4.53 Angstroms. Next, and without further comment, he inserted  $r_c = 4.53$  Angstroms into the Gibbs-Thomson equation (5) along with numerical values for all quantities appearing therein except  $T$ , and solved for  $T$ . His result was  $-41^{\circ}\text{C}$ , in excellent numerical agreement with Cwilog's (1947) observed value for the transition point. He concluded that this argument had demonstrated that the transition must be dependent upon homogeneous nucleation. For several reasons this argument of Lafargue's cannot be accepted. First, although the fact that the radius of the second sphere of coordination in liquid water is about 4.5 Angstroms is well established, there is no good *a priori* reason why one should insert this particular distance rather than, say, the first or the third, or even some higher order coordination radius into the Gibbs-Thomson equation as an alleged critical radius. It is an essential feature of the homogeneous nucleation process that  $r_c$  is not a constant, as this step of Lafargue's assumes, but is instead a quantity which decreases with decreasing temperature. Second, for Lafargue to have sought an explanation of the  $-40^{\circ}\text{C}$  transition in terms of an essentially static model rather than to grapple with the critically important notion of the *rate* of nucleation was to ignore the intrinsically kinetic nature of the nucleation process; namely, that at all times there exists a spectrum of rates of chance formation of embryos of various sizes from two molecules on up, and that spontaneous crystallization only occurs when the rate of formation of embryos of critical size becomes of the order of one per volume unit and time unit characteristic of the experiment. Lafargue was effectively saying that the ice-like short-range order

in supercooled water waits passively for the temperature to fall far enough for the local structure to simulate an ice embryo of size sufficient to satisfy the Gibbs-Thomson relation. This view ignores the fundamental role played by statistical fluctuations in the nucleation process. Third, Lafargue used the value of  $L_f$  corresponding to  $0^{\circ}\text{C}$  in a calculation referring to  $-41^{\circ}\text{C}$ . Had he used the value of  $L_f$  appropriate to  $-41^{\circ}\text{C}$  (see section 5) with all other variables unchanged, he would have found a transition temperature of  $-58^{\circ}\text{C}$  instead of  $-41^{\circ}\text{C}$ , and the agreement with observation would have disappeared. It would seem to follow from these objections, unfortunately, that the problem of explaining the  $-40^{\circ}\text{C}$  transition was certainly not solved by Lafargue.

A valuable x-ray diffraction study of the molecular structure of supercooled water (Dorsch and Boyd, 1951), which appears to have been stimulated in part by Lafargue's paper, revealed that the peak in the angular intensity pattern for water at a scattering angle of  $18^{\circ}$  becomes increasingly better resolved as the degree of supercooling increases down to those investigators' lower limit of observation of  $-16^{\circ}\text{C}$ . Since this peak is due to x-ray scattering by the second sphere of coordination at about 4.5-Angstrom radius, Dorsch and Boyd concluded that the structure of water does grow increasingly ice-like as supercooling proceeds, as suggested a number of years ago by Bernal and Fowler (1933). They pointed out that this trend suggests that at the still greater degree of supercooling prevailing near the  $-40^{\circ}\text{C}$  point, the structure of liquid water might be so nearly isomorphic with ice as to justify Lafargue's disregard of the whole concept of the work of formation of an ice embryo. However, the work of formation (properly the free energy of formation) of a nucleus goes to zero, according to (4) only if  $\sigma_s$  goes to zero; and if isomorphism developed to this extent near  $-40^{\circ}\text{C}$ , then Lafargue's calculation would become invalid for still another reason, since his result requires a value of  $10.5 \text{ erg cm}^{-2}$  for  $\sigma_s$ . There seems no way to justify Lafargue's approach.

A still more recent effort to account for the  $-40^{\circ}\text{C}$  transition in terms of homogeneous nucleation is due to Mason (1952). Unlike Krastanow who did not have available the quantum-statistical expression for the rate factor in the nucleation equation, and unlike Lafargue who may have been unaware of it, Mason proceeded from Turnbull and Fisher's equation (3) above. Finally, unlike Fisher, Hollomon and Turnbull, he did not merely use the equation to make an estimate of  $\sigma_s$  by reasoning backward from the observed  $-40^{\circ}\text{C}$  transition temperature assuming the very thing which the meteorologist seeks to confirm. Instead, Mason made a direct attack on the problem by estimating  $\sigma_s$  on theoretical grounds, and then used this estimated value in (3) to study the behavior of  $J$ .

In several of the following sections, a number of refinements of detail in Mason's treatment will be discussed. Here only one general objection must be raised to the basis upon which Mason sought to demonstrate agreement between theory and observation. Aware of the inherent uncertainty in his theoretical estimate of  $\sigma_s$ , Mason found that values of  $\partial(\log_{10} J)/\partial T$  were less sensitive to uncertainties in  $\sigma_s$  than were values of  $\log_{10} J$  itself, and so he only discussed the former in his paper. On calculating values of that derivative near  $-40^\circ\text{C}$ , he found a nearly ten-fold increase in  $J$  per Centigrade degree in that vicinity, and he offered the rapidity of this increase, *per se*, as the explanation of the experimental observations of a sudden transition of supercooled clouds in the neighborhood of  $-40^\circ\text{C}$ .

Now a rapid temperature variation in the nucleation rate near  $-40^\circ\text{C}$  is certainly necessary to any statistical explanation of the observations, but it is not by itself sufficient. One must ask whether the nucleation rate might not vary just as rapidly at some temperatures other than  $-40^\circ\text{C}$ ; and (3) yields the answer that it does. Indeed, near  $-30^\circ\text{C}$  the rate of formation of nuclei is found, from (3) by use of Mason's figures, to change by a factor much greater: 250 per degree; and at  $-20^\circ\text{C}$  it changes by a factor of one hundred million per degree! Hence the mere ten-fold change per degree near  $-40^\circ\text{C}$  can certainly not *by itself* be regarded as implying that the neighborhood of  $-40^\circ\text{C}$  will be a preferred region for transition. Consequently, it becomes logically indispensable to consider not just the steepness of the temperature variation in the nucleation rate, but also the absolute values of that rate.

By means of this latter approach, an explanation for the observed phenomena might have been presented in a rather more convincing form than that chosen by Mason. A further important modification in approach should then have been to evaluate the nucleation rates not simply in terms of nuclei per cubic centimeter per second but rather in terms of nuclei per drop per second.<sup>5</sup> The latter is the pertinent rate here since each drop is essentially an isolated physical system in the process in question, and if a given drop is to crystallize within a reasonable length of time  $t$ , there must be a high probability of at least one nucleus forming somewhere within that drop during the time  $t$ . Failure on the part of Fisher, Hollomon and Turnbull (1949) to look at the  $-40^\circ\text{C}$  problem in this manner has already been cited. A measure of the average time between nucleation events within each drop is given

<sup>5</sup> Mason has pointed out (private communication) that his original approach was exactly this one, but that his recognition of the difference in sensitivity to  $\sigma_s$  of  $J$  and of  $\partial J/\partial T$  led him to discuss only the temperature derivatives. In so doing he apparently overlooked the fallacy of this approach occasioned by the even steeper  $J$  variations at temperatures warmer than  $-40^\circ\text{C}$ . And, indeed, a merely large value of  $\partial J/\partial T$  occurs at  $-40^\circ\text{C}$  for almost any halfway plausible numerical values one may insert into (3).

by the reciprocal of the nucleation rate per drop. Using the several tentative numerical values suggested by Mason for the parameters entering into (3), one finds for this "average nucleation time" the values shown in table 1 for drops of 1-, 5- and 10-micron radii. It is in considering the absolute values of these tabulated times *as well as* their rapid temperature variation that one finds quite nice apparent agreement between observation and Mason's work.

TABLE 1. Average time between nucleation events within water drops of radius  $r$  at various temperatures.  
Revised from Mason (1952).

Temperature	$r = 1$ micron	$r = 5$ microns	$r = 10$ microns
$-36^\circ\text{C}$	187 days	32 hr	4.5 hr
$-37^\circ\text{C}$	6.9 days	80 min	10 min
$-38^\circ\text{C}$	11 hr	5 min	40 sec
$-39^\circ\text{C}$	42 min	20 sec	2.5 sec
$-40^\circ\text{C}$	5 min	2 sec	0.3 sec
$-41^\circ\text{C}$	30 sec	0.2 sec	0.03 sec

In experiments where supercooling is produced in an adiabatic expansion, the entire nucleation process must occur in times of the order of seconds (unless the chamber is unusually well insulated). Hence the times shown in table 1 suggest that no crystals should be observed in a cloud of drops whose radii are of the order of microns until the peak expansional cooling extends down to near  $-40^\circ\text{C}$ , but that near that point the probability of nucleation finally rises to a level at which every drop in the 5- to 10-micron range may be expected to experience a nucleation event within the sensitive time of the chamber. In a natural cloud where the period during which a given drop exists at a given temperature is of the order of minutes, one would expect, from the implications of table 1 that spontaneous freezing could occur at a higher temperature, but only a degree or two higher because of the extreme temperature sensitivity of nucleation. Thus, to emphasize the basic issue here, the apparent success of a statistical theory of homogeneous nucleation is to be assessed not just on the basis of its prediction of a rather steep ascent of the nucleation probability per drop in the  $-40^\circ\text{C}$  region, as Mason tacitly suggested, but much more on the basis of whether it predicts that this ascent will, in fact, carry that probability to values implying that a majority of drops will be nucleated at least once in the time interval characteristic of the cooling process involved.<sup>6</sup>

Judged on both these grounds, the version of Mason's work shown in table 1 looks nearly perfect. Even the slight spread of the experimentally observed

<sup>6</sup> The calculated rates shown in table 1 have been given here despite their now recognized lack of validity, partly to document a logical objection to Mason's mode of assessing his results, but much more to illustrate, for the reader not familiar with nucleation theory, exactly the sort of numerical behavior of the dropwise nucleation rates which one would *hope* to find in searching for a statistical explanation of the  $-40^\circ\text{C}$  transition.

transition temperatures is readily understood in terms of table 1 if different observers worked with clouds of slightly different drop-size distributions, and particularly if the sensitive times of their chambers varied from fractions of a second to several seconds. Both types of dispersion in experimental conditions are entirely plausible. The writer's first interest in nucleation theory was aroused by these implications of table 1. It is with some regret, then, that he must next point out that an extensive study of the basis of Mason's calculations has uncovered a number of defects which, when removed in the best way recognized by the writer, destroy the neat agreement between table 1 and the experimental observations. The next six sections will be devoted to a critical examination of these points and to efforts to improve, in every way possible, the basis of the calculations of the dropwise nucleation rates.

#### 4. The Gibbs-Thomson equation

The theoretical nucleation rate is determined jointly by (3), (4) and (5). The writer has been unable to find any basis for modifying (3) or (4), though (4) will be incomplete if one can demonstrate that edge energies are being ignored at the expense of numerical accuracy. The Gibbs-Thomson equation (5), however, appears to require a slight change. Mason followed Frenkel (1946, p. 415) in using the form (5); but an examination of Frenkel's derivation of this relation reveals that it is only approximately correct for such large values of  $T_0 - T$  as one encounters in the present problem. From a thermodynamic argument which need not be reproduced here (Frenkel, 1946, p. 368), one can show that

$$(v_l - v_s) dp = 2\sigma_s v_s d(1/r),$$

where  $v_l$  and  $v_s$  are the specific volumes of the liquid and solid phases, respectively, and  $p$  is the external pressure on the system. Eliminating  $(v_l - v_s)$  between this equation and the differential form of Clapeyron's equation, and integrating between the limits  $r = r_c$  at  $T$ , and  $r = \infty$  at  $T_0 = 273\text{K}$ , one gets as a more generally applicable form of the Gibbs-Thomson equation,

$$r_c = 2\sigma_s / \rho_s L_f \ln (T_0/T). \quad (6)$$

The form (5) given by Frenkel and used by Mason is an approximation to (6) obtainable by expanding  $\ln (T_0/T)$  into a series and using only the first term. For only very small degrees of supercooling, negligible error is introduced by using (5); but when, as here,  $T_0 - T$  becomes 40C, there is about an 8 per cent error in (5), which means about a 16 per cent error in the computed value of  $F_c$ , and finally a much larger error in  $J$ . It may be well to state here that though this elimination of an error of less than 10 per cent in  $r_c$

represents a rather slight improvement when viewed against the large uncertainties which will be shown to exist in  $\sigma_s$  in section 7, still it enters (6) factorially and not additively, and so the revision is meaningful. A more concrete measure of the significance of the replacement of (5) by (6) is found in the fact that, with all other parameters left unchanged in Mason's calculations, this modification raises  $J$  by a factor of  $10^4$  for drops at  $-40\text{C}$ , and thereby raises the predicted "spontaneous freezing point" by about 4C, from near  $-40\text{C}$  as shown in table 1 to about  $-36\text{C}$ . That is, the change from (5) to (6) already alters appreciably the close agreement with observation which made table 1 seem so promising an explanation of the  $-40\text{C}$  transition.

#### 5. Latent heat of fusion of ice

It has been pointed out above that previous investigators of the problem of homogeneous nucleation of supercooled water have failed to take account of the temperature dependence of the latent heat of fusion of ice. It will next be shown that this oversight has introduced a quite large error into this previous work, including Mason's work as modified in table 1.

A general thermodynamic relation, sometimes referred to as Kirchoff's equation (Glasstone, 1947),

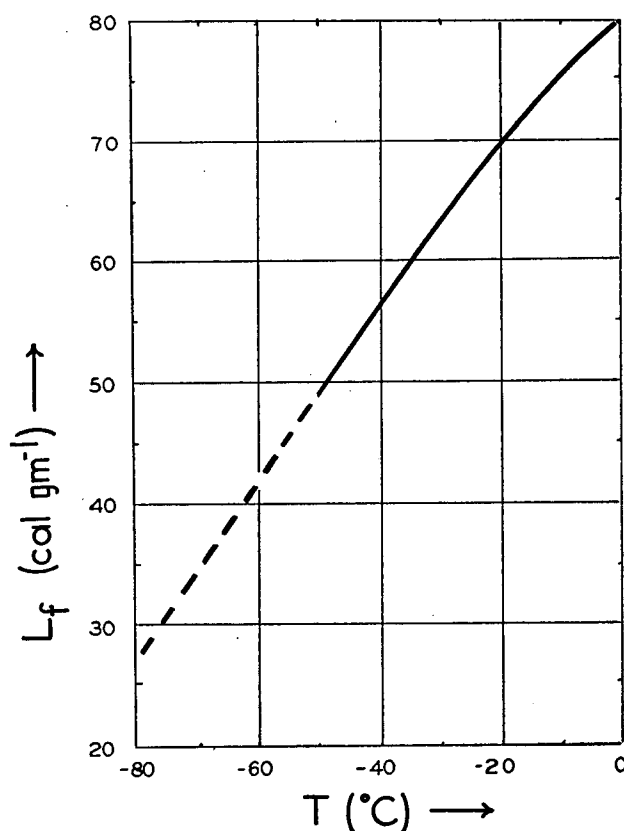


FIG. 1. Temperature dependence of latent heat of fusion of ice,  $L_f$ . Values from 0C to  $-50\text{C}$  after Goff. Values from  $-50\text{C}$  to  $-80\text{C}$  obtained by linear extrapolation.

relates the isobaric temperature variation of the latent heat of fusion to the difference in specific heats at constant pressure for the liquid phase  $c_{pl}$ , and the solid phase  $c_{ps}$ , according to

$$(\partial L_f / \partial T)_p = c_{pl} - c_{ps}. \quad (7)$$

For water substance at 0C,  $c_{pl} \approx 1$  cal gm<sup>-1</sup> deg<sup>-1</sup>, while  $c_{ps} \approx 0.5$  cal gm<sup>-1</sup> deg<sup>-1</sup>, so the latent heat of fusion of ice decreases with decreasing temperature at a rate of about 0.5 cal gm<sup>-1</sup> deg<sup>-1</sup> just below the melting point. If this rate held constant down to -40C,  $L_f$  would decrease to about 60 cal gm<sup>-1</sup> at that temperature. Actually the situation is slightly worse, since  $c_{ps}$  is known to decrease with decreasing temperature (Giaque and Stout, 1936), and at the same time  $c_{pl}$  increases with decreasing temperature according to experimental results extending to -15C (Scheel and Heuse, 1909) plus theoretical extrapolation to -50C (Goff, 1949) based on thermodynamic relations between  $c_{pl}$  and  $de/dT$ .

Values of  $L_f(T)$  are shown in fig. 1. The dashed portion of the curve in fig. 1 below -50C is the writer's own simple *linear* extrapolation beyond Goff's values. Although this part of the curve is a gross extrapolation, it will be used in certain estimates made in section 10. The very careful nature of Goff's extrapolation to -50C from experimental data extending to -15C warrants considerable faith in the values down to well below the -40C transition point, which is fortunate here. It is clear from fig. 1 that previous analyses of the homogeneous nucleation of supercooled water, in which a value of 80 cal gm<sup>-1</sup> has repeatedly been used for  $L_f$  in the Gibbs-Thomson equation, have thereby been very seriously in error inasmuch as this roughly 40-per cent overestimate of  $L_f$  is raised to the second power and then used in an exponential. For example, if just this one correction is made in Mason's work it shifts the predicted transition point from near -40C as implied in table 1 to the very much lower temperature of -68C. Comment has already been made on what the same type of error did to Lafargue's work. In section 7 below, it will be shown that failure to recognize that  $L_f$  decreases with decreasing temperature produced still another type of error in Krastanov's (1941) estimate of  $\sigma_s$ .

There is a second, less obvious correction of  $L_f$  that must be considered. This second correction has also been overlooked in previous studies, though fortunately without numerical error since still another oversight closely compensates this one, as will be shown later. Despite this near-cancellation of one error against another, it seems advisable to examine each here to avoid future possibility of one of them being detected and corrected and not also the other. The present point hinges upon the fact that the ice whose fusion is involved in homogeneous nucleation occurs

in the form of extremely small embryos with radii of the order of 10-20 Angstroms. For particles of such small radii of curvature, there appears the same sort of geometric effect on binding energy as was referred to above in a footnote in section 2 for the case of liquid embryos. The binding energy (and hence the latent heat of fusion) must decrease with decreasing embryo radius, and although this decrease is entirely negligible for radii above, say, 10<sup>-6</sup> cm, it becomes numerically significant for particles of the size of those here in question.

To obtain thermodynamically a measure of the reduction of  $L_f$  due to surface curvature effects, consider a spherical ice embryo of radius  $r$  from which a small mass  $dm$  of water molecules is removed by melting. Let  $L_f$  now denote the latent heat of fusion for  $r = \infty$  at the temperature in question. Then the amount of energy  $dQ$  that must be supplied to melt off  $dm$  grams of ice from the sphere is *less* than  $L_f dm$  by the amount of the decrease of surface energy  $\sigma_s dA$ , where  $dA$  is the change in surface area of the embryo accompanying the spherically symmetric stripping of the  $dm$  grams. Thus, inasmuch as  $dm = 4\pi\rho_s r^2 dr$  and  $dA = 8\pi r dr$ , and since  $dQ = L_f dm - \sigma_s dA$ , it follows that

$$L_{fr} \equiv dQ/dm = L_f - (2\sigma_s/\rho_s r), \quad (8)$$

where  $L_{fr}$  is the latent heat of fusion per gram of ice at a radius of curvature  $r$ . It may be noted that  $\sigma_s$  itself is size dependent, but allowance for this would only introduce second-order corrections into (8).

The numerical magnitude of this size correction of  $L_f$  is subject to the same relative error as is the value assigned to  $\sigma_s$ , so it will turn out that its precise value cannot be determined here since  $\sigma_s$  will finally turn out to be uncertain. However, an estimate of its effect can be made by consideration of a nuclear radius of 10 Angstroms (approximate size in water nucleation at -40C) and the assumption that  $\sigma_s \approx 20$  erg cm<sup>-2</sup> (rough average of three estimates of  $\sigma_s$  given in section 7 below). In this case the correction term amounts to about 13 per cent of  $L_f$ . This correction is thus about half again as large as the correction due to the revision in form of the Gibbs-Thomson equation, which was shown in section 4 to shift the theoretically predicted transition temperature by about 4C.

It is interesting to compare (8), which has been obtained here thermodynamically, with the results of an approximate molecular argument given by Benson and Shuttleworth (1951). They calculated the ratio of the molecular heat of *vaporization* for a small cluster of molecules to that of a plane surface on the assumption that all pairs of molecules interact according to an inverse twelfth power repulsive potential plus an inverse sixth power attractive potential. For the simplest case of a central molecule surrounded by twelve close-packed neighbors, they computed the ratio to

be about 0.4. Since Benson and Shuttleworth's model implies that this ratio may be expected to vary approximately as  $1 - cN^{-1/3}$ , where  $c$  is a constant and  $N$  is the number of molecules in the cluster, their value of 0.4 for thirteen molecules may be raised to about 0.6 for a cluster of the size referred to in the preceding paragraph, since such a cluster would comprise 25 to 30 water molecules. The corresponding ratio for latent heats of fusion predicted by (8) is 0.87. This order-of-magnitude agreement with Benson and Shuttleworth's result is surprisingly good in view of the present uncertainty in  $\sigma_s$ , and in view of the other approximations involved in both approaches to this ratio. It seems appropriate to regard this agreement in size-effect estimates as providing mutual support for these quite independent methods of estimating latent heats of small aggregates of molecules.

## 6. Density of ice

The coefficient-of-volume expansion of ice near 0°C is  $1.5 \times 10^{-4} \text{ deg}^{-1}$  (Dorsey, 1940). It follows that even at  $-50^\circ\text{C}$ , thermal contraction has increased the density of ice by only about one per cent of its value of 0.92 at 0°C. This change is too small to be considered here. It will, furthermore, be opposed by a decrease of density associated with surface distortion of the ice lattice (Brown, 1947). Since nuclei have relatively large surface/volume ratios, this latter type of density change may become sensible. Shuttleworth (1949) calculates that it amounts to several per cent for homopolar crystals, but this density reduction is localized almost entirely to a surface monolayer. Pending further developments in the theory of dipole-bonded crystals like ice, the effect must be ignored.

## 7. Surface free energy of a water-ice interface

To the writer's knowledge, no one has yet devised an experimental technique for directly measuring  $\sigma_s$  for an interface between supercooled water and ice, nor even for water and ice at the triple point. Nothing could be more unfortunate for the problem at hand. Inspection of (3), (4) and (6) reveals that  $\sigma_s$  has a controlling influence on the homogeneous nucleation rate since it enters to the third power in an exponential in the  $J$  equation. It follows that major efforts should be devoted to getting improved estimates of  $\sigma_s$  by any available theoretical means. In the present section, attempts will be made to refine Krastanow's (1941) and Mason's (1952) values. The present study has not led to any essentially new basis for estimating  $\sigma_s$ , but it has revealed that numerically significant changes have to be made in both of these existing methods.

Krastanow's basis for estimating  $\sigma_s$  depends upon a general relationship rather casually suggested by Volmer (1939, p. 181). The latter proposed that one

might get a rough value of this quantity from the proportion

$$\sigma_s/L_f \approx \sigma_l/L_v. \quad (9)$$

The validity of such a proportion depends on how surface free energies and latent heats are related, respectively, to intermolecular binding energies, and depends particularly on whether that relationship is identically the same for the solid and the liquid states. It must not be thought that this identity has been proved by either Volmer or Krastanow; in fact, neither has given any comment of justification for (9). Since Krastanow's estimates of  $\sigma_s$  as derived from (9) have been used without apparent question in subsequent studies by other investigators (Lafargue, 1950; Weickmann, 1951), and will also be used below, it becomes a matter of some interest to try to assess this equation's validity, even if only to a first approximation.

In the latter spirit, the writer offers the following crude derivation of Volmer's equation based upon a result of a theoretical analysis of the relation between surface energies and latent heats of sublimation of crystals (Shuttleworth, 1949). From direct molecular calculations of the surface energy, Shuttleworth found that an expression of the form  $a_s^2\sigma_s'/L_s = K$  holds for homopolar crystals, where  $a_s$  is the intermolecular (or interatomic) distance in the solid,  $\sigma_s'$  is the surface free energy of the solid against its vapor, and  $K$  is a constant depending upon the interatomic potential used and on the lattice geometry involved. For a (111) face in a face-centered cubic homopolar crystal,  $K$  is about 0.2 for one plausible potential. Shuttleworth discussed quantitatively the effect on  $\sigma_s'$  due to surface distortion of the lattice of van der Waals crystals, but could only point out qualitatively that, for crystals in which permanent dipoles influence the bonding,  $\sigma_s'$  will be appreciably lower due to greater contribution of distortion energy. Since water is a substance of particularly marked dipole-dipole bonding (hydrogen bonding), one would expect a  $K$  value somewhat below 0.2, in the case of interest here.

If one next considers the liquid state, he observes that an interaction picture very much like that assumed by Shuttleworth exists as far as concerns the short-range order important in homopolar or dipole bonding, and particularly so in the case of supercooled water, which appears to have a very ice-like structure—at least out as far as second-nearest neighbors (Dorsch and Boyd, 1951). Hence one might expect that supercooled water should also be characterized by a Shuttleworth relation of the form  $a_l^2\sigma_l/L_v \approx K'$ , where  $a_l$  is the intermolecular distance in the liquid structure and  $K'$  is the new constant for liquid water. But since  $a_s \approx a_l$ , within the limits of accuracy of the present discussion, and since structural similarities and interaction similarities should imply  $K \approx K'$ , it should

follow that a proportion of the form

$$a_s^2 \sigma_s' / L_s \approx a_l^2 \sigma_l / L_v \quad (10)$$

might hold approximately. Furthermore, each ratio in (10) would be expected, as Shuttleworth noted, to be somewhat smaller than 0.2. Actually, the right-hand member, which is readily evaluated, equals 0.08 at 0C.<sup>7</sup> From the 0C value of  $L_s$ , one finds from (10) that  $\sigma_s'$  is about 85 erg cm<sup>-2</sup>. Then invoking Antonov's rule (Adam, 1949) to estimate  $\sigma_s$ , one finds

$$\sigma_s \approx \sigma_s' - \sigma_l \approx (85-75) \text{ erg cm}^{-2} = 10 \text{ erg cm}^{-2}.$$

Finally, putting this estimated 0C value of  $\sigma_s$  back into Volmer's equation (9), one finds that the left- and right-hand members have numerical values of  $2.98 \times 10^{-9}$  and  $3.01 \times 10^{-9}$ , respectively, when the latent heats are once again expressed in ergs per gram. This agreement of the two members of (9) to better than one per cent is almost certainly fortuitous because of the many approximations involved in the preceding discussion. What can be said, however, is that Volmer's equation has now been provided with at least some theoretical support, which has not been true previously, to the writer's knowledge. Briefly, one can regard (10) as following from Shuttleworth's relation and the similarity in structures of ice and supercooled water; and Volmer's equation (9) then appears to be related to (10) through Antonov's rule. It should be strongly emphasized, however, that (9) has been justified here in only a very approximate manner; so computations based upon it simply cannot yet be regarded as definitive—a point which has not been given deserved emphasis in previous applications.

Since (9) has now been rendered at least plausible as one relation for making approximate calculations of  $\sigma_s$ , the next step is to examine whether Krastanow's (1941) applications of (9) can merely be taken over here for later use in estimating  $J$ . Although Krastanow did not state the numerical values he used to compute his  $\sigma_s$  values, the writer finds that Krastanow's results can be reproduced to within one per cent by introducing into (9) temperature-dependent values of  $\sigma_l$  extrapolated below 0C from data such as those given by Zemansky (1943) and temperature-dependent values of  $L_v$  (List, 1951), and by use of a *constant* value of  $L_f$  equal to 80 cal gm<sup>-1</sup>. This last feature of Krastanow's approach was erroneous because of the temperature dependence of  $L_f$ . His original computed values of  $\sigma_s$  are shown in the first line of table 2. By using  $L_f$  values taken from fig. 1, one obtains the set of values shown in the second line of table 2.

Whereas Krastanow's values increase slowly with decreasing temperature, the temperature-corrected values *decrease* appreciably. That the latter sort of

TABLE 2. Water-ice interfacial free energy  $\sigma_s$  (erg cm<sup>-2</sup>) computed from Volmer's equation.

Temperature (deg C)	0	-10	-20	-30	-40	-50
Krastanow's $\sigma_s$ based on $L_f = 80 \text{ cal gm}^{-1}$	10.0	10.2	10.4	10.6	10.8	11.0
Corrected $\sigma_s$ based on $L_f(T)$ from fig. 1	10.0	9.6	9.1	8.5	7.7	6.8

temperature dependence is the more reasonable would seem to follow from Dorsch and Boyd's (1951) x-ray diffraction studies, which indicate that as the degree of supercooling of water increases, the liquid becomes increasingly ice-like in structure. As the structures of the two phases grow increasingly more similar, it should follow that the surface free energy of the interface between the two phases should decrease towards the zero value that it must exhibit in the limit of complete isomorphism. Consequently the present revision of Krastanow's computation must be regarded as more nearly correct than the original values, and they will be used later in section 10. Note that in the neighborhood of the -40C point, Krastanow's value is about 40 per cent too large, if the present revision is taken as the reference value.

Although Krastanow's estimates of  $\sigma_s$  were substantially in error, it must next be noted that since  $\sigma_s$  and  $L_f$  enter the Gibbs-Thomson equation only in the form of the ratio  $\sigma_s/L_f$ , and since exactly this ratio forms the left side of (9), Krastanow's errors in  $\sigma_s$  and  $L_f$  inevitably cancel each other exactly as far as any calculations of  $r_c$  from (5) are concerned. Nevertheless,  $F_c$  varies as  $\sigma_s r_c^2$ , so Krastanow's roughly 40-per-cent overestimate of  $\sigma_s$  itself near -40C would still remain to throw off any nucleation-rate calculations based on his results. It can be seen that some extenuating remarks might be made along the same line about Lafargue's (1951) calculation; but Lafargue used a 0C value of  $L_f$  with a value of  $\sigma_s$  which appears to have been interpolated linearly between Krastanow's 0C value and his -40C value. This prevents cancellation of one error by the other, so the point will not be amplified here—especially since Lafargue's whole approach is fundamentally unsound.

Having examined in some detail, and refined in one way, the Volmer-Krastanow method for estimating  $\sigma_s$ , we will now focus attention on a second method, first used in a meteorological application by Mason (1952). Mason's approach was as follows: Using crystallographic data for ice, he computed the total number of hydrogen bonds per unit area of a (0001) plane in ice, combined this with an estimate of the energy required to break one hydrogen bond, and therefrom determined the cleavage work per unit area required to pull an ice crystal apart perpendicular to the basal plane. Since this cleavage process creates two units of new surface area per unit area of basal plane, he identified one-half of the computed cleavage work (one-half of

<sup>7</sup> One must use the latent heats per molecule in Shuttleworth's relation.

204 erg cm<sup>-2</sup> or 102 erg cm<sup>-2</sup>) with  $\sigma_s'$ , the specific surface free energy of ice against water vapor. Next he implicitly introduced Antonov's rule to obtain  $\sigma_s$  by subtracting the specific surface free energy of water against vapor from 102 erg cm<sup>-2</sup>. Using a value of 80 erg cm<sup>-2</sup> for the surface tension of water at -40C, he obtained 22 erg cm<sup>-2</sup> for  $\sigma_s$ . This value, then, underlies the results shown in table 1 above. In view of the extreme sensitivity of calculated  $J$  values to the value used for  $\sigma_s$ , it is immediately disturbing to see that Mason's estimate is about three times as large as that which has been obtained above for -40C from a refinement of the Volmer-Krastanow method. This discrepancy demands that a careful evaluation of Mason's method of estimating  $\sigma_s$  be made; for although it has been emphasized above that the Volmer-Krastanow method remains open to serious question, choice between it and Mason's method cannot be made until the latter's validity is also assessed.

A first, and rather obvious question concerns the value which Mason took for  $\sigma_l$  at -40C, namely, 80 erg cm<sup>-2</sup>. Although he did not so state, perhaps Mason may have been influenced in this choice by a suggestion due to Sander and Damköhler (1943) to the effect that a value of about 78 erg cm<sup>-2</sup> is required for  $\sigma_l$  near -40C to make certain experimental data on water-vapor nucleation agree with theory. Bradley (1951) as well as LaMer and Pound (1951) have suggested that the decrease in  $\sigma_l$  below values extrapolated from experimental data above 0C may actually have been due to the effect of high surface curvature of the water nuclei involved. This explanation seems quite plausible to the writer (see comments at the end of this section on a similar phenomenon in ice nucleation). If true, then it is definitely incorrect to make size corrections in  $\sigma_l$  and then use this in Antonov's rule as has to be done in Mason's approach. Fortunately, some observational data exist to throw light on this question. Hacker (1951) has recently carried out an excellent experimental study of  $\sigma_l$  for water supercooled down to as low as -22C. His results are in very good agreement with the International Critical Tables to as far as the latter's data extend, -10C, and confirm the existence of the slight inflection point in  $\sigma_l(T)$  near 0C that can be discerned in the I.C.T. values. Hacker's results definitely contradict the deductions of Sander and Damköhler (to the extent that the latter investigators' conclusions are applied to plane surfaces of water rather than to highly curved surfaces); for near -20C, Hacker's curve is curving slightly upward while that of Sander and Damköhler is curving downward and lies already well below Hacker's absolute values. It may be mentioned that there is little ground for questioning Hacker's results on the basis that surface contamination might have affected his results, since contamination can easily lower surface tensions, but almost never raises them.

An extrapolation of Hacker's experimental curve to -40C, preserving the slight curvature of the 0C to -22C range, yields a value of about 84 erg cm<sup>-2</sup>; so it appears necessary to alter Mason's value of 80 erg cm<sup>-2</sup>, and hence in turn to revise immediately his value of  $\sigma_s$  from 102 - 80 = 22 erg cm<sup>-2</sup> to 102 - 84 = 18 erg cm<sup>-2</sup>. This rather slight revision in  $\sigma_s$ , it must be noted, has marked effects on calculated values of  $J$  and raises the theoretically predicted transition temperature by about 6C. It is clear that rather slight changes in one's basis for assigning numerical values to either  $\sigma_s'$  or  $\sigma_l$  will have rather large effects on  $\sigma_s$ , since, unfortunately, the latter is obtained from Antonov's rule as a small difference,  $\sigma_s' - \sigma_l$ , in two large terms.

The above revision has sent the present estimate of  $\sigma_s$  downward to improve somewhat the agreement between the Volmer-Krastanow estimate and that obtained from the cleavage-work approach. The sensitivity of  $\sigma_s$  to the calculated value of  $\sigma_s'$  requires that the latter quantity be scrutinized next. There appears to be no possibility of revising Mason's purely crystallographic arguments concerning the density of hydrogen bonds per unit area of a (0001) plane, a density which can be expressed inversely as an area per bond of  $1.77 \times 10^{-15}$  cm<sup>2</sup>; but two objections must be raised against his method of calculating the energy per bond.

Mason follows Pauling (1940, p. 304) in assigning a value of 4500 cal mole<sup>-1</sup> to the hydrogen bond energy at 0C, but then states with no explanation that the corresponding value at -40C should be about 5100 cal mole<sup>-1</sup>. Now the temperature variation of the heat of sublimation (the quantity from which the hydrogen-bond energy is determined by Pauling's argument) can be estimated from Kirchoff's equation, applied now to the solid-vapor transition:

$$(\partial L_s / \partial T)_p = c_{pv} - c_{ps},$$

where  $c_{pv}$  and  $c_{ps}$  are the specific heats at constant pressure for the vapor and solid phases, respectively. Near 0C,  $c_{pv} = 0.443$  cal gm<sup>-1</sup> deg<sup>-1</sup>, and  $c_{ps} = 0.468$  cal gm<sup>-1</sup> deg<sup>-1</sup>, so  $(\partial L_s / \partial T)_p \approx -0.025$  cal gm<sup>-1</sup> deg<sup>-1</sup>. Both  $c_{pv}$  and  $c_{ps}$  decrease with  $T$ , but in such a way that their difference remains nearly constant. Hence, extrapolating to -40C from the 0C value,  $L_s = 677$  cal gm<sup>-1</sup>, one finds that near -40C,  $L_s \approx 678$  cal gm<sup>-1</sup>. This change represents an increase of less than 0.2 per cent over the 0C value, in serious disagreement with Mason's roughly 13-percent increase in the hydrogen-bond energy over this temperature interval.

Since the discrepancy between the above thermodynamic estimate of the temperature effect on  $L_s$  and Mason's unexplained adjustment is so large and has a marked effect on the calculated value of  $\sigma_s$ , it is fortunate that at least a crude independent check can be effected as follows: The coefficient of expansion of ice is about  $5 \times 10^{-5}$  deg<sup>-1</sup>, so the 40-deg temperature

change from 0C to  $-40\text{C}$  will decrease all lattice distances by about two parts per thousand if the effects of the slight anisotropy of ice are ignored. Now by Badger's rule (Pauling, 1940, p. 171), the force constant  $k_0$  for a bond varies about as  $d^{-3}$ , where  $d$  is the pertinent interatomic distance. Since the range of forces here involved is only of the order of  $d$  itself, the work of breaking a bond is of the order of  $k_0 d^2$ , or  $d^{-3} d^2$ , or  $d^{-1}$ . Badger's rule is only an empirical relationship, but that it yields tolerably good approximations can be shown by checking it against heats of dissociation of two different hydrogen-bonded substances having known bond distances (*e.g.*, water and formic acid dimer). Combining the thermal expansion datum with Badger's rule, one predicts that the bond energy in ice should increase by about 0.2 per cent, just the value estimated on purely thermodynamic grounds above.

Since Mason gave no justification for his 13-percent increase in the bond energy associated with the temperature change from 0C to  $-40\text{C}$ , and since two independent estimates assign it a value of only about 0.2 per cent, it appears necessary to reject Mason's figure of  $5100 \text{ cal mole}^{-1}$  in favor of the 0C value of  $4500 \text{ cal mole}^{-1}$  for the hydrogen-bond energy per mole (simply ignoring the 0.2-percent increase at  $-40\text{C}$  predicted here). This revision of Mason's estimate of  $\sigma_s'$  yields a value of  $102(4500/5100) \approx 90 \text{ erg cm}^{-2}$ . Applying Antonov's rule and using  $\sigma_l = 84 \text{ erg cm}^{-2}$  at  $-40\text{C}$ , one now gets only  $6 \text{ erg cm}^{-2}$  for a second-revised value of  $\sigma_s$ . This revision has sent  $\sigma_s$  below the revised Volmer-Krastanow value of  $7.7 \text{ erg cm}^{-2}$ .

However, a further error appears to have entered Mason's calculation of  $\sigma_s'$ , and this error more than cancels the two errors now cited in his  $\sigma_s$  calculation. In computing the work that must be expended in cleaving an ice crystal parallel to the basal plane, Mason took account of only a part of the total bond energy, that ascribable to hydrogen bonding. That is, the value of  $4500 \text{ cal mole}^{-1}$  which he quotes from Pauling was obtained in turn by Pauling from the  $12,200 \text{ cal mole}^{-1}$  heat of sublimation of ice by observing that only about three fourths of the total bond energy in an ice crystal is due to hydrogen bonding. The remaining one fourth is due to van der Waals forces. Now in the conceptual experiment of cleaving an ice crystal, work would be done *both* in breaking hydrogen bonds and in separating neighboring molecules against the van der Waals attractions, so Mason was incorrect in ignoring the latter. The van der Waals attractions in question here are mainly of the type known as London-dispersion forces, and arise in ice because of dipole-dipole interactions between adjacent oxygen atoms. Fluctuations in the instantaneous dipole moment of one oxygen-atom nucleus and its surrounding electron cloud induce instantaneous di-

poles in neighboring oxygen atoms, and the time average of these fluctuating dipole-induced-dipole interactions constitutes an attractive effect. The exact nature of these forces is quite pertinent here because all of the available electrons in water may be regarded as surrounding the oxygen nuclei, so that it becomes clear that the effective areal density of van der Waals bonds on a (0001) plane will be identical with that of the hydrogen bonds (if we ignore all but nearest-neighbor interactions). The two types of bonding will, in fact, act coaxially along the oxygen-oxygen axes. Hence Mason's figure of  $4500 \text{ cal mole}^{-1}$  has only to be replaced by  $6100 \text{ cal mole}^{-1}$  to give a new estimate for  $\sigma_s'$  of  $90(6100/4500) = 122 \text{ erg cm}^{-2}$ . Applying Antonov's rule as before, one gets  $\sigma_s = 38 \text{ erg cm}^{-2}$  as a final revised value resulting from Mason's approach.

Neglect of the van der Waals bonding was the most numerically serious error in Mason's work and is seen to lead to a value of  $\sigma_s$  which is about five times greater than the revised Volmer-Krastanow value for the same temperature. This large discrepancy in values of  $\sigma_s$  predicted by the two available methods leads to vastly different values of  $J$  near  $-40\text{C}$ , as will be shown below, and demands that search be made for still further refinements in the two calculational approaches so that the discrepancy may be reduced. In particular, it would be very helpful even to know if the revised Volmer-Krastanow method somehow tends to underestimate  $\sigma_s$ , or if the revised Mason method tends to overestimate the same quantity. A comment will next be made concerning the latter probability.

In the estimation of the cleavage work by the method that gave Mason a value of  $102 \text{ erg cm}^{-2}$  for  $\sigma_s'$ , and which has here yielded  $122 \text{ erg cm}^{-2}$ , no explicit allowance has been made for the reduction in the work of separation occasioned by the distortion of the lattice in the vicinity of the two newly created (0001) faces. The local density of atoms in the surface layer of a crystal is slightly lower than the value characteristic of the deep interior; and as a result, a newly created surface, of the sort envisioned in the cleavage operation, will relax into a state of lower potential energy during the separation following cleavage. The result (Brown, 1947; Shuttleworth, 1949) is that the net-cleavage work is reduced by an amount dependent upon the degree of surface distortion peculiar to the crystalline substance in question. Shuttleworth has succeeded in calculating this reduction term for the case of inert-gas crystals near absolute zero, and finds that it is of the order of only a few per cent of the gross cleavage work. However, Shuttleworth observes that for a crystal in which permanent dipoles contribute to the total bonding, this reduction term will become appreciably larger, though by an amount which he indicates is not easily computed. Since the ice lattice is chiefly held together by hydrogen bonds

of the permanent dipole type, it would seem to follow that one must obtain an excessive value of  $\sigma_s'$  if no reduction is applied to the cleavage work to allow for surface distortion. This would mean that  $38 \text{ erg cm}^{-2}$  would, in turn, be an overestimate of  $\sigma_s$ .

Although the writer has not succeeded in making any precise determination of the distortion correction, the following crude argument is offered as an indication of the order of magnitude of the effect: One can make a theoretical calculation of  $\sigma_l$  by the cleavage-work method used above; but to get  $\sigma_l$ , one must, of course, base the calculation on  $L_v$  rather than  $L_s$ . The result for 0C is  $107 \text{ erg cm}^{-2}$ , which is  $32 \text{ erg cm}^{-2}$  greater than the known value of  $75 \text{ erg cm}^{-2}$ . At  $-40\text{C}$  one gets  $112 \text{ erg cm}^{-2}$ , which exceeds by  $28 \text{ erg cm}^{-2}$  the  $-40\text{C}$  value used here on the basis of Hacker's study. Since the sort of surface distortion which occurs in a crystal lattice also occurs in a liquid (see, for example, Brown, 1947), one may take  $30 \text{ erg cm}^{-2}$  as an average distortion energy for liquid water over the temperature range of interest here. That this is a percentually very much larger correction than the distortion correction Shuttleworth found for inert-gas crystals is not surprising in view of the very different force laws involved in the bonding of the two types of substances; but whether this figure may be regarded as a close estimate of the distortion correction cannot be said to be certain. It will be a good estimate only if the cleavage calculation upon which the uncorrected values of  $\sigma_l$  were based do take appropriate account of all other factors. The writer proceeds tentatively on the assumption that the latter is so.

Since the dipole and higher multipole binding in water substance involves significant interactions out to and possibly beyond next-nearest neighbors (Campbell, 1952), one must expect that the surface structure in water would be somewhat more open than that of ice, since in water only short-range order exists, while in ice long-range order prevails. Consequently the distortion energy in ice must be slightly less than that in water, and roughly in inverse proportion to the latent heats of vaporization of the two phases. Hence, the distortion correction in ice may be taken here as about  $30(L_v/L_s) \approx 26 \text{ erg cm}^{-2}$  for the temperature range from 0C to  $-40\text{C}$ . Applying this correction to the previously obtained value  $\sigma_s' = 122 \text{ erg cm}^{-2}$ , one gets  $96 \text{ erg cm}^{-2}$  as a crudely distortion-corrected estimate of the specific free energy of a vapor-ice interface.

Two distinct values have now been found for  $\sigma_s'$  from the cleavage-work approach:  $122 \text{ erg cm}^{-2}$  as a value uncorrected for distortion, and  $96 \text{ erg cm}^{-2}$  as a value very roughly corrected for distortion. Using Antonov's rule with values of  $\sigma_l$  taken from Hacker (1951) and from a smooth extrapolation to  $-50\text{C}$  of Hacker's data, one gets the two sets of  $\sigma_s$  values shown in table 3. For reference, the first line contains the  $\sigma_l$  values used in the calculations.

TABLE 3. Values of  $\sigma_s$  ( $\text{erg cm}^{-2}$ ) calculated from work of cleaving ice crystal along (0001) plane.

Temperature (deg C)	0	-10	-20	-30	-40	-50
Value of $\sigma_l$ used ( $\text{erg cm}^{-2}$ )	75	77	80	82	84	86
$\sigma_s$ uncorrected for distortion energy	49	45	43	40	38	36
$\sigma_s$ "corrected" for distortion energy	21	19	16	14	12	10

A last point to be considered under the heading of surface free energy of a water-ice interface concerns the question of the size-dependence of  $\sigma_s$ . It has been argued theoretically (e.g., Tolman, 1948) that surface energy must, in general, be a function of surface curvature. Indeed, the sort of simple molecular model, in terms of which the  $r$ -dependence of  $L_f$  was obtained earlier here, demands  $r$ -dependence also in  $\sigma_s$  since both of these parameters are largely determined by surface binding forces and the net effect of the latter is dependent upon surface curvature. LaMer and Pound (1951) have considered the experimental evidence for a decrease of surface tension of liquid water with decreasing radius of surface curvature, and have discerned what may be such an effect in the experimental data of Sander and Damköhler (1943). Bradley (1940) made a calculation based on an inverse-seventh power law of attraction inserted into the Laplacian theory of capillarity, and concluded that the surface free energy might drop by slightly less than 10 per cent at radii equal to ten molecular diameters, and by perhaps 13 per cent for drops with radii equal to only five molecular diameters (order of magnitude of critical ice embryos). More recently, Benson and Shuttleworth (1951) have made a similar calculation, except that they included repulsive interactions. They found that for clusters of as few as thirteen molecules the size-reduction amounts to perhaps 15 per cent of the plane-surface value.

The fairly close numerical agreement between Bradley's, and Benson's and Shuttleworth's estimates of 10–15 per cent for the particle-size range here involved, coupled with the further agreement between this estimate and the writer's size correction for the parameter  $L_f$  (section 5 above), has led him to treat  $\sigma_s/L_f$  as size-independent in the Gibbs-Thomson equation (6). This leaves just the explicit factor  $\sigma_s$  in (4) to produce net size dependence in the nucleation rates; and the writer chooses to employ a uniform 10-percent reduction of  $\sigma_s$  whenever  $F_c$  is being computed, since the embryo radii are in just the size range where the above evidence suggests a correction of this order of magnitude. Clearly, there is room for improvement here, but it does not seem likely that much will be possible until a more complete theoretical treatment of the surface energy of small aggregates is forthcoming.

## 8. The nuclear shape factor $g$

Once all parameters entering the Gibbs-Thomson

equation are specified, the value of  $F_c$  is still dependent upon the shape factor  $g$  in (4). Mason chose  $g \approx 23$ , the value appropriate to a hexagonal prism whose height equals three times its apical semidiameter, but he did not discuss the basis for this particular choice. Since all of the thermodynamic arguments that underlie the Gibbs-Thomson equation assume spherical nuclei, and since  $g$  for a sphere is only  $4\pi \approx 12.6$ , the use of any other value calls for some justification. However, as soon as one gives explicit attention to this matter he recognizes that here is still another of the numerous details of nucleation theory which pose fairly subtle problems. In considering nuclear shapes, one must cope with the constraint imposed by the lattice geometry characteristic of ice; and for such small crystallites as those comprising nuclei in supercooled water near  $-40^\circ\text{C}$  it is not clear that one can choose arbitrarily either a sphere or any other shape. One guiding principle here is that the most probable nuclear shape should be that which is both representable by a microlattice and consistent with the requirement that the total free energy shall be a minimum for the given number of member molecules. By analogy with gross crystal morphology, one would expect that the crystal faces of high specific surface free energy would rapidly grow out, leaving the faces of low specific free energy best developed. Since Weickmann (1947) has clearly established the dominance of elongated hexagonal prisms near the  $-40^\circ\text{C}$  point, one concludes that near that temperature the basal planes must be characterized by somewhat larger specific surface free energy than are the prism faces. It follows (by direct deduction from Weickmann's observations) that the preferred shape for nuclei near  $-40^\circ\text{C}$  ought to be elongated prisms, unless curvature effects somehow alter this problem seriously. Since Mason's choice of  $g$  corresponds to a shape that might be built up from the basic lattice geometry of ice while a sphere does not (in the limit of aggregates of nuclear size), and furthermore because the same  $g$  seems consistent with Weickmann's observations on macroscopic crystals, the writer chooses to follow Mason in using  $g \approx 23$ .

As for the implications of inconsistency this choice seems to introduce, in view of the spherical shapes assumed in all underlying thermodynamic arguments, the writer would make the following observation: It has been pointed out earlier that (4) is correct only as long as edge energies are unimportant, and the ratio of the contribution of edge energies to that of surface energies grows large for exactly the size limit near which one works in nucleation theory. It is of double interest, then, to note that in Benson's and Shuttleworth's (1951) analysis of the surface energy of small nuclei, their term which represents the contribution of edge energy to the total surface energy of a polyhedral cluster can be shown to comprise a term of identical

functional form and approximately equal numerical magnitude as that which has been discussed above at the end of section 7 in connection with the size-dependence of  $\sigma_s$ . That is, if one uses a value of  $\sigma_s$  corrected for size-dependence, it appears that he is essentially making an edge-energy correction for what is, in microscopic reality, a polyhedral crystalline rather than a true sphere.

### 9. Activation energy for self-diffusion

The most essential difference between the solid phase and the liquid phase of a given substance is that in the former, long-range order exists in the form of a truly crystalline structure, while in the latter only a short-range order exists. Yet in many liquids, of which water is an excellent example, this short-range order is well enough developed, so that one seems forced to regard each molecule as being rather well locked into a local structure which, in the case of water, is known to be tetrahedrally bonded. In view of this tendency towards a crystal-like local structure, molecules cannot move in a truly gas-like fashion among each other in a liquid. Hence the phenomena of self-diffusion and viscosity come to depend upon the probability with which an individual molecule may break one or more of the bonds which hold it to its nearest neighbors, preparatory to moving relative to the local structure. The energy  $A$  required thus to attain the more mobile state of higher potential energy is drawn from the thermal energy distribution by the mechanism of random vibrational collisions, and the fractional probability that a given liquid molecule may have acquired this so-called "activation energy for self-diffusion" is given by the factor  $\exp[-A/kT]$ . This probability factor enters into the nucleation equation because each molecule (including the last one just needed to attain critical size) must first free itself from the liquid structure near the water-ice interface and then diffuse from the liquid region over onto the crystal lattice. The activation-energy barrier may be thought of loosely as being made up of the work needed to break one intermolecular bond prior to the molecule's chance rotation into an orientation compatible with entry into the local lattice. In the limit of very low temperatures, where  $F_c$  becomes negligibly small, the rate of growth of embryos becomes limited almost entirely by the diffusional barrier, and a true ice lattice may have to give way to a vitreous form of the solid phase.

Since exactly the same activation energy enters, in an inverse manner, into viscous processes, it becomes possible to determine  $A$  from empirical viscosity data. Although there have been proposed many different expressions for describing the temperature dependence of viscosity (Partington, 1951), the most widely accepted, on both theoretical and observational grounds, is

$$\eta(T) = C \exp [A/kT], \quad (11)$$

where  $\eta$  is the coefficient of viscosity and  $C$  is a constant. Mason (1952) made use of (11) to determine  $A$ , using viscosity data of White and Twining (1913). He obtained the value  $A = 3.3 \times 10^{-13}$  ergs, and it is of immediate interest to note that this is of the order of magnitude of the energy per bond in water, as would be expected on the basis of the physical picture suggested above.

It should be mentioned here that Krastanow (1941) gave an estimate for  $A$  of  $2 \times 10^{10}$  erg gm $^{-1}$ , or about  $6 \times 10^{-13}$  ergs per molecule, which he obtained from a suggestion due to Volmer (1939) that  $A$  must be somewhat less than the molecular heat of vaporization of the substance in question. That Krastanow's value is about twice as large as that found by Mason from (11) is due to the fact that an estimate based upon  $L_v$  (Krastanow actually used 500 cal gm $^{-1}$ ) inevitably measures the energy needed to break two intermolecular bonds, whereas diffusion actually appears to proceed primarily by a sequence of single-bond ruptures followed by rotations about the remaining bond,—even in ice (Owston, 1951).

To complete this brief examination of previous treatments of  $A$  in nucleation studies, it may be recalled that one of the objections raised in section 3 to the calculations of Fisher, Hollomon and Turnbull (1949) concerned their complete omission of a term of the form  $\exp[-A/kT]$  in their nucleation equation. In terms of the physical picture suggested above, it seems clear that this omission left out an effect which, especially for large degrees of supercooling, assumes appreciable importance in inhibiting embryo growth. Finally, it may be noted in passing that a diffusional barrier does *not* affect nucleation of either liquid or solid embryos forming in supersaturated *vapor*, because the nearest-neighbor distance in a vapor is generally so great as to preclude the sort of interactions which inhibit diffusion in a liquid.

In estimating  $A$ , Mason's approach is followed here. However, Mason did not take cognizance of the fact that  $A$  increases with decreasing temperature due to the increasing order in the liquid structure at lower temperatures. From viscosity data given by Dorsey (1940, tables 82, 85), the writer has computed  $A(T)$  in the temperature range from  $-10^\circ\text{C}$  to  $70^\circ\text{C}$ . The results are shown in fig. 2 as the solid portion of the curve. Mason's value of  $3.3 \times 10^{-13}$  erg is seen to correspond to a temperature of about  $5^\circ\text{C}$ , while in the temperature range of interest in the problem,  $A$  is clearly going to be larger. In view of the fact that the functional form of (11) is not indisputably established, the writer has only felt justified in making a simple linear extrapolation down to the temperature limits of interest here. This procedure probably tends to underestimate slightly the activation energy barrier, but is clearly an improvement over the use of a constant value corresponding to a temperature near  $0^\circ\text{C}$ .

## 10. Calculations

The primary objective of the present study has been to determine, if possible, whether the  $-40^\circ\text{C}$  transition can be explained theoretically in terms of the homogeneous nucleation process. The test of this hypothesis consists of calculating  $J$  from (3), (4) and (6) for water drops of specified size and for a number of different temperatures, to see what degree of supercooling is required to raise the nucleation rate per drop per second to the order of unity (*cf.* discussion of table 1 in section 3 above). This will now be done, by use of the revised numerical values of the several parameters discussed in sections 5 through 9.

In the calculations, the value of  $n$  in (3) will be taken to be the number of water molecules in an isolated drop of 10-micron radius. From the values of  $J$  calculated here, one may readily obtain the corresponding values for smaller or larger radii to form a table similar to table 1, since  $J$  varies linearly with  $n$ . A radius of 10 microns is selected here as being typical of the drop size reported in laboratory studies of the  $-40^\circ\text{C}$  transition (*e.g.*, Schaefer, 1949). It also serves reasonably well to represent the natural cloud physical situation.

Since (3) is transcendental in  $T$ , one cannot simply put  $\log_{10} J = 0$  and solve directly for  $T$  to determine the theoretical transition temperature. Instead, one may compute and plot  $\log_{10} J(T)$  and then read the value of  $T$  where the curve crosses the axis of abscissas. This has been done here in three separate series of calculations, one corresponding to each of the methods for estimating  $\sigma_s$ . The results, displayed in part in fig. 3, are as follows:

1. Using  $\sigma_s$  as obtained by the revised Volmer-Krastanow method (table 2), one obtains curve I of

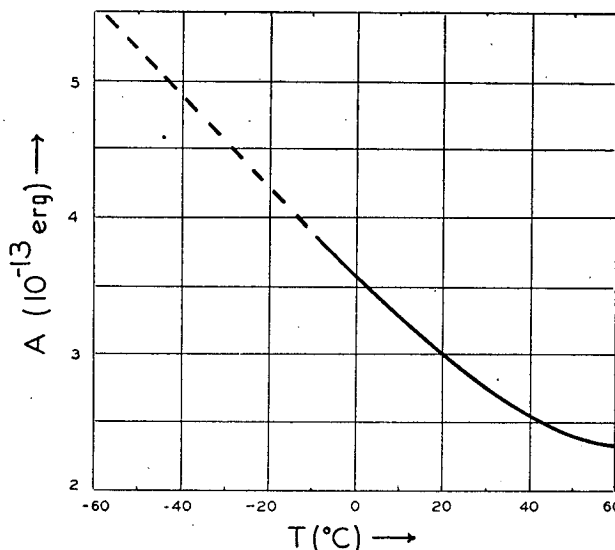


FIG. 2. Temperature dependence of activation energy for self-diffusion in water.  $A$  in units of  $10^{-13}$  ergs per molecule. Values from  $60^\circ\text{C}$  down to  $-10^\circ\text{C}$  calculated from empirical viscosity data (Dorsey). Values from  $-10^\circ\text{C}$  down to  $-50^\circ\text{C}$  obtained by linear extrapolation.

fig. 3. It is seen that the temperature for spontaneous nucleation of 10-micron drops is predicted to be about  $-10^{\circ}\text{C}$ , according to this calculation.

2. Next, using values of  $\sigma_s$  obtained from the present revision of Mason's approach (table 3), one obtains values of  $J$  which are so minute as to preclude spontaneous nucleation anywhere near  $-40^{\circ}\text{C}$ . The lowest temperature to which the writer extended this part of the calculations was  $-70^{\circ}\text{C}$ ; and even for that extreme degree of supercooling, a drop of 10-micron radius would experience a nucleation only once in about  $10^{68}$  sec, if this second set of  $\sigma_s$  values was correct. The age of the universe is believed to be of the order of  $10^{17}$  sec. Such low nucleation rates cannot conveniently be shown in fig. 3, and would clearly be of no meteorological interest anyway.

3. Finally, using the values of  $\sigma_s$  based on the present revision of Mason's approach but corrected very roughly for distortion effects in the manner indicated earlier (table 3), one gets the curve shown as II in fig. 3, from which the theoretically predicted transition temperature is found to be about  $-26^{\circ}\text{C}$ .

Before a discussion of these results is presented, one additional calculation will be examined. Fisher, Hollomon and Turnbull (1949) have used (3) to compute the value which  $\sigma_s$  must have if the  $-40^{\circ}\text{C}$  transition really is due to homogeneous nucleation. In section 3 several objections to their calculation have been noted. It is of interest here to repeat that calculation on the basis

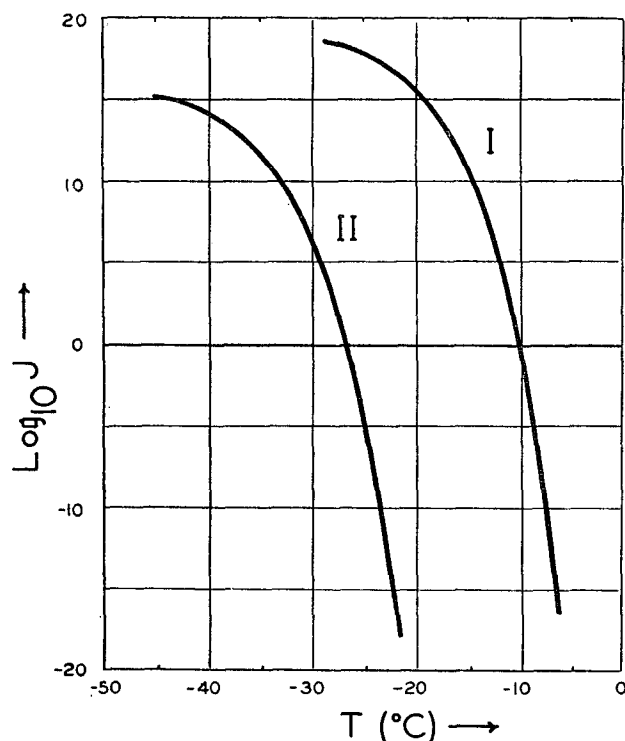


FIG. 3. Temperature dependence of nucleation rate  $J$  for supercooled water drops of 10-micron radius. Curve I computed by use of  $\sigma_s$  as estimated by revised Volmer-Krastanow method; curve II computed by use of  $\sigma_s$  as estimated by revised Mason method with approximate correction for surface distortion energy.

of such revisions as have been made in the course of the present study (excepting, of course, revisions in methods of calculating  $\sigma_s$  itself). Assuming that the laboratory observations of the  $-40^{\circ}\text{C}$  transition apply to drops of 10-micron radius, one finds by this sort of inverse calculation that a value of  $\sigma_s$  of  $18 \text{ erg cm}^{-2}$  would bring the present theory into accord with laboratory observations. This figure is to be compared with the  $-40^{\circ}\text{C}$  values of 7.7, 38 and  $12 \text{ erg cm}^{-2}$  obtained in this study by three different methods, and with the value of  $33 \text{ erg cm}^{-2}$  deduced by Fisher, Hollomon and Turnbull.

## 11. Discussion

On the basis of a rather large number of revisions of previous efforts to examine the  $-40^{\circ}\text{C}$  problem, three separate calculations have been made here employing three different sets of estimated values of  $\sigma_s$ , the variable having dominant numerical influence on the theoretical nucleation rates.

The first of these calculations (curve I, fig. 3) implies a far too efficient nucleation process. If all of the other parameters controlling  $J$  are reliable (and they are certainly much more reliable than  $\sigma_s$ ), then one can conclude that the values of  $\sigma_s$  estimated by the Volmer-Krastanow method must surely be lower than the correct values, because it is well known that liquid-water drops often exist in clouds at temperatures substantially below  $-10^{\circ}\text{C}$ . It must be recalled that no really firm basis for accepting the Volmer-Krastanow method for estimating  $\sigma_s$  has yet been given, although the writer has suggested earlier here one way in which it can at least be rendered qualitatively plausible.

The second calculation predicts an effectively zero nucleation rate down to regions of supercooling well beyond those of meteorological interest. That is, when the writer calculates  $\sigma_s$  after the manner suggested by Mason, but with Mason's apparent errors corrected in the best way recognized by the writer, the implied nucleation rates are found to fail completely to account for a  $-40^{\circ}\text{C}$  transition. This, plus the results of the first calculation, seem to place the burden of the argument squarely on the correction for distortion energy in the cleavage computations.

In the third calculation, where a crude, though at least not arbitrary correction for the lattice distortion effect has been included, the predicted transition temperature still falls outside the range of observed transition points, though by an amount which is only about half as great as the discrepancy for the first of the three calculations. The phenomenal increase of computed nucleation efficiency that accompanies the application of the distortion energy correction is very disquieting in view of the uncertain grounds on which a distortion correction was made here. Consequently, it becomes important to examine the possibility that

one could make a more straightforward attack on the problem of determining the distortion energy.

If one had experimental data concerning the lattice expansion in the outer two or three molecular layers near an ice surface, he might calculate the distortion energy fairly accurately from the known compressibility coefficient of ice; but unfortunately x-ray data inevitably provide only a picture of the average structure down to many tens of molecular or atomic distances. Perhaps electron-diffraction methods hold somewhat more promise, but the difficulty in adequately preparing a sample surface in the case of ice would probably be a limiting factor here.

On the theoretical side, it might be hoped that a direct calculation modeled upon that made by Shuttleworth for inert-gas crystals would be the answer, and this is indeed so in principle. In fact, however, such a calculation would be extremely difficult. Following Shuttleworth, one would seek a general expression for the potential energy of a surface molecular plane with respect to all of the rest of the crystal, minimize this with respect to the interplane distance, solve for the implied equilibrium interplane distance, and then insert this back into the general energy expression to compute the reduction in energy due to surface distortion. But whereas the interatomic attractive potential in an inert-gas crystal decreases according to  $r^{-6}$ , that for dipolar ice would contain terms decreasing only according to  $r^{-3}$ ; so one would have to minimize jointly the potential energy of at least the two uppermost planes of water molecules, and this might be only a first approximation. This complication would not be so serious by itself, but each of the involved potentials would have to be expressed as a sum over the lattice of a Taylor series expansion (multipole expansion) of the charge distribution around each  $H_2O$  molecule. Campbell (1952) has examined the problem of calculating the lattice energy of ice (for fixed intermolecular distances) in terms of multipoles, and has found that even when one includes all terms up to fifth-order (e.g., octupole-octupole interactions) for nearest-neighbors, the agreement with the corresponding thermodynamic data is unsatisfactory. Furthermore, Campbell found that interactions between next-nearest neighbors are still significant out to beyond third-order terms. From Campbell's table II, one can see that this means that the potential energy for each molecule in a plane near the surface must contain approximately fifteen terms in the variable interplane distance, and since one must find a joint minimum for at least the first two interplane distances, it follows that at least thirty terms are involved in the function whose minimum would be sought. Finally a *very* serious further complication enters by virtue of the fact that these multipole interactions, unlike the dispersion forces (London, 1937) with which Shuttleworth dealt, are not simply additive, so the type of

lattice sums which were usable in Shuttleworth's calculation are not applicable here.

In all, it seems questionable whether the heroic efforts that would have to be made to effect this lattice calculation of the distortion energy are meteorologically justifiable. This last step required to complete the theoretical exploration of the problem of homogeneous nucleation of supercooled water drops appears to be of an order of difficulty far exceeding that of any solid-state calculations that have yet been carried out for ice or other dipole crystals. Consequently, the writer feels that the fact that even a crude estimate of the distortion has here yielded a theoretically predicted temperature of  $-26^{\circ}C$  may for the present be taken as a fair indication that the  $-40^{\circ}C$  transition is truly an effect of homogeneous nucleation; an effect whose precise nature cannot be specified quantitatively in the present state of knowledge of the solid-state physics of ice. Careful scrutiny of the present revisions of previous investigators' work will have to be made by others before this conclusion can be accepted; but if the present calculations can be regarded as essentially correct up to the last step of making the distortion correction, and particularly if experimental evidence clearly contradicting the homogeneous nucleation hypothesis is not forthcoming, then there would seem to be a reasonable basis for concluding that  $-40^{\circ}C$  is the temperature to which water droplets of cloud-particle size must be supercooled in order that there shall be nearly unit probability of the formation of an ice embryo of critical size somewhere inside each drop within a period of time of the order of the lifetime of the cloud; that is, that near  $-40^{\circ}C$ , clouds of pure water drops undergo homogeneous nucleation.

## 12. Summary

Previous investigations of the  $-40^{\circ}C$  transition in supercooled water drops have been shown to contain a variety of inaccuracies which have had marked effect on predicted nucleation rates. After a number of modifications were made in existing approaches to the homogeneous nucleation problem, three different estimates of the specific surface free energy of a water-ice interface were used to estimate the temperature dependence of the dropwise nucleation rate. Of the three results, the one in which the most confidence can be placed yielded a predicted transition temperature substantially too high,  $-26^{\circ}C$ , but was based on a correction for surface-distortion effects that is recognized to be quite crude. There seems little immediate hope for gaining improved precision in the estimate of the distortion correction on theoretical grounds, since the required calculation poses very formidable difficulties.

The fact that one rough estimate of the distortion energy has led to a predicted transition threshold even as close to the observed value as  $-26^{\circ}C$  is tentatively

taken to indicate that the  $-40^{\circ}\text{C}$  transition probably is an effect of homogeneous nucleation whose precise explanation will have to await further developments in the solid-state physics of ice.

### 13. Suggestion for future research

It would be of the greatest interest to have some sort of experimental determination of the surface free energy of a water-ice interface. Although a direct evaluation of this parameter for supercooled water seems quite out of question, it may not be entirely impossible to determine this quantity at the triple point of water by employment of sufficiently elaborate thermostatic controls. It should be clear from the previous discussions of the distortion-energy correction that immeasurable improvement in one's understanding of the nucleation problem would result even from a reasonably accurate determination of  $\sigma_s$  at the triple point.

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